

Response to the comments of referee #1:

We thank the reviewer for the helpful comments.

Comment: The authors should examine the tenses used in the paper. It is usual to use the past tense for experiments (e.g. p9 l1, should be “MVK...was injected...”) and the present tense for results etc.

Response: The manuscript was checked and tenses are corrected.

Comment: P4, l9. Change to “...prevents ambient air entering...” and P4, l21. change to “...detection limit of the instruments.”

Response: This is changed as suggested.

Comment: Either square brackets or the word concentrations should be inserted. i.e. “...OH concentrations agree...”. This error occurs on a number of occasions (e.g. later on the same line)

Response: This was checked and is corrected for the entire manuscript.

Comment: The sentence beginning “The predicted rate constant...” would be helped by inserting a diagram into the SI – I presume the term “limited protruding section” means that part of the forward barrier that lies above the reactant energy, but it is not obvious. The comment on the reversibility of the alkoxy decomposition is not very clear – again this would be helped by a diagram of the PES and some additional comment in the SI.

Response: The paragraph is rephrased to explain more clearly what was meant, i.e. a barrier protruding less than 2 kcal/mol above the products, and hence a low barrier for the reverse H-migration. SAR-derived energy barriers for the alkoxy product decomposition (≥ 4 kcal/mol) are also mentioned now to further emphasize the potential competition on the product fate. Table 2 was found to contain a typo which added to the confusion. (a reaction energy of 2.40 which should have read 20.4). Finally, we show an energy diagram in the supporting information.

Comment: P11, R7. The mechanism would be clearer if the underlined phrase below were inserted: “...HMVKA02 1,4 H migration ...-OH group, followed by H abstraction at the -OH site by O2 forming HO2...” Also the O2 in reaction R7 is not involved in the rate determining step and so + O2 should be placed in brackets. Generally speaking, it is necessary to have the MCM site open on reading the paper to appreciate the details of the reactions being discussed. While this is OK, it does slow reading down – the authors might consider putting the structures, with MCM names, in the SI.

Response: The phrase is added as suggested. Structures of all molecules relevant for the discussion are given together with their names in the MCM in Figure 1. We have the feeling that this is sufficient for the reader to follow the discussion.

Comment: P13, l4. The first sentence needs rephrasing – the word rates should be inserted and a reference made to the steady state (the reaction rates are equal – they are not genuinely in equilibrium.) I suggest “OH is in steady state because of its short lifetime, so that its rates of production and destruction are equal.”

Response: The sentence is changed accordingly.

Response to the comments of referee #2:

We thank the reviewer for the helpful comments.

Comment: Have the authors investigated the details of the RO₂ rate constants used in the MCM mechanism and the effect these might have on the results? For example, are rate constants appropriate for each RO₂ structure used or some kind of average? Furthermore, there are few rate constants available for multifunctional RO₂ radicals that capture the effects of neighboring functional groups.

Response: The RO₂ reaction rate constants are used as suggested in the MCM. Because there are no specific measurements of reaction rate constants of MVK derived RO₂, we tested the effect of faster reaction rate constants to increase product concentrations that are smaller in the model than measured values. An increase of the reaction rate constant with HO₂ would further deplete the modelled HO₂, which is not consistent with measurements. In addition, the effect on the glycolaldehyde yield is small, because glycolaldehyde is only formed in the subsequent photolysis of the product of the HO₂+RO₂ reaction, if the additional reaction channels suggested by Praske et al are not taken into account. Because of the low NO concentration in the “low-NO”-experiment, the sensitivity of the model results to an increased reaction rate constant of the RO₂+NO reaction is rather small. We add on p7 I22: “No measurements for the reaction rate constants of RO₂ species from MVK exist. The sensitivity of model results to a change of the RO₂ reaction rate constants, however, is rather small so that their uncertainties could not explain observed model-measurements discrepancies.”

Comment: What role might reactions of RO₂ radicals with particles or the walls play? These do not appear to be considered here (probably since its difficult to know what happens), even though they seem likely to compete with other RO₂ reaction pathways under low NO conditions when RO₂ lifetimes are long.

Response: The experiments were performed without seed particles and particle formation in the chamber during these experiments were not sufficient to build-up substantial aerosol surface area. Therefore, effects from heterogeneous reaction on aerosol can be neglected. The SAPHIR chamber has a large volume to surface ratio to minimize wall loss effects. Experiments from the past do not hint that RO₂ loss reaction significantly impact the results. In addition, we observe the formation of product species (glycolaldehyde) in the experiments here, which would not be expected, if RO₂ was lost. We add on p4 I30: “No significant particle formation was observed in the experiments so that only gas-phase chemistry needs to be considered in the evaluation.”

Investigation of the oxidation of methyl vinyl ketone (MVK) by OH radicals in the atmospheric simulation chamber SAPHIR

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Abstract. The photooxidation of methyl vinyl ketone (MVK) was investigated in the atmospheric simulation chamber SAPHIR for conditions at which organic peroxy radicals (RO₂) mainly reacted with NO (“high NO” case) and for conditions at which other reaction channels could compete (“low NO” case). Measurements of trace gas concentrations are compared to calculated concentration time series applying the Master Chemical Mechanism (MCM version 3.3.1). Product yields of methylglyoxal and glycolaldehyde are determined from measurements. For the high NO case, the methylglyoxal yield is (19 ± 3) % and the glycolaldehyde yield is (65 ± 14) % consistent with recent literature studies. For the low NO case, the methylglyoxal yield reduced to (5 ± 2) % because other RO₂ reaction channels that do not form methylglyoxal become important. Consistent with literature data, the glycolaldehyde yield of (37 ± 9) % determined in the experiment is not reduced as much as implemented in the MCM suggesting additional reaction channels producing glycolaldehyde. At the same time, direct quantification of OH radicals in the experiments shows the need for an enhanced OH radical production at low NO conditions similar to previous studies investigating the oxidation of the parent VOC isoprene and methacrolein, the second major oxidation product of isoprene. For MVK the model–measurement discrepancy is up to a factor of 2. Product yields and OH observations are consistent with assumptions of additional RO₂ plus HO₂ reaction channels as proposed in literature for the major RO₂ species formed from the reaction of MVK with OH. This study, however, shows that also HO₂ radical concentrations are underestimated by the model, suggesting that additional OH is not directly produced from RO₂ radical reactions, but indirectly via increased HO₂. Quantum chemical calculations show that HO₂ could be produced from a fast 1,4-H shift of the second most important MVK derived RO₂ species (reaction rate constant 0.003 s⁻¹). However, additional HO₂ from this reaction is not sufficiently large to bring modelled HO₂ radical concentrations into agreement with measurements due to the small yield of this RO₂ species. An additional reaction channel of the major RO₂ species with a reaction rate constant of (0.006 ± 0.004) s⁻¹ would be required that produces concurrently HO₂ radicals and glycolaldehyde to achieve model–measurement agreement. A unimolecular reaction similar to the 1,5-H shift reaction that was proposed in literature for RO₂ radicals from MVK would not

explain product yields for conditions of experiments in this study. A set of H-migration reactions for the main RO₂ radicals were investigated by quantum chemical and theoretical kinetic methodologies, but did not reveal a contributing route to HO₂ radicals or glycolaldehyde.

1 Introduction

Isoprene (C₅H₈) emitted by plants (Guenther et al., 2012) has the highest emission rate among non-methane organic compounds. Isoprene is mainly oxidized by the photochemically generated hydroxyl radical (OH) forming the first-generation organic compounds methacrolein (MACR), methyl vinyl ketone (MVK), formaldehyde (HCHO and isoprene hydroxyperoxides (ISOPOOH) (e.g. Karl et al., 2006). The latter ones are formed without the involvement of nitric oxide (NO) so that ISOPOOH becomes increasingly important with decreasing concentrations of nitrogen oxides (St. Clair et al., 2015) which are mainly released by anthropogenic activities. The formation of MVK and MACR is accompanied by the production of HO₂, which can further recycle OH, whereas ISOPOOH formation is a radical termination reaction. However, field studies have shown that also in environments where NO concentrations are less than a few 100 pptv a high OH regeneration rate can be maintained which is not explained by chemical models (Tan et al., 2001; Lelieveld et al., 2008; Hofzumahaus et al., 2009; Whalley et al., 2011). The gap between measured and modelled OH is correlated with the abundance of isoprene (Lu et al., 2012). Since then, it has been recognized that organic peroxy radical (RO₂) pathways which do not require NO as reaction partner can also significantly recycle OH (Wennberg et al., 2018). These reactions include

- hydrogen-shift reactions of RO₂ radicals forming OH or HO₂,
- reaction of peroxy radicals with HO₂.

These pathways have both been identified in the oxidation chain of isoprene (Peeters et al., 2009, 2014). 1,6 H-shift of RO₂ formed in the reaction of isoprene with OH leads to the formation of hydroxyperoxy aldehydes (HPALD) and HO₂. The photolysis of HPALD gives even additional OH radicals. Its relevance for the atmosphere has been shown in laboratory experiments (Crouse et al., 2011; Wolfe et al., 2012) and chamber experiments (Fuchs et al., 2013). In the supplement of the first publication of the LIM (Peeters et al., 2009) the authors also suggested that a 1,5-H-shift reaction could be relevant for MVK and MACR. For MACR, however, an 1,4 H-shift reaction for RO₂ was found, which efficiently recycles OH (Crouse et al., 2012). Its impact on the radical budget has been shown in chamber experiments (Fuchs et al., 2014). H-shift reactions have also been proposed to be important for RO₂ radicals which are formed in the oxidation chain of ISOPOOH (D'Ambro et al., 2017) also potentially enhancing the OH regeneration rate.

The reaction of peroxy radicals with HO₂ forms not only hydroxyperoxides, but also OH together with an alkoxy radical. This was shown for the acetylperoxy radical with an OH yield of 50 % (Dillon and Crowley, 2008; Winiberg et al., 2016). In a recent study by Praske et al. (2015), product yields from the reaction of MVK derived peroxy radicals with HO₂ were investigated. Similar to the acetylperoxy radical, product yields demonstrated that only one third of the reaction yields hydroxyperoxides and that two additional reaction channels exist, both of which could lead to the reformation of OH.

In this study, the oxidation of MVK by OH was investigated in the atmospheric simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a Large Reaction Chamber) at Forschungszentrum Jülich. Experiments were performed under controlled conditions with atmospheric trace gas and radical concentrations. In these experiments, not only organic compounds like in previous studies were measured, but also radical species (OH, HO₂, and RO₂) allowing for an analysis

of the OH budget. In the low NO case, NO mixing ratios were kept below 100 pptv so that different RO₂ radical reactions, i.e. reaction with HO₂ and unimolecular isomerization reactions, can compete. Measured time series of radical concentrations are compared to model calculations applying the Master Chemical Mechanism version 3.1.1 (MCM, 2017) and modifications suggested in literature.

5 2 Methods

2.1 Simulation experiment in SAPHIR

Experiments were performed in the outdoor atmospheric simulation chamber SAPHIR. Details of the chamber can be found in previous publications (e.g. Rohrer et al., 2005). SAPHIR has a cylindrical shape (length 18 m, diameter 5 m, volume 270 m³ and consists of a double-wall FEP (fluorethylene-propylene) film. A small overpressure (45 Pa) prevents ~~ambient air entering~~ ~~that ambient air can enter~~ the chamber. The replenishment flow that is required to maintain this pressure leads to a dilution of all trace gases by approximately 3 to 5 % per hour. A shutter system shades the chamber before the photooxidation experiment is started. Natural sunlight is used to irradiate the mixture. Small sources of nitrous acid (HONO) and formaldehyde (HCHO) are present in the sunlit chamber (100 to 200 pptv/h). The photolysis of HONO is typically the primary source for OH radicals and nitrogen oxides.

15 In total, four experiments were conducted in this study, two of them at low NO (23 June 2016: NO < 70 pptv and 23 May 2017: NO < 40 pptv) and two of them at high NO conditions (20 August 2014: 0.7 to 6 ppbv NO and 17 May 2017: approximately 0.1 to 0.4 ppbv NO). Results from experiments performed at similar conditions gave consistent results. The discussion of results focus on the two experiments for which the number of trace gas measurements was highest and results for the other experiments are shown in the Supporting Information.

20 The experiments started with cleaning the chamber air by flushing out impurities from previous experiments until trace gas concentrations were below the ~~limit of detection of~~ ~~limit-of-detection-of~~ instruments. The chamber air was first humidified by flushing water vapour from boiling water into the dark chamber (relative humidity approximately 70 %). In the low NO experiments, approximately 140 ppbv ozone produced from a silent discharge ozoniser (O3onia) was injected in the dark, in order to suppress NO concentrations. In contrast, 6 to 10 ppbv of NO₂ or NO were injected from a gas mixture in case of the
25 high NO experiments. In one of the two low NO experiments (23 May 2017), 20 ppbv MVK (Sigma-Aldrich, purity 99 %) in water was injected in the dark chamber from a Liquid Calibration Unit (LCU, Ionicon). MVK (1.5 ppbv) was reinjected after 3.5 hours of photooxidation. In the other experiments, MVK was injected several times during the experiment after an initial phase of illumination of the chamber air without additional OH reactants by injecting liquid MVK into a heated inlet line that is flushed by synthetic air. This procedure was similar to that applied in previous studies (e.g. Fuchs et al., 2013, 2014;
30 Kaminski et al., 2017). The photooxidation of MVK was then observed for several hours. **No significant particle formation was observed in the experiments so that only gas-phase chemistry needs to be considered in the evaluation.**

2.2 Instrumentation

Trace gas concentrations were measured with a comprehensive set of instruments. Nitric oxide (NO) was detected by chemiluminescence (Eco Physics) and nitrogen dioxide (NO₂) by the same instrument but with a blue-light converter in the inlet. In one of the experiments (17 May 2017), no NO_x measurements were available. A cavity ring-down instrument (Picarro) monitored water vapour and carbon monoxide and a UV photometer (Ansyco) detected ozone.

The total OH reactivity (inverse lifetime of OH) was measured by a pump-probe method (Lou et al., 2010; Fuchs et al., 2017), in which the decay of OH radicals produced by laser flash photolysis of ozone is observed by laser-induced fluorescence (LP-LIF). OH reactivity gives a measure of all OH reactant concentrations, so that potential gaps in the detection of e.g. organic compounds that are relevant for the radical chemistry can be identified (e.g. Nölscher et al., 2012). Unfortunately, the instrument failed in 2014, so that OH reactivity was only measured in one of the two high NO experiments.

Organic compounds were measured by a proton-transfer time-of-flight mass spectrometer (PTR-TOF-MS, Ionicon), which was calibrated to quantify MVK, Methylglyoxal (CHOC(=O)CH₃, MGLYOX), and glycolaldehyde (HOCH₂CHO) were quantified in one low and one high NO experiment. In the other two experiments, performed in different years, the PTR-TOF-MS was calibrated for MVK, but not for methylglyoxal and glycolaldehyde for all experiments so that these species could not be quantified in all experiments. Acetic acid was detected on the same mass as glycolaldehyde in the PTR-TOF-MS instrument. However, model calculations suggest that the contribution of acetic acid was less than 10% of the total signal. Therefore, measurements represent glycolaldehyde concentrations reasonably well.

A second PTR-TOF-MS instrument (PTR-3, Ionicon) quantified MVK concentrations in the experiment on 23 May 2017. Measurements of both instruments agreed within 20%. In addition to direct measurements of MVK concentrations, measurements of the OH reactivity can be used to calculate the MVK concentration that was injected in the experiments because the increase in OH reactivity at that point in time can be attributed to the MVK concentration increase. The comparison with the increase in MVK measurements by the PTR-TOF-MS instrument shows good agreement.

In the experiments in 2017, formaldehyde was measured by the same differential optical absorption spectroscopy (DOAS) instrument that also detects OH radicals in the chamber (Dorn et al., 1995). In the other years, HCHO was measured by a Hantzsch monitor. The 1 σ -precision of the formaldehyde measurement of 230 pptv is less than that of the Hantzsch monitor (20 pptv), but it is sufficiently high for the detection of HCHO in the experiments here.

OH was detected by DOAS (Dorn et al., 1995) in all experiments except for the high NO experiment in 2014. In addition, OH, HO₂ and RO₂ radicals were measured by laser-induced fluorescence (LIF). The instrument has been described in detail elsewhere (Fuchs et al., 2008, 2011, 2016). OH concentrations measured by LIF in the SAPHIR chamber have been shown to agree with measurements by DOAS in several comparison exercises (e.g. Schlosser et al., 2009; Fuchs et al., 2012). Good agreement was also observed in this work so that significant potential artefacts in the LIF detection scheme as reported for some instruments in the field (Mao et al., 2012; Novelli et al., 2014; Rickly and Stevens, 2018) can be excluded.

HO₂ and RO₂ are chemically converted to OH by the reaction with NO prior to OH detection by laser-induced fluorescence in the LIF instrument. The conversion of RO₂ requires at least two subsequent reactions with NO. First, RO₂ is converted by

added NO to HO_x in a flow reactor upstream of the fluorescence cell. Added CO in the reactor ensures that the HO_x consists predominantly of HO₂, which has a small wall loss compared to OH. The reactor is operated at higher pressure (25 hPa) compared to the low-pressure (4 hPa) LIF detection cell (Fuchs et al., 2009). The HO_x is sampled from the reactor into the LIF detection cell where HO₂ is converted by a large excess of added NO to OH. Operational parameters of the RO₂ system are optimized for the efficient detection of RO₂ radicals that have a similar reaction rate with NO as methylperoxy radicals. As a consequence, RO₂ radicals are not efficiently detected, if their reaction with NO does not directly and quantitatively result in the production of HO₂. This is for example the case for the peroxy radical HMVKBO₂ (as named in the MCM) that is formed from the reaction of MVK with OH (see below for details). This has to be taken into account, if measured RO₂ radicals are compared with model calculations.

The HO₂ detection cell consists of a fluorescence cell, in which HO₂ reacts with excess NO that is injected behind the inlet nozzle. As shown for several LIF instruments, the HO₂ signal can also contain contributions from RO₂ radicals that rapidly form HO₂ in the reaction with NO (Fuchs et al., 2011; Whalley et al., 2013; Lew et al., 2018). This applies for those RO₂ radicals which form an alkoxy radical (RO) in the reaction with NO that rapidly produces HO₂ and other products. The interferences from RO₂ can be minimized, however, if the instrument is operated with an NO concentration, for which the HO₂ to OH conversion efficiency is only approximately less than 10 %. In this case, the RO₂ to OH conversion efficiency becomes much smaller for all RO₂ species, because the two reactions with NO needed to produce OH limit the overall conversion efficiency. In this study, the HO₂ channel of the LIF instrument was operated such that RO₂ interferences can be assumed to be negligible.

In one of the experiments (23 May 2017), HO₂ was additionally detected by a newly developed chemical ionization mass spectrometry (CIMS) instrument using Br⁻ as ionization reagent. HO₂ is detected as cluster ion similar to the approaches reported by Veres et al. (2015); Sanchez et al. (2016) using an I⁻ and Br⁻ CIMS, respectively. Details of this new instrument will be presented in a separate publication. HO₂ measurements of the CIMS instrument agreed with [HO₂] detected by the LIF instrument within 15 %.

Solar radiation was measured outside the chamber using a spectroradiometer. Photolysis frequencies were then calculated by applying a model to transfer outside conditions to conditions inside the chamber (Bohn et al., 2005; Bohn and Zilken, 2005). Latest recommendations for absorption spectra and photolysis yields were used.

2.3 Model calculations

Model calculations were performed using the Master Chemical Mechanism in its latest version 3.3.1 (MCM, 2017). A simplified reaction scheme is shown in Fig. 1. The MCM mechanism was modified (MCM*) to take results reported in literature into account and findings in this work. Details are listed in Table 1.

Chamber specific properties were added such as dilution of traces gases due to the replenishment flow. Sources for HONO and HCHO production from the chamber were parametrized as described in previous publications (e.g. Fuchs et al., 2014; Kaminski et al., 2017).

Model calculations were constrained to physical parameters (pressure, temperature, photolysis frequencies, dilution rate of trace gases). A small, constant background OH reactivity of unknown OH reactants that was measured by the OH reactivity instrument after humidification of the chamber air was modelled as an OH reactant that converts OH to HO₂. However, the magnitude of this background reactivity was small ($< 1 \text{ s}^{-1}$) compared to the OH reactivity from MVK during the experiment
5 ($> 15 \text{ s}^{-1}$) so that it did not affect the chemistry.

Injections of trace gases were modelled as sources during the time of injection, but injected trace gases were not constrained to measured values at later times. [NO], [NO₂] and [O₃] [~~NO~~], ~~NO₂~~ and ~~O₃~~ were only constrained to measurements for the high NO_x experiment, because differences between modelled and measured values would have led to significant differences in other observables. No modelling could be performed for one of the high NO experiments (17 May 2017) due to the lack
10 of NO_x measurements. **No measurements for the reaction rate constants of RO₂ species from MVK exist. The sensitivity of model results to a change of the RO₂ reaction rate constants, however, is rather small so that their uncertainties could not explain observed model-measurements discrepancies.**

2.4 Quantum-chemical calculations

A set of H-migration reactions for the main MVK-derived peroxy radicals was investigated by quantum chemical and theoretical kinetic methodologies. The reactions studied included migration of hydroxyl, of α -OH, and of methyl H-atoms; direct
15 HO₂ elimination forming an enol was also investigated (Table 2).

Several methodologies were applied, as detailed in the supporting information. From these data, the M06-2X/cc-pVTZ rovibrational data (Dunning, 1989; Zhao and Truhlar, 2008), with CCSD(T)/aug-schwartz4(DT) single point energy calculations extrapolated to the basis set limit (Purvis and Bartlett, 1982; Martin, 1996) were selected. All quantum chemical calculations
20 were performed using the Gaussian-09 program suite (Frisch et al., 2010). The high-pressure rate coefficients for each of the elementary processes was then calculated using multi-conformer canonical transition state theory, MC-CTST (Vereecken and Peeters, 2003; Zheng and Truhlar, 2013) based on a rigid rotor harmonic oscillator paradigm, an exhaustive search of the reactants and TS conformers, and asymmetric Eckart tunneling and WKB zero-curvature (ZCT) tunneling. For the 1,4- and 1,6-H-shift in HMVKAO₂, a large difference between Eckart and ZCT tunneling was found; the geometric average is reported
25 here (see Supporting Information).

3 Results

3.1 Product yields

The reaction of OH with MVK leads to the addition of OH to either one of the double-bonded C-atoms so that two different RO₂ radical species can be formed (Fig. 1):



Yields are from current recommendations (Atkinson et al., 2006) that are also used in the MCM. The further reaction chain with NO gives glycolaldehyde and an acetylperoxy radical for HMVKBO₂ and methylglyoxal, formaldehyde and HO₂ for HMVKAO₂. In the low NO experiment (23 May 2017), approximately 30 % of the RO₂ reacted with NO assuming that the reaction with HO₂ was the only competing reaction. In contrast, more than 90 % of RO₂ reacted with NO in the high NO experiment. Mixing ratios of the major products formaldehyde, glycolaldehyde and methylglyoxal increased to 6, 8, and 1.3 ppbv, respectively, in the high NO experiment when 13 ppbv MVK was oxidized (Fig. 2). Less of these products was observed in the low NO experiment with 4.5 ppbv formaldehyde, 5 ppbv glycolaldehyde and 1 ppbv methylglyoxal (Fig. 3) when 17 ppbv MVK is oxidized. The smaller concentrations of these products in the low NO case might be expected, because other products can be formed in the competing RO₂ reaction channels (Fig. 1).

Because part of the products are oxidized during the experiment, a correction procedure described in detail by Galloway et al. (2011) and Kaminski et al. (2017) is applied, in order to calculate products yields originating from the oxidation of MVK. This correction takes loss of products due to the reaction with OH and photolysis into account and also small production from chamber sources. The relationship between consumed MVK and corrected product concentrations gives the yield of the product species (Table 3, Figure in Supporting Information).

For the high NO experiment, when RO₂ nearly exclusively reacted with NO, the ratio of product yields for glycolaldehyde (0.65 ± 0.14) and methylglyoxal (0.19 ± 0.03) can be related to the branching ratio of the MVK reaction with OH (Reactions R1 and R2), because these products are formed in either one of the two reaction channels. The values derived from this experiment agree within their uncertainties with studies by Galloway et al. (2011); Tuazon and Atkinson (1989); Praske et al. (2015) all reporting lower methylglyoxal yields than suggested by current recommendations (Atkinson et al., 2006). This indicates that the branching ratio assumed in the MCM of 0.7:0.3 needs to be shifted towards HMVKBO₂. Praske et al. (2015) suggests a branching ratio of 0.76:0.24. The formaldehyde yield of 0.73 ± 0.15 is higher than the methylglyoxal yield, because formaldehyde is not only a co-product of methylglyoxal in the reaction chain of HMVKAO₂ (Fig. 1), but can also be formed from secondary products in the oxidation scheme of MVK. This might also explain why the HCHO yield in this chamber experiment is higher than that in the study by Tuazon and Atkinson (1989). Product yields reported by Grosjean et al. (1993) differ for all three species (largest difference for formaldehyde) from the other studies for unclear reasons.

In the low NO case, other RO₂ reaction channels than reaction with NO gain in importance. Lower yields of methylglyoxal (0.05 ± 0.002) and glycolaldehyde (0.37 ± 0.09) compared to the high NO experiment are therefore found in this case. However, the relative decrease of glycolaldehyde is much smaller than that of methylglyoxal. This indicates that glycolaldehyde is also formed from other reaction channels than the reaction of HMVKBO₂ with NO. This agrees with results reported by Praske et al. (2015). In that study, a glycolaldehyde yield of 0.38 ± 0.05 was determined in experiments, in which RO₂ exclusively reacted with HO₂.

3.2 Modelled and measured time series of radical concentrations

Time series of trace gas and radical concentrations are shown together with model calculations using the MCM without modifications for one of the high NO experiments (Fig. 2, 20 August 2014) and for one of the low NO experiments (Fig. 3, 23

May 2017). Although the instrumentation that performed measurements in the experiments ~~were~~ partly different specifically for experiments done in different years, consistent results are obtained. In addition, parameters that are measured by two instruments agree within their combined uncertainties.

MVK (12 ppbv) ~~was~~ injected at two times into the sunlit chamber in the high NO experiment (Fig. 2). Approximately 5 half of the MVK reacted away before the second MVK addition ~~was~~ done. The NO mixing ratio ~~decreased~~ over the course of the experiment from nearly 6 to 0.5 ppbv, but ~~was~~ sufficiently high that 90 % of HO₂ ~~reacted~~ with NO for most of the time. OH concentrations ~~ranged~~ from $(2-4) \times 10^6 \text{ cm}^{-3}$ modulated by changes of the OH reactivity and radiation. Model calculations of ~~[OH]~~ agree with measurements within 20 % at all times during the oxidation of MVK. This corresponds to a good description of the measured MVK concentration by the model (deviations less than 5 %) demonstrating 10 that the OH concentration fits the observed oxidation rate of MVK.

HO₂ and RO₂ radical concentrations ~~were~~ rather small ($< 2 \times 10^8 \text{ cm}^{-3}$) due to their fast loss in the presence of high NO. Measured and modelled HO₂ concentrations show good agreement until the NO mixing ratio ~~decreased~~ below 0.5 ppbv (at 11:00, Fig 2). In the case of RO₂, the model yields significantly larger concentrations than measurements. This discrepancy is plausible due to the incomplete conversion of the peroxy radical HMVKBO₂ in the pre-reactor. The trans- 15 formation to HO₂ requires more than one NO reaction step and therefore remains incomplete during the transit through the reactor. If the modelled concentration of ~~[HMVKBO₂]~~ is subtracted from the total modelled ~~[RO₂]~~, good model-measurement agreement is obtained.

Overall, the good agreement between modelled and measured radical concentrations demonstrates that radical chemistry during the oxidation of MVK is well described by state-of-the-art chemical models, if RO₂ radicals are mainly lost in the 20 reaction with NO.

In the low NO experiment (Fig. 3), approximately 20 ppbv of MVK ~~was~~ injected, before photooxidation ~~started~~. As a consequence of the low NO ($< 40 \text{ pptv}$), RO₂ radicals formed in the reaction of MVK with OH not only ~~reacted~~ with NO, but reaction with HO₂ and RO₂ ~~were~~ competitive. Model calculations using the MCM (Fig. 3) suggest that at least half of the RO₂ ~~reacted~~ with HO₂ and a smaller fraction (10 to 20 %) with other RO₂ radicals.

25 After nearly 6 hours of oxidation, only 4 ppbv MVK ~~was~~ left in the presence of $(2-4) \times 10^6 \text{ cm}^{-3}$ OH. The amount of MVK that is injected in the model is adjusted to the increase in OH reactivity during the time of injection. The 10 % discrepancy to measured MVK mixing ratios is within the uncertainty of the PTR-TOF-MS calibration. However, the decay of the measured ~~[MVK]~~ is slightly faster than the decay in the model specifically during the first two hours of oxidation. This corresponds to modelled OH concentrations, which are up to a factor of 2 smaller than measured OH ~~concentrations~~ during 30 this time. At later times of the experiment, measured and modelled ~~[OH]~~ as well as the relative change in ~~[MVK]~~ are matched. Differences between measured and modelled OH ~~concentrations~~ in the first phase of the experiment are accompanied by HO₂ concentrations, which are approximately $2 \times 10^8 \text{ cm}^{-3}$ lower in the model compared to measured values. Measured ~~[HO₂]~~ increases from $(4-8) \times 10^8 \text{ cm}^{-3}$ during the first 2 hours. Modelled values match measurements at later times of the experiment like observed for ~~[OH]~~. The concurrent underestimation of ~~[OH]~~ and ~~[HO₂]~~ suggests that a radical 35 source is missing in the model.

In a sensitivity run (MCM*), modifications of reactions that are reported in literature, but do not directly affect the fate of RO₂ are implemented:

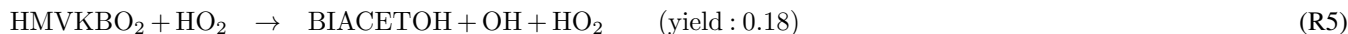
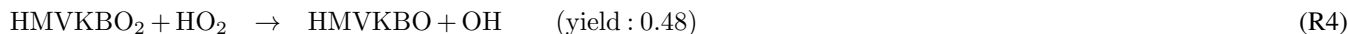
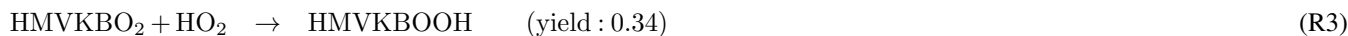
- The reaction rate constant of glycolaldehyde with OH is lowered by 20 % following measurements by Karunanandan et al. (2007).
- 5 – Following the results of the product analysis (see above), the branching ratio of Reaction R1 and R2 is changed from 0.3:0.7 to 0.24:0.76 as suggested by Praske et al. (2015).
- OH yield from ozonolysis of MVK is lowered to 16 % as determined by Aschmann et al. (1996); Paulson et al. (1998) compared to 36 % assumed in the MCM.

Details are listed in Table 1. Differences to results with the current version of the MCM are rather small (not shown here) so
10 that these modifications do not significantly affect the model–measurement agreement. They are included in the sensitivities model runs shown below.

4 Discussion

4.1 Additional RO₂+HO₂ reactions

Product yields indicate that an additional source for glycolaldehyde that is not included in the MCM is required to explain
15 observations in the low NO experiment. This is consistent with chamber experiments by Praske et al. (2015), which were performed under conditions that RO₂ exclusively reacted with HO₂. In this case, the glycolaldehyde yield is expected to be small, because glycolaldehyde is mainly formed in the subsequent reaction of RO₂ with NO (Fig. 1). In that study, also a C₄α–diketone (CH₃COCOCH₂OH, MCM name: BIACETOH) was measured with a yield of 0.14. From these product yields, the authors suggest that there are reaction channels of the HMVKBO₂ plus HO₂ reaction in addition to the formation
20 of hydroxyperoxides (Praske et al., 2015):



Including Reactions R3–R5 in the MCM* mechanism (M1 Table 1) results in an improved description of observations
25 for the low NO experiment (Fig. 4). Modelled [OH] agrees with measurements within 20 %. The largest increase of modelled [OH] is obtained 1 to 2 hours after starting the oxidation due to the additional radical regeneration from Reactions R4 and R5. The model–measurement agreement is worsened for [RO₂] compared to the MCM model run, but still within the uncertainty of the measurement. The additional production of glycolaldehyde from the subsequent chemistry of Reaction R4 brings modelled organic product species into agreement with measurements within 20 % so that all observations
30 except for [HO₂] can be explained by the new reactions of HMVKBO₂ with HO₂. HO₂ concentrations, however, are

still significantly lower in the model compared to measurements. Results are consistent with experiments by Praske et al. (2015), but a potential underestimation of $[\text{HO}_2]\text{HO}_2$ could not be recognized, because HO_2 radicals were not measured in their experiments.

4.2 RO_2 isomerization reactions

5 RO_2 isomerization reactions have been shown to be of importance for the atmospheric fate of RO_2 from isoprene (Peeters et al., 2014). Peeters et al. (2009) also suggested from quantum-chemical calculations that HMVKBO_2 undergoes a fast 1,5-H shift with subsequent decomposition (Fig. 1 and Table 1):

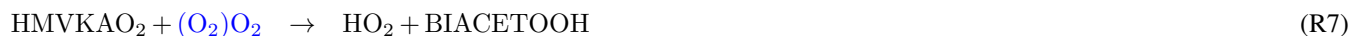


Here, the possibility of RO_2 isomerization reactions for both major RO_2 species formed from the reaction of MVK with OH were investigated in detail by means of quantum-chemical calculations.

Table 2 shows the reaction pathways that were examined for the HMVKAO_2 and HMVKBO_2 peroxy radicals. More information can be found in the Supporting Information. For both radicals, 1,5-H-migration of the hydroxyl H-atom is energetically most favourable with a barrier of 22 kcal mol^{-1} . The predicted reaction rate constant remains below $5 \times 10^{-4} \text{ s}^{-1}$, mostly due to limited tunnelling owing to the large reaction endothermicity, and the broad energy barrier protruding less than 2 kcal mol^{-1} above the reaction products. ~~owing mostly to limited tunnelling due the large endothermicity, the broad energy profile, and limited protruding section.~~ The concomitant low reverse energy barrier for the reverse H-migration in the product also implies that the reaction might be competitive against the alkoxy product decomposition with estimated barriers 4 kcal mol^{-1} (Vereecken and Peeters, 2009). ~~possibly be reversible prior to alkoxy radical decomposition.~~ Most of the other reactions considered are several orders of magnitude slower and can be neglected. The predicted rates for all processes considered remain over an order of magnitude below that required to fit the measured OH, HO_2 , and glycolaldehyde concentrations so that these H-migration reactions do not have a discernible impact on the MVK oxidation chemistry radical budget or product yields at room temperature. As such, the subsequent chemistry after these reactions was not investigated.

The isomerization rate constant estimated by Peeters et al. (2009) for Reaction R6 of 0.01 s^{-1} is about two orders of magnitude faster than calculated here. This is mainly related to the higher energy barriers found at the levels of theory applied in this work. The small reaction rate constant for this reaction is consistent with the small product yield for methylglyoxal found in the low NO experiment, which would need to be significantly higher than calculated, if Reaction R6 was competitive with the other RO_2 reaction channels. A similar conclusion was drawn from product yields obtained in the study by Praske et al. (2015).

The fastest reaction rate coefficient of RO_2 isomerization reactions calculated here is found to be the HMVKAO_2 1,4-H-migration of the hydrogen atoms adjacent to the $-\text{OH}$ group, followed by H abstraction at the $-\text{OH}$ site by O_2 forming HO_2 together with a bi-ketone (named BIACETOOH in the MCM):



A reaction rate constant of 0.003 s^{-1} is calculated making this reaction competitive with the reaction of HVMKAO_2 with HO_2 and NO in the low NO experiments. Approximately 20 to 30 % of the HVMKAO_2 undergoes the 1,4-H shift reaction in this experiment. However, the resulting increase of the HO_2 concentration is rather small ($< 0.5 \times 10^8 \text{ cm}^{-3}$) because of the small HVMKAO_2 yield in the reaction of MVK with OH . This reaction is included in the model sensitivity runs M2.

5 4.3 Potential additional RO_2 reaction channel

A fast conversion of HVMKBO_2 to HO_2 would be required to fit HO_2 measurements. Glycolaldehyde would need to be a co-product to match measured values:



X represents an unknown reaction partner not needed in case of a unimolecular reaction. M2 in Fig. 4 gives the model result, if Reaction R8 is included in the MCM* in addition to the 1,4-H shift of HVMKAO_2 (Reaction R7) and the additional channels of the reaction of HVMKBO_2 with HO_2 (Reactions R3–R5).

In order to fit HO_2 and glycolaldehyde concentration measurements, a reaction rate constant of $0.006 \pm 0.004 \text{ s}^{-1}$ is required. This reaction rate makes the Reaction R8 competitive with the reaction of RO_2 with NO (reaction rate approximately 0.004 s^{-1}) and HO_2 (reaction rate approximately 0.008 s^{-1}). In M2, 40 % of HVMKBO_2 reacts with HO_2 and 30 % of HVMKBO_2 forms directly HO_2 and glycolaldehyde in Reaction R8 for conditions of this experiment. In comparison, 60 % of HVMKBO_2 reacts with HO_2 in the model run M1. The overall effect on the $[\text{OH}]/[\text{OH}]$, however, is similar in both model runs so that modelled $[\text{OH}]/[\text{OH}]$ becomes consistent with measurements. This is due to the conversion of HO_2 produced in Reaction R8 to OH . Overall, however, the major difference in the results of M1 and M2 is in the improved model–measurement agreement of $[\text{HO}_2]/[\text{HO}_2]$.

Unfortunately, experiments here do not give hints about the exact nature of Reaction R8. Quantum-chemical calculations (see above) shows that Reaction R8 cannot be a unimolecular reaction such as H-atom migration, because they are not fast enough to compete with other RO_2 reaction channels. Photolysis of RO_2 that could result in OH/HO_2 have been observed for acetylperoxy radicals (Cox et al., 1990) and isoprene derived RO_2 (Hansen et al., 2017). However, the reaction rate constant of $0.006 \pm 0.004 \text{ s}^{-1}$ needed here to explain observations would require an unrealistically high absorption cross section. A reaction partner in Reaction R8 could also be a RO_2 radical. In this case, however, products of the HVMKBO_2 plus RO_2 reaction that are assumed in the MCM would need to be changed according to Reaction R8 and the reaction rate constant would need to be increased by a large factor of 20 to 50 compared to recommendations for RO_2 self-reaction rate constants in order to make this reaction competitive with the other RO_2 reaction channels.

4.4 Model–measurement agreement of nitrogen oxide species

So far, only radicals and organic products have been discussed. However, there is also disagreement between measured and modelled NO_2 mixing ratios. The NO_2 concentration produced by the model is 30 % smaller in the low NO experiment (23 May 2017)) compared to measured values. This discrepancy increases to 40 %, if the OH concentration and therefore the MVK

oxidation rate is increased. This is due to the increased production of peroxy radicals, which form peroxy acyl nitrate (PAN) or PAN like species, which act as nitrogen oxide reservoirs. Acetylperoxy radicals forming PAN are mainly produced from HVMKBO₂ as a co-product of glycolaldehyde, but another PAN-like species (MCM name PHAN) is additionally produced by the oxidation of glycolaldehyde. If no production of PHAN is assumed, measured and modelled NO₂ mixing ratios agree within 100 pptv (M2 in Fig. 4), less than the accuracy of the NO_x formation in the chamber. However, also reduction of the production of acetylperoxy radicals could improve the model–measurement agreement. The change in NO and peroxy radical concentrations is rather small, because of the suppression of NO by O₃ and the overall small turnover rate of HO₂ and NO. More specific experiments concerning the NO_x budget would be required to decide, which NO_x reservoir species is overestimated by the model.

10 4.5 OH budget analysis

OH is in steady state because of its short lifetime, so that its rates of production and destruction are equal. ~~OH production and destruction are in equilibrium due to the short lifetime of OH.~~ Therefore, OH reactivity together with OH concentration measurements allows determination of the total OH production rate from only two measured quantities. Under conditions with high NO concentrations, only few chemical reactions are typically controlling the OH production. The dominating process is usually the recycling of HO₂ by its reaction with NO. In addition, photolysis of ozone and HONO make significant contributions. For low NO conditions and in the presence of high VOC concentrations, field and chamber experiments often show larger total OH productions rates (derived from measured OH and OH reactivity) than can be explained by the above processes. Under these conditions, other OH sources linked to the degradation of VOCs become relevant.

Figure 5 shows the OH budget for the low NO experiment (23 May 2017) using model results (M2, Table 1) to calculate contributions to the OH production. In addition, total OH production is calculated from measured and modelled OH concentrations and OH reactivity. Results from calculations using either modelled or measured values give similar numbers that agree within the uncertainty of the calculation of 20 %.

The OH production rate is dominated by HO₂ recycling reactions and primary OH production (HONO and O₃ photolysis). These contributions explain 70 to 80 % of the total OH production during the MVK oxidation. The model would give lower OH production compared to calculations using measurements if Reaction R8 was not included because HO₂ concentrations and therefore OH recycling by HO₂ would be underpredicted in this case. This reaction is responsible for approximately half of the HO₂ concentration during the first two hours of MVK oxidation. This demonstrates the importance of including all HO₂ sources in models.

Another 10 to 15 % of the total OH production rate is due to the OH formation from the additional HO₂ plus RO₂ reaction channel suggested by Praske et al. (2015) (Reaction R4). A large number of other OH forming reactions included in the model such as photolysis of hydroperoxides fills the remaining gap between these major contributions and the total calculated OH production.

5 Summary and conclusions

The photooxidation of MVK, one of the major oxidation products of isoprene, was investigated at atmospheric conditions in the simulation chamber SAPHIR. NO was varied from high to low concentrations. For high NO, RO₂ is mainly lost in the reaction with NO and current chemical models can describe radical concentrations within 20 %. Product yields of the major oxidation products glycolaldehyde (0.65 ± 0.14) and methylglyoxal (0.19 ± 0.03) are consistent with previous measurements (Tuazon and Atkinson, 1989; Galloway et al., 2011; Praske et al., 2015).

OH radical concentrations are underestimated (maximum factor 2) by the MCM at low NO concentrations (< 100 pptv), when other RO₂ reaction channels can compete with the reaction of RO₂ with NO. At the same time, also HO₂ and glycolaldehyde concentrations are smaller in the model compared to measurements. Only part of the model–measurements discrepancies can be explained by findings in recent studies investigating the MVK photooxidation. The higher glycolaldehyde yield is consistent with a study by Praske et al. (2015). The additional channels for the RO₂ plus HO₂ reaction suggested by these authors can reproduce glycolaldehyde and OH concentrations, but do not explain the model–measurement discrepancy for replaced[HO₂]HO₂.

The possibility of RO₂ isomerization reactions for both major RO₂ species formed from the reaction of MVK with OH were investigated in detail by means of quantum-chemical calculations. Additional HO₂ can be produced from the 1,4-H shift reaction of HVMKAO₂. The reaction rate constant of 0.003 s⁻¹ is competitive with other RO₂ reaction channels at low NO conditions. The overall impact, however, is small due to the small HVMKAO₂ yield. Other reactions considered here can be neglected for atmospheric conditions. This also includes the isomerization reaction suggested by Peeters et al. (2009) (Reaction R6). The rate constant for this reaction is about two orders of magnitude smaller than calculated by Peeters et al. (2009) due to the higher energy barriers found at the higher levels of theory applied in this work.

Because HO₂ and glycolaldehyde concentrations are underestimated at the same time, a reaction that converts RO₂ to HO₂ and glycolaldehyde (Reaction R8) would explain observations in these experiments. A reaction rate constant of 0.006 ± 0.004 s⁻¹ is required to bring measured and modelled values into agreement. Unimolecular H-shift reactions are found to be too slow. Alternatively, reaction of HMKBO₂ with RO₂ that would produce directly HO₂ and glycolaldehyde would explain [HO₂]HO₂ observations and would give similar OH and glycolaldehyde concentrations as the mechanism by Praske et al. (2015). However, not only product species would need to be different from what is described in the MCM, but also the reaction rate constants would need to be increased by a large factor of 20 to 50 for the HMKBO₂ plus RO₂ reaction. More studies will be needed to explore the exact role of HO₂ in the MVK oxidation scheme. In addition, open questions remain concerning the fate of nitrogen oxides in the MVK oxidation scheme. The MCM suggests the built-up of nitrogen oxide reservoirs by the formation of PAN and PAN-like species. Experiments here indicate that these reservoirs are less important.

The need for an additional HO₂ source was also found in the oxidation of monoterpenes. Field studies, in which OH reactivity was dominated by monoterpenes, showed that models underestimate HO₂ and OH concentrations (Kim et al., 2013; Hens et al., 2014). A chamber study investigating the photochemistry of β-pinene found that an additional HO₂ source is

required to explain observed HO₂ and OH and suggested a rearrangement of radical intermediates as explanation (Kaminski et al., 2017).

The impact on the OH recycling efficiency and observed organic products in the MVK oxidation are the same regardless whether OH is directly produced from HO₂ plus RO₂ like in the Praske et al. (2015) mechanism or if OH is produced from enhanced HO₂ as suggested by experiments here. The enhanced OH recycling is demonstrated in this study by the direct quantification of the OH radical concentration during the photochemical oxidation of MVK. Similar as for isoprene (Peeters et al., 2014; Fuchs et al., 2013) and the second major organic product from isoprene oxidation, methacrolein, (Crouse et al., 2011; Fuchs et al., 2014), HO_x radicals are faster recycled in the MVK oxidation scheme than previously assumed. For all three species, OH concentrations are found to be a factor 2 to 3 higher than calculated by models for atmospheric conditions with low NO concentrations. Current state-of-the-art models increased already OH production for isoprene and methacrolein oxidation by including additional reaction pathways. The study here shows that this is also needed for the MVK oxidation scheme.

Competing interests. The authors declare to have no competing interests.

Data availability. Data of the experiments in the SAPHIR chamber used in this work is available on the EUROCHAMP data homepage (<https://data.eurochamp.org/>).

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Table 1. Changes of reactions and additional reactions applied to the MCM.

reaction	reaction rate constant	reference
MCM*:		
R1: OH+MVK→HMKVKA ₂ O ₂	$0.24 \times 2.6 \times 10^{-12} \exp(610\text{K}/\text{T}) \text{ cm}^3 \text{ s}^{-1}$	Praske et al. (2015)
R2: OH+MVK→HMKVKB ₂ O ₂	$0.76 \times 2.6 \times 10^{-12} \exp(610\text{K}/\text{T}) \text{ cm}^3 \text{ s}^{-1}$	Praske et al. (2015)
HOCH ₂ CHO+OH→products	$8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	Karunanandan et al. (2007)
MVK+O ₃ →OH+products	$0.16 \times 8.5 \times 10^{-16} \exp(-1520\text{K}/\text{T})$	Aschmann et al. (1996); Paulson et al. (1998)
M1 (includes MCM*):		
R3: HMKVKB ₂ O ₂ +HO ₂ →HMKVKB ₂ OOH	$0.34 \times 0.625 \text{ KRO2HO2}^a$	Praske et al. (2015)
R4: HMKVKB ₂ O ₂ +HO ₂ →HMKVKB ₂ O+OH	$0.48 \times 0.625 \text{ KRO2HO2}^a$	Praske et al. (2015)
R5: HMKVKB ₂ O ₂ +HO ₂ →BIACETOH+OH+HO ₂	$0.18 \times 0.625 \text{ KRO2HO2}^a$	Praske et al. (2015)
M2 (includes M1 and MCM*):		
R7: HMKVKA ₂ O ₂ →HO ₂ +BIACETOOH	0.003 s^{-1b}	this work
R8: HMKVKB ₂ O ₂ (+X) ^c →HO ₂ +HOCH ₂ CHO +HCHO+CO	$(0.006 \pm 0.004) \text{ s}^{-1}$	this work
HOCH ₂ CO ₃ + NO ₂ →PHAN	0	this work

^a value from MCM: $0.625 \text{ KRO2HO2} = 2.91 \times 10^{-13} \exp(1300\text{K}/\text{T}) \text{ cm}^3 \text{ s}^{-1}$ (MCM, 2017)

^b from theoretical calculation (see Table 2)

^c a reaction partner could not be determined from these experiments

Table 2. H-migration and HO₂ elimination in hydroxy–MVK–peroxy radicals. Barrier height E_b , reaction energy E_{react} and the rate coefficient k at a temperature of 300 K are listed. Arrhenius expressions for a temperature range between 200 and 400 K are available in the Supporting Information.

Reactant	Reaction class	Product	E_b kcal mol ⁻¹	E_{react} kcal mol ⁻¹	k (300K) s ⁻¹
HMVKAO₂	–OH 1,5-H-shift	CH ₃ –C(=O)–CH(O•)–CH ₂ OOH	21.6	20.42,40	5.0 × 10 ⁻⁴
	α–OH 1,4-H-shift	CH ₃ –C(=O)–C•(OH)–CH ₂ OOH	24.7	-6.2	3.3 × 10 ⁻³
	–CH ₃ 1,6-H-shift	C•H ₂ –C(=O)–CH(OH)–CH ₂ OOH	23.1	10.2	5.9 × 10 ⁻⁴
HMVKBO₂	–OH 1,5-H-shift	CH ₃ –C(=O)–CH(OOH)–CH ₂ O•	22.5	20.6	8.8 × 10 ⁻⁵ ^a
	α–OH 1,4-H-shift	CH ₃ –C(=O)–CH(OOH)–C•HOH	25.1	6.5	3.2 × 10 ⁻⁵
	–CH ₃ 1,6-H-shift	C•H ₂ –C(=O)–CH(OOH)–CH ₂ OH	27.4	10.0	3.8 × 10 ⁻⁵
	HO ₂ elimination	CH ₃ –C(=O)–CH=CHOH + HO ₂	30.0	-1.5	6.1 × 10 ⁻¹⁰

^a estimated at 0.01 s⁻¹ by Peeters et al. (2009)

Table 3. Yields of organic products from photooxidation of MVK by OH from this work and from literature. Errors of values from this work take into account the accuracy of measurements and precision of the calculation. HCHO is not only produced in the first oxidation step of MVK but also produced in the subsequent oxidation of glycolaldehyde and methylglyoxal. Therefore, the yield can increase over the course of the experiment.

species	yield	$\frac{\text{loss}(\text{RO}_2+\text{HO}_2)}{\text{loss}(\text{RO}_2+\text{NO})}$	reference
HCHO	0.24 ± 0.08^a	2:1 ^c	this work
	0.46 ± 0.04^b	2:1 ^c	this work
	0.73 ± 0.15	1:9	this work
	0.54 ± 0.04	0:1	Tuazon and Atkinson (1989)
	0.28	0:1	Grosjean et al. (1993)
MGLYOX	0.05 ± 0.02	2:1 ^c	this work
	0.04 ± 0.01	1:0	Praske et al. (2015)
	0.19 ± 0.03	1:9	this work
	0.24 ± 0.001	0:1	Galloway et al. (2011)
	0.25 ± 0.08	0:1	Tuazon and Atkinson (1989)
	0.32	0:1	Grosjean et al. (1993)
HOCH ₂ CHO	0.37 ± 0.09	2:1 ^c	this work
	0.38 ± 0.05	1:0	Praske et al. (2015)
	0.65 ± 0.14	1:9	this work
	0.74 ± 0.06	0:1	Praske et al. (2015)
	0.67 ± 0.04	0:1	Galloway et al. (2011)
	0.64 ± 0.16	0:1	Tuazon and Atkinson (1989)
	0.60	0:1	Grosjean et al. (1993)

^a approximately after 1 hour of oxidation

^b after 3 hours of oxidation

^c RO₂+RO₂ contribution to the total RO₂ loss: <20 %

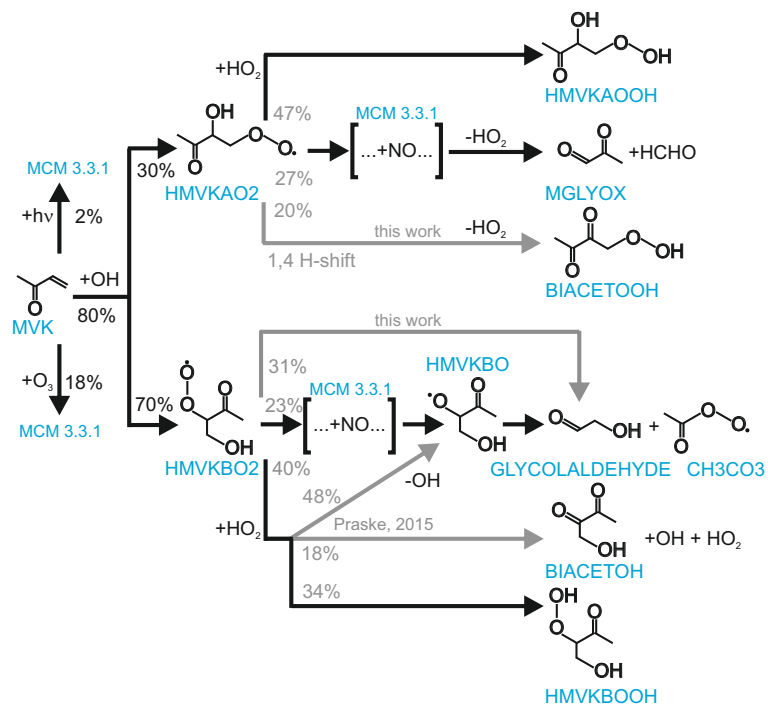


Figure 1. Simplified OH oxidation scheme for MVK. Names of compounds are assigned similar to MCM. Modifications to the MCM mechanism (M2) applied in model sensitivity runs M1 and M2 (Table 1) are shown as grey arrows. Reaction yields are calculated for conditions of the experiment with low NO (high ozone concentrations) on 23 May 2017. Grey numbers refer to model run M2.

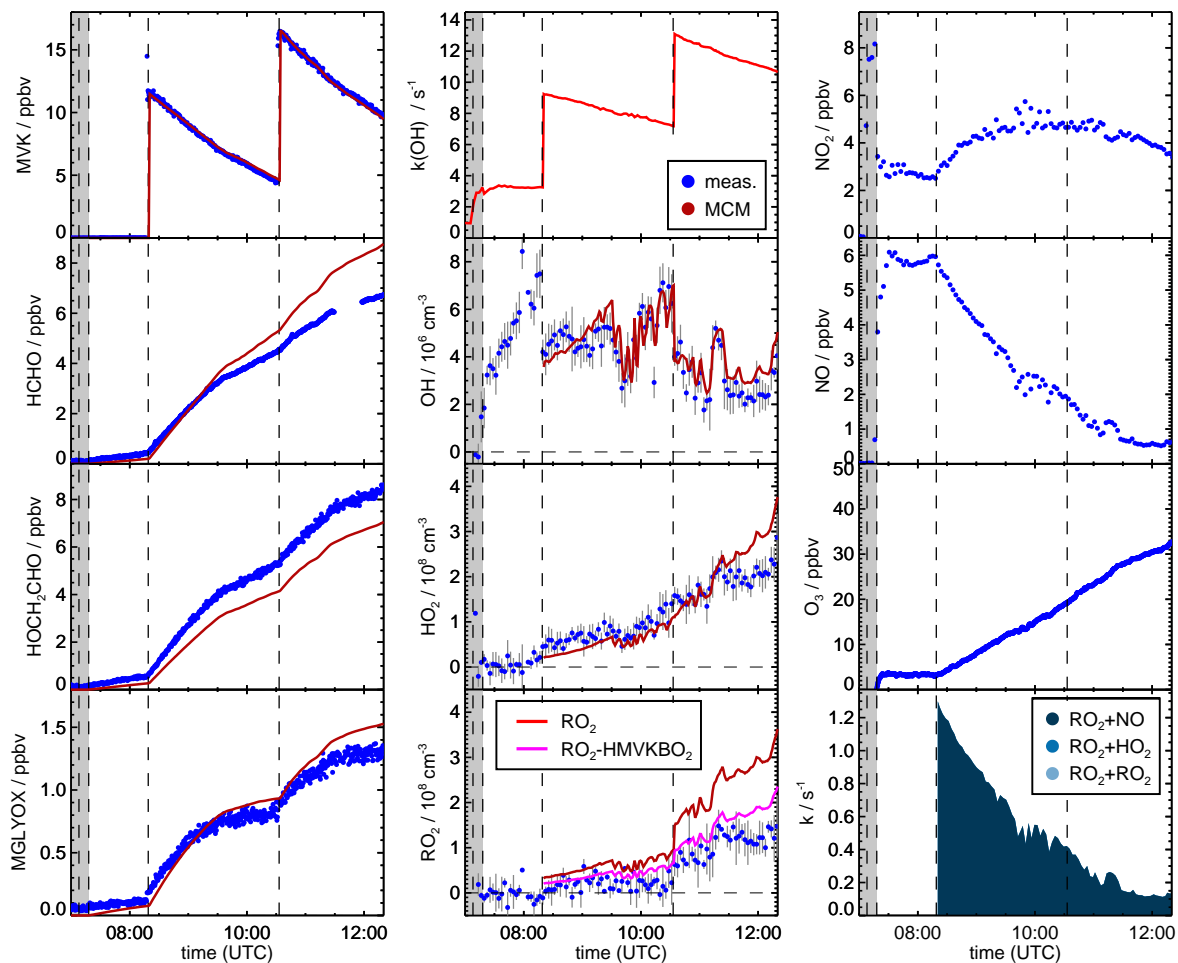


Figure 2. Time series of radicals, inorganic and organic species during the MVK photooxidation for the high NO experiment (20 August 2014) together with results from model calculations applying MCM. Dark shaded areas indicate the time before opening the chamber roof and vertical dashed line times when trace gases were injected into the chamber. OH reactivity was not measured during this experiment. NO, NO₂ and O₃ are constrained to measurements in the model. RO₂ loss rates (most lowest right panel) are calculated from modelled HO₂, RO₂ and NO concentrations. However, contributions from the reactions with RO₂ and HO₂ or RO₂ are too small to be visible. Modelled acetic acid concentrations are small compared to modelled glycolaldehyde concentrations (measured together in the PTR-TOF-MS).

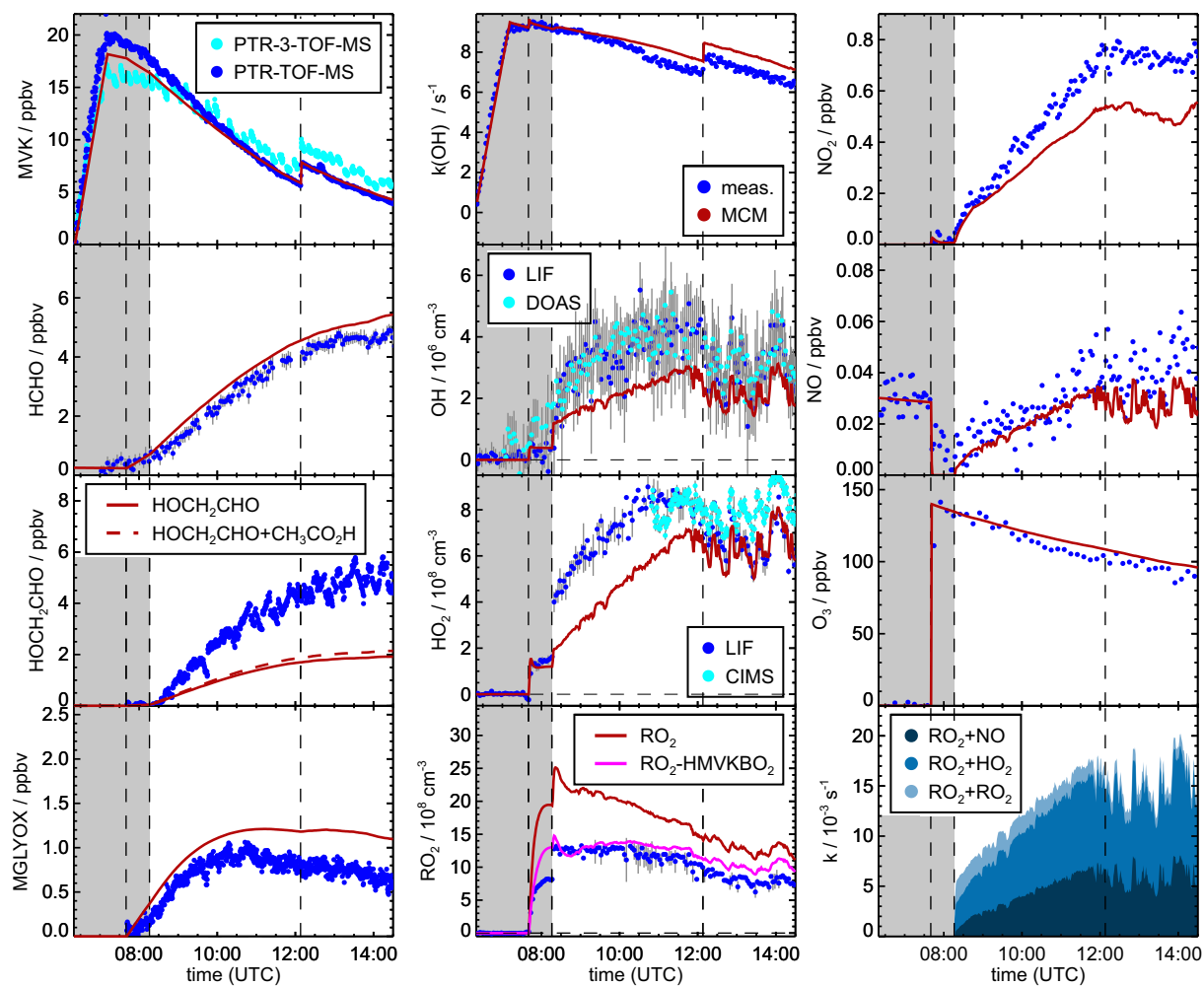


Figure 3. Time series of radicals, inorganic and organic species during the MVK photooxidation at low NO (23 May 2017) together with results from model calculations applying MCM. Dark shaded areas indicate the time before opening the chamber roof and vertical dashed line times when trace gases were injected into the chamber. RO₂ loss rates (most lowest right panel) are calculated from modelled HO₂, RO₂ and NO concentrations.

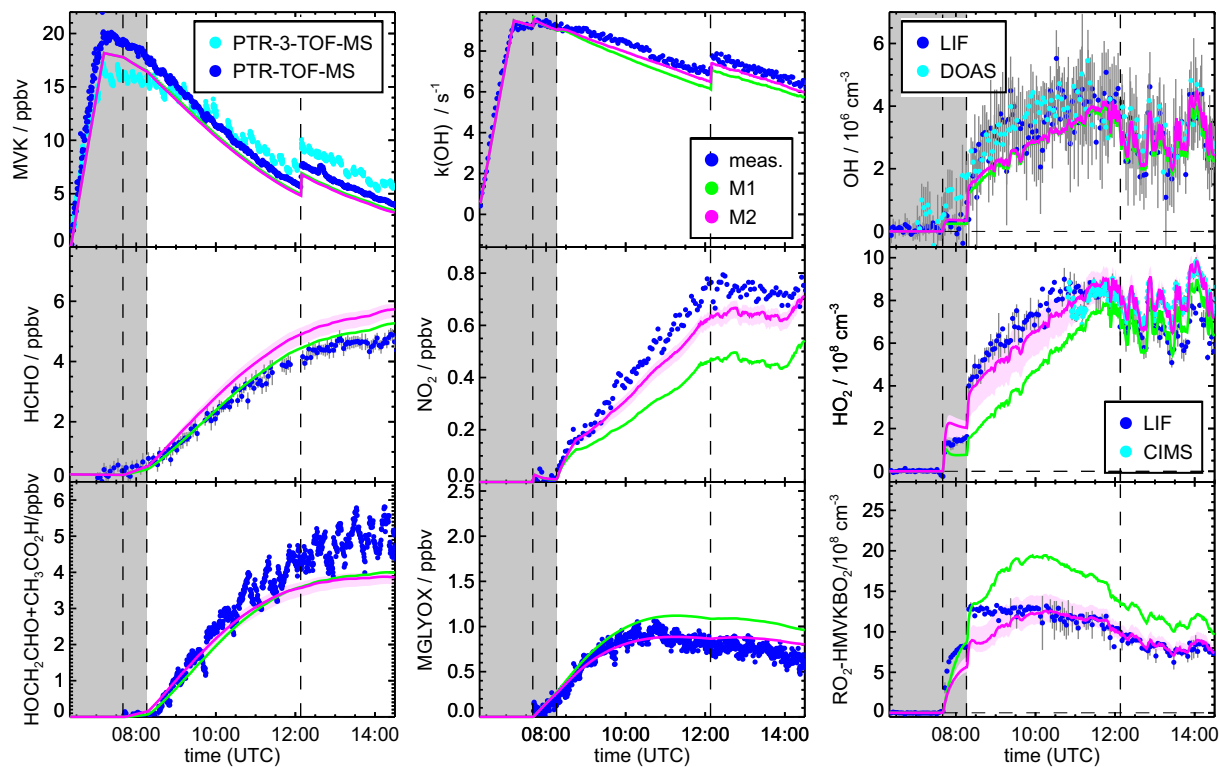


Figure 4. Time series of radicals, inorganic and organic species during the MVK photooxidation at low NO (experiment on 23 May 2017). Dark shaded areas indicate the time before opening the chamber roof. Model sensitivity runs M1 and M2 include modifications listed in Table 2.

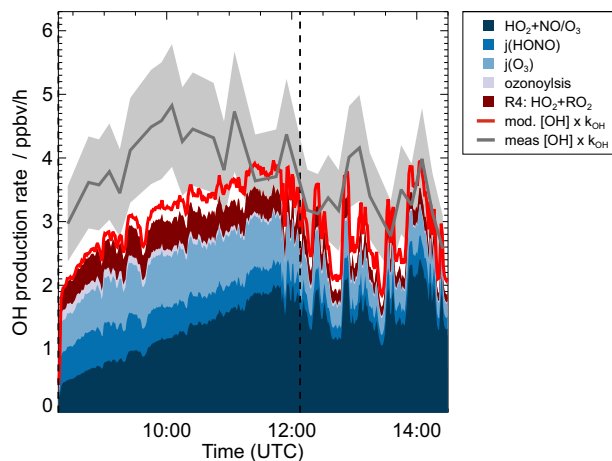


Figure 5. OH budget during the experiment at low NO concentration (23 May 2017) for the period, when MVK photooxidation took place. The vertical dashed line indicates when MVK was reinjected into the chamber. Red and blue coloured areas add contributions to the OH production calculated from the model results (M2 sensitivity run in Fig. 4). The contribution RO_2+HO_2 refers to the OH production from Reaction R4. In addition to modelled OH production contributions, total OH production calculated from the product of OH concentration and OH reactivity (k_{OH}) is shown. These quantities are either taken from the model results (M2) or from measurements. The coloured grey area gives the uncertainty of the total OH production calculation, if measured OH concentrations and measured OH reactivity are used.

Supporting Information to “Investigation of the oxidation of methyl vinyl ketone (MVK) by OH radicals in the atmosphere simulation chamber SAPHIR”

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1 Additional Figures

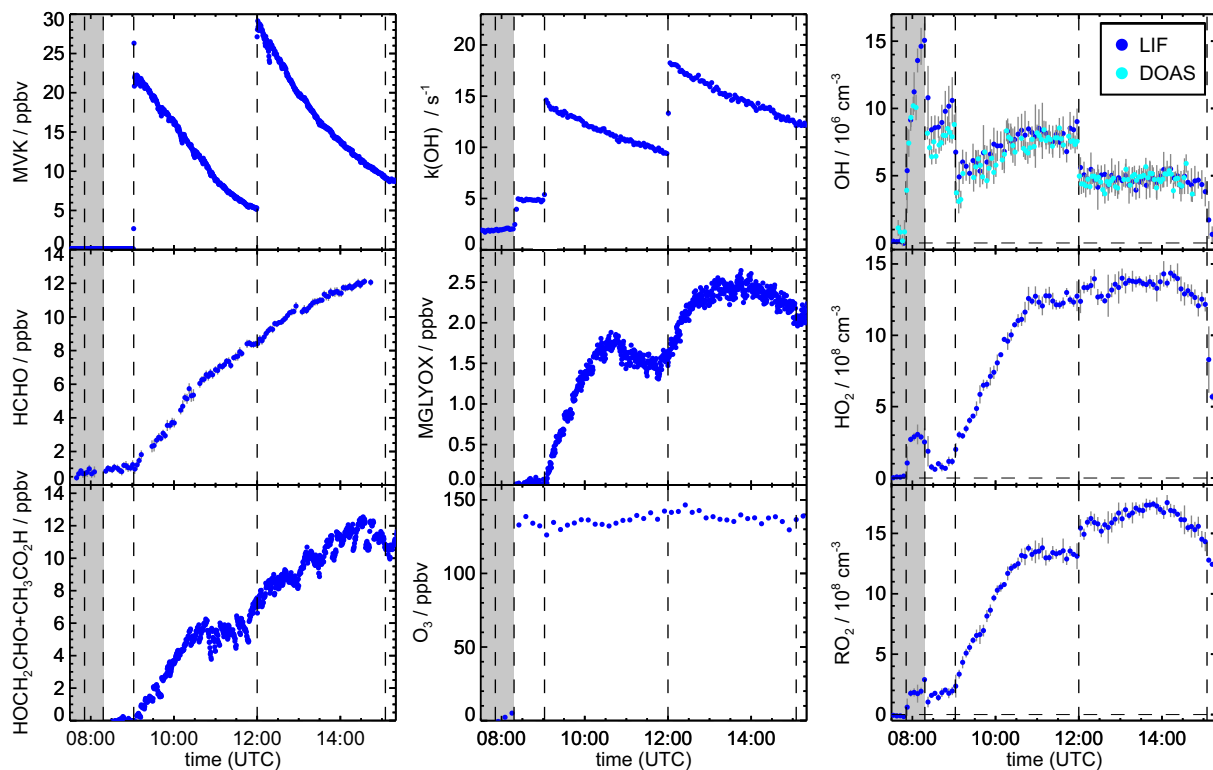


Figure 1. Time series of radicals, inorganic and organic species during the MVK photooxidation for the high NO experiment (17 May 2017). Dark shaded areas indicate the time before opening the chamber roof and vertical dashed line times when trace gases were injected into the chamber. Model calculations were not performed due to the lack of reliable NO_x measurements in this experiment. Approximately 8 ppbv NO₂ was injected at the beginning of the experiment.

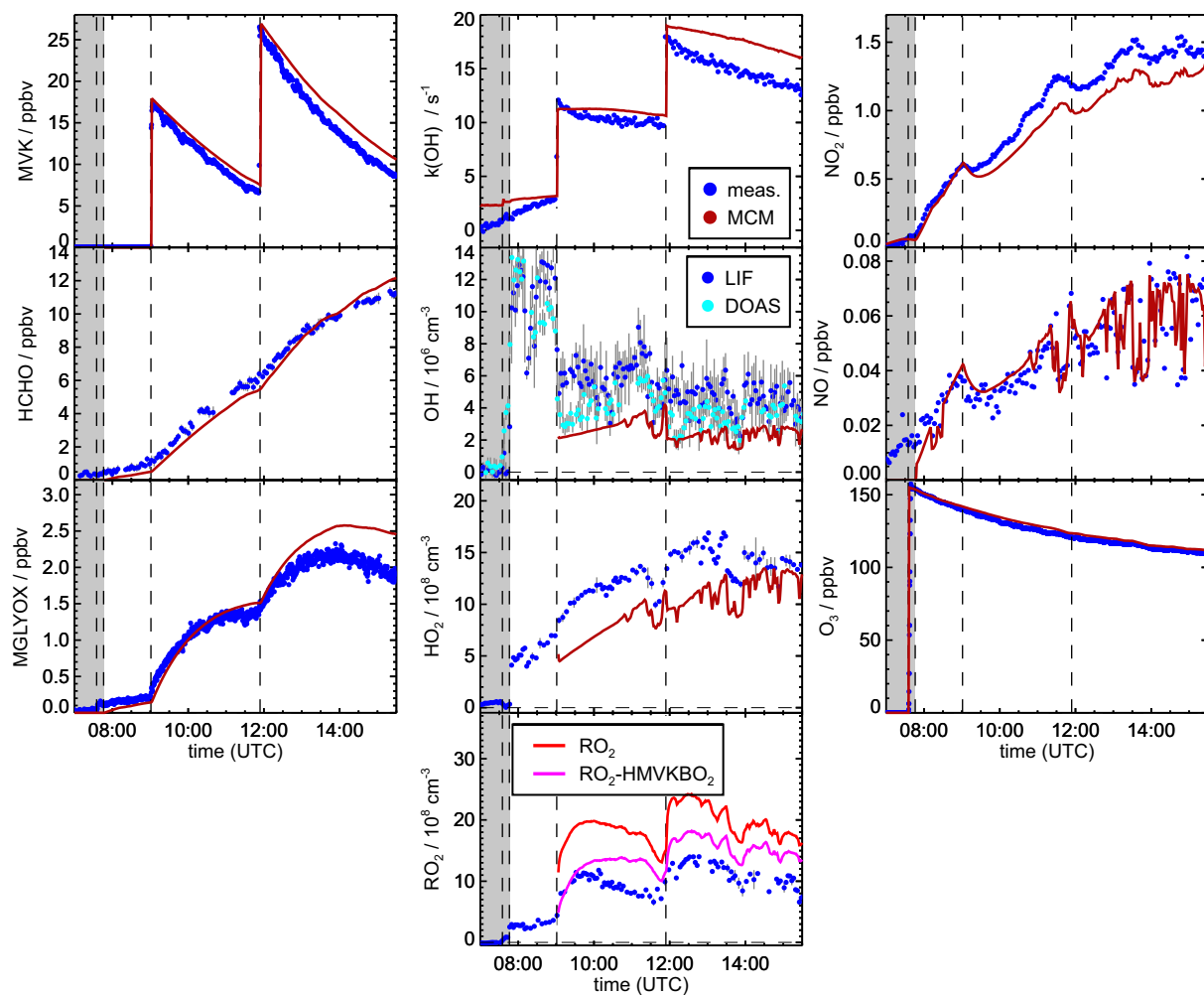


Figure 2. Time series of radicals, inorganic and organic species during the MVK photooxidation for the low NO experiment (23 June 2016) together with results from model calculations applying MCM. Dark shaded areas indicate the time before opening the chamber roof and vertical dashed line times when trace gases were injected into the chamber. Glycolaldehyde could not be derived from PTR-TOF-MS measurements for this experiment because no calibration was available.

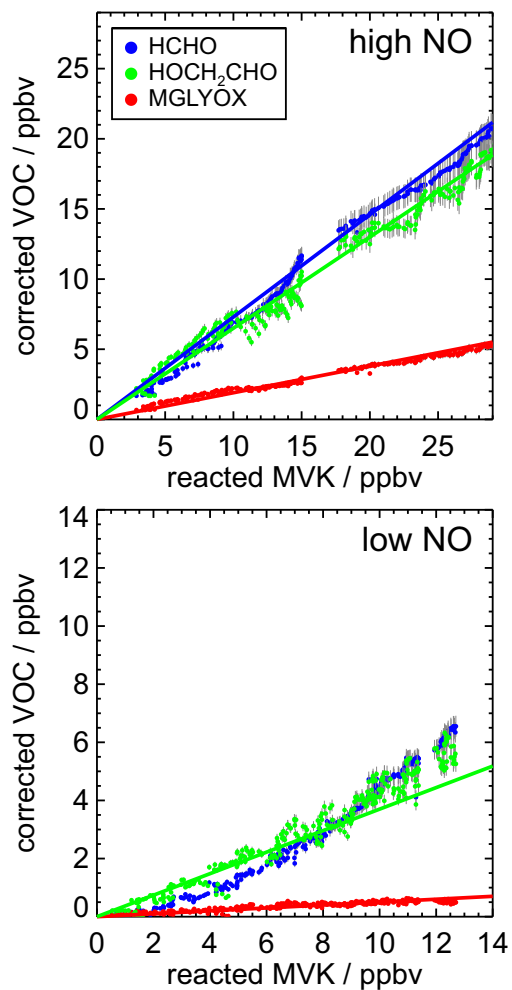


Figure 3. Corrected product concentrations versus the MVK that reacted away. Corrections are applied to account for production not connected to the oxidation of MVK (small chamber source) and additional loss processes (reaction with OH, photolysis). The slope gives the product yield of the organic compound in the MVK reaction with OH

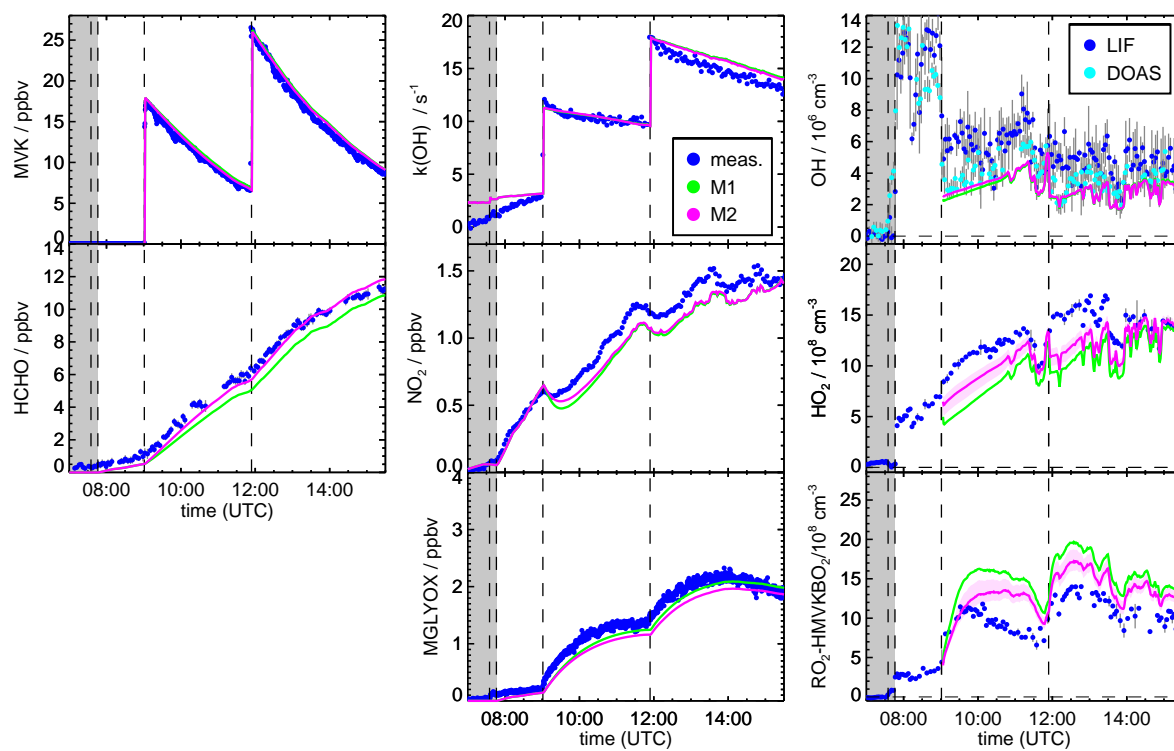


Figure 4. Time series of radicals, inorganic and organic species during the MVK photooxidation at low NO (experiment on 16 June 2016). Dark shaded areas indicate the time before opening the chamber roof and vertical dashed line times when trace gases were injected into the chamber. Model sensitivity runs include additional reaction pathways listed in Table 2 in the main paper.

2 Theoretical analysis of unimolecular reactions of the primary peroxy radicals

2.1 Theoretical methodology

The geometries of the reactants and transition states are optimized at the M06-2X/cc-pVTZ level of theory (Dunning, 1989; Zhao and Truhlar, 2008), exhaustively searching the entire conformer space afforded by the internal rotors. The lowest-lying structures, i.e those contributing 0.1 % to the population at 300 K, are then re-optimized at the M06-2X/aug-cc-pVTZ level of theory, and their harmonic vibrational wavenumbers are calculated and scaled by 0.971 (Alecu et al., 2010; Bao et al., 2017). Finally, the relative energies of the barrier heights are refined by CCSD(T)/aug-cc-pVxZ (x=D,T) single point energy calculations (Purvis and Bartlett, 1982) on the most stable conformer for each critical point, and extrapolated to the complete basis set using the aug-Schwartz4(DT) method described by (Martin, 1996). These CCSD(T)/CBS(DT)//M06-2X/aug-cc-pVTZ energies and rovibrational characteristics (see Table 1) are selected for theoretical kinetic calculations.

For the chemically most critical transition state, i.e. the 1,5-H-shift of the hydroxy-H-atom in the HMVKBO₂ radical, we have performed additional calculations using the B3LYP and M05-2X DFT functionals with various basis sets, as well as CBS-QB3, G3X, and G3SX calculations (Becke, 1992; Curtiss et al., 2001; Lee et al., 1988; Montgomery et al., 1999; Zhao et al., 2006). All quantum chemical calculations are performed using the Gaussian-09 program suite (Frisch et al., 2010).

The high-pressure rate coefficients for each of the elementary processes is calculated using multi-conformer canonical transition state theory, MC-CTST (Vereecken and Peeters, 2003; Zheng and Truhlar, 2013), as implemented in our in-house software. The rate is predicted based on a rigid rotor harmonic oscillator paradigm using M06 2X/aug-cc-pVTZ rovibrational characteristics and CCSD(T) barrier heights, where the population includes all conformers that contribute more than 0.1 %. The temperature range considered is 200 to 400 K. Tunnelling is included by asymmetric Eckart tunnelling (Johnston and Heicklen, 1962) with unscaled imaginary frequency, where the conformer-specific reactant and product for the lowest TS are discovered by IRC calculations. The tunnelling correction for the lowest TS is then used for all TS. For one reaction channel, we have also performed WKB tunnelling corrections (Garrett and Truhlar, 1979) based on the M06-2X/aug-cc-pVTZ minimum energy path.

2.2 Theoretical results

Table 1 lists barrier heights for the various reaction pathways studied in this work , with the preferred values shown in Fig. 5. For the 1,5-H-migration in HMVKBO₂, we find that our calculations using a wide range of methodologies yield significantly higher energy barriers than the earlier predictions by Peeters et al. (2009). Partly, this is due to the methodologies used, where the B3LYP functional in particular is known to underestimate H-migration barrier heights, and yield TS geometries that are not ideal for single-point energy calculations. Another reason for the systematic underprediction in the earlier work is that the conformer space of the reactant was not examined exhaustively. Several lower-lying conformers were identified since, leading to a higher effective barrier height and hence lower rate coefficients for all reaction channels. The M05-2X functional seems to overpredict barrier heights somewhat, whereas the M06-2X functional leads to good agreement with higher-level single-

point energy calculations. Extrapolation to the complete basis set limit appears to have only a limited influence, though the computational cost prohibited us from applying basis sets above aug-cc-pVTZ.

The rate coefficient predictions are listed in Table 1 and Table 2. Compared to the earlier predictions by Peeters et al. (2009), we find rate coefficients that are about two orders of magnitude slower; this is mainly related to the higher energy barriers found at the levels of theory applied in this work, as discussed above. Tunnelling has a large contribution for the α -OH 1,4-H-shift and $-\text{CH}_3$ 1,6-H-shift, with rate enhancements between 10^2 and 10^4 ; as expected, HO_2 elimination is not affected much by tunnelling (factor 4 at 300 K) due to its high reduced mass and concomitant low imaginary wavenumber of $\approx 1060i \text{ cm}^{-1}$. Tunnelling has the lowest impact on the $-\text{OH}$ 1,5-H-migrations, with enhancements of a factor 2 to 3 only, with similar values obtained when using Eckart and WKB tunnelling corrections. This is related directly to the high endoenergeticity of the reaction, which leads to a broad energy profile (imaginary wavenumber $\approx 1200i \text{ cm}^{-1}$) with a limited energy range accessible for tunnelling (reverse barrier only $\approx 2.5 \text{ kcalmol}^{-1}$). Despite having the lowest energy barrier of the processes discussed here, its rate coefficient thus remains rather low. The highest rate coefficient is predicted for the 1,4-H-migration of the α -OH hydrogen atom in HMKAO_2 . This channel is entropically slightly more favourable than a 1,5-H-shift, with less degrees of freedom for internal rotation converted to more rigid vibrations in the cyclic transition state. This channel also has the highest tunnelling factor, 2×10^4 at 300 K, using asymmetric Eckart tunnelling.

The two fastest reactions, both H-migrations in the HMKAO_2 radicals lead to a product radical that is stabilized by vinyloxy resonance; delocalization of the unpaired electron only becomes active after the migrating H-atom is transferred to the peroxy group. It is conceivable that an Eckart potential energy barrier shape is not appropriate for these reactions. For example, allyl resonance has been shown to produce a non-Eckart energy profiles, with an minimum energy profile that cannot be reproduced accurately by the Eckart barrier shape (Nguyen et al., 2010; Peeters et al., 2009, 2014). To probe the reliability of the Eckart tunnelling, a zero-curvature tunnelling (ZCT) correction using the WKB methodology was implemented, based explicitly on the shape of the minimum energy path. In both cases, a significantly lower tunnelling correction was found, about an order of magnitude below the Eckart correction at 300 K (see Table 1). The ZCT values are expected to be a lower bound to the tunnelling correction, as corner-cutting will increase tunnelling. The effective rate coefficient is expected to be bracketed by the two tunnelling predictions. As our final rate coefficient prediction, we then employ the geometric average of the two tunnelling corrections, but with a large uncertainty of a factor 5. As none of the reactions studied theoretically in this work are contributing significantly to the oxidation of MVK, we choose not to perform additional calculations to reduce the uncertainty interval further.

Table 1. H-migration and HO₂ elimination in hydroxy–MVK–peroxy radicals. Barrier height E_b and the rate coefficient k at a temperature of 300 K are listed. aVxZ is used as abbreviation for aug-cc-pVxZ ($x = D,T$); CBS(DT) refers to extrapolation to the complete basis set using the aug-Schwartz4(DT) method.

Reactant	Reaction class	Level of theory	E_b kcal mol ⁻¹	$k(300)$ K s ⁻¹	
HMVKAO₂ CH ₃ –C(=O)–CH(OH)–CH ₂ OO•	–OH 1,5-H-shift	CCSD(T)/aVTZ//M06-2X/aVTZ	22.0	2.9×10^{-4}	
		CCSD(T)/CB S(DT)//M06-2X/aVTZ	21.6	5.0×10^{-4}	
	α –OH 1,4-H-shift	CCSD(T)/aVTZ//M06-2X/aVTZ	24.7	1.3×10^{-2}	
		CCSD(T)/CBS(DT)//M06-2X/aVTZ	24.7	1.5×10^{-2}	
	–CH ₃ 1,6-H-shift				7.7×10^{-4} ^a
		CCSD(T)/aVTZ//M06-2X/aVTZ	23.1	1.5×10^{-3}	
		CCSD(T)/CBS(DT)//M06-2X/aVTZ	23.1	1.4×10^{-3}	
					2.5×10^{-4} ^a
HMVKBO₂ CH ₃ –C(=O)–CH(OO•)–CH ₂ OH	–OH 1,5-H-shift	B3LYP/6-31+G(d,p)	17.7 ^b		
		CBS-QB3	21.3 ^b		
		M05-2X/6-31+G(d,p)	24.3		
		M05-2X/aVDZ	24.0		
		M06-2X/cc-pVTZ	22.3		
		M06-2X/aug-cc-pVTZ	22.2		
		CBS-QB3//M05-2X/6-311G(d,p)	23.0		
		CBS-Q//QCISD/6-311G(d,p)	20.6 ^b		
		CBS-APNO	20.0 ^b	7×10^{-3} ^{b,c}	
		CCSD(T)/aVDZ//M05-2X/aVDZ	24.2		
		CCSD(T)/CBS(DT)//M05-2X/6-311G(d,p)	22.4		
		G3X/B3LYP/6-31G(2df,p)	24.7		
	G3SX/B3LYP/6-31G(2df,p)	23.8			
	α –OH 1,4-H-shift	CCSD(T)/aVTZ//M06-2X/aVTZ	22.7	6.0×10^{-5}	
		CCSD(T)/CBS(DT)//M06-2X/aVTZ	22.5	8.8×10^{-5}	
		CCSD(T)/aVTZ//M06-2X/aVTZ	25.2	2.7×10^{-5}	
		CCSD(T)/CBS(DT)//M06-2X/aVTZ	25.1	3.2×10^{-5}	
	–CH ₃ 1,6-H-shift	CCSD(T)/aVTZ//M06-2X/aVTZ	27.4	3.6×10^{-5}	
		CCSD(T)/CBS(DT)//M06-2X/aVTZ	27.4	3.8×10^{-5}	
	HO ₂ elimination	CCSD(T)/aVTZ//M06-2X/aVTZ	29.7	9.5×10^{-10}	
CCSD(T)/CBS(DT)//M06-2X/aVTZ		30.0	6.1×10^{-10}		

^aBased on WKB zero-curvature tunnelling

^bPeeters et al. (2009)

^creported as 0.01 s^{-1} by Peeters et al. (2009)

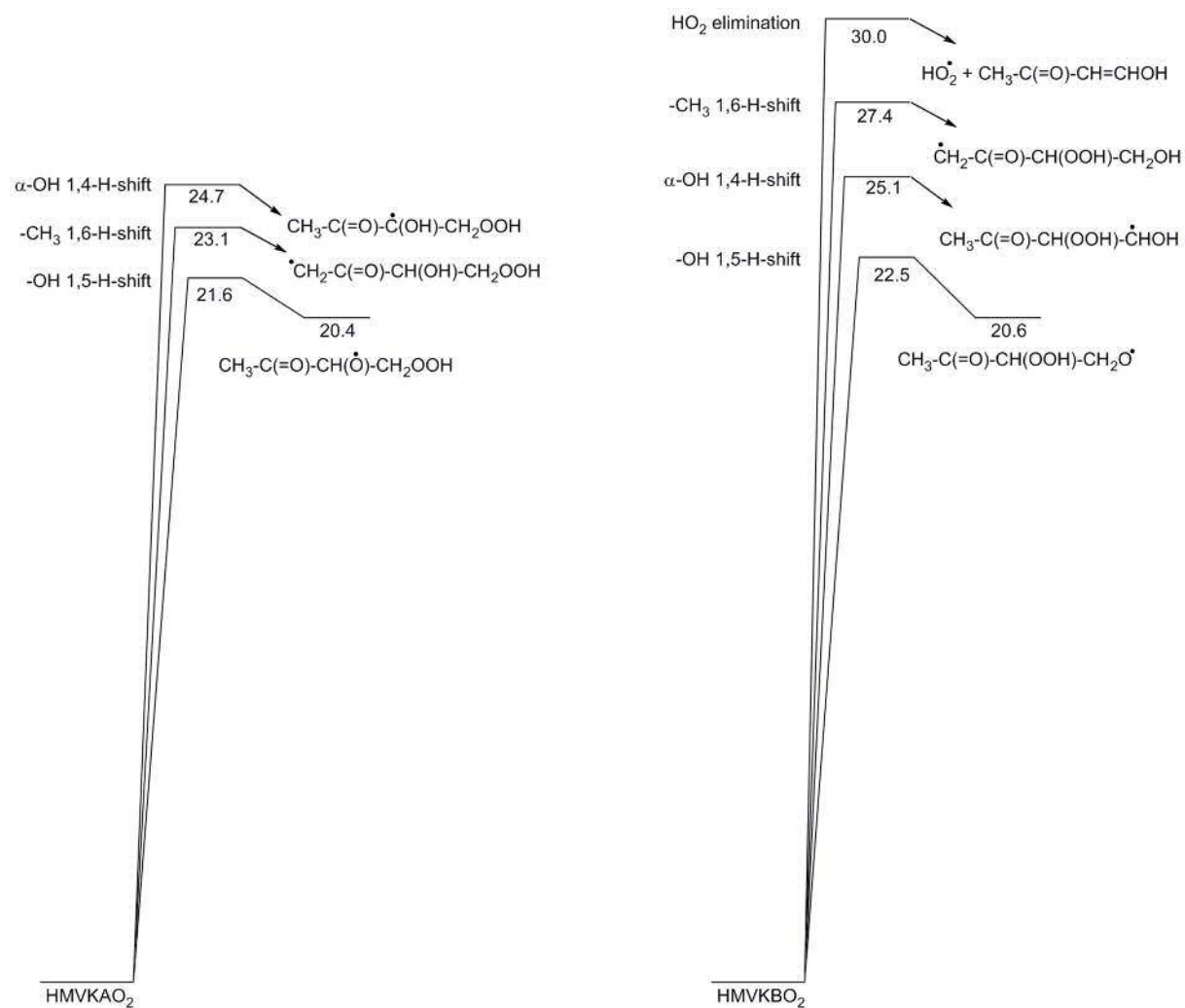


Figure 5. ZPE-corrected potential energy surface at the CCSD(T)/CBS(DT)/M06-2X/aug-cc-pVTZ level of theory, showing the energetics of the HMVKAO₂ and HMVKBO₂ reactions.

Table 2. Temperature dependence of the rate coefficients between 200 and 400 K as a Kooij expression: $k(T) = AT^n \exp(-E_a/T)$. The rates are based on the CCSD(T)/CBS(DT)//M06-2X/aug-cc-pVTZ quantum chemical data.

Reactant	Reaction class	A $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	n	E_a K
HMVKAO_2	-OH 1,5-H-shift	1.25×10^{11}	-0.03	9897
CH ₃ -C(=O)-CH(OH)-CH ₂ OO•	α -OH 1,4-H-shift	4.12×10^{-67}	24.46	-2295
	-CH ₃ 1,6-H-shift	8.97×10^{-29}	12.54	4308
	all unimolecular	7.4×10^{-109}	39.35	-5769
HMVKBO$_2$	-OH 1,5-H-shift	7.13×10^{11}	-0.24	10571
CH ₃ -C(=O)-CH(OO•)-CH ₂ OH	α -OH 1,4-H-shift	3.11×10^{-81}	29.64	-1790
	-CH ₃ 1,6-H-shift	2.05×10^{-57}	21.74	1083
	HO ₂ elimination	2.15×10^{-45}	18.86	7811
	all unimolecular	6.71×10^{-112}	41.14	-3722

^a Geometric average across the Eckart and WKB tunneling corrections

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Quantum chemical data

a. Population analysis at the M06-2X/cc-pVTZ level of theory

Relative energies in kcal mol⁻¹
Population contribution in %

HMVKAO2 Conformer	Erel	%
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HMVKAO2.mppt	0.34	23.2
HMVKAO2.mpmt	0.00	19.4
HMVKAO2.hptp	0.68	13.9
HMVKAO2.mmpt	1.08	8.33
HMVKAO2.mtmt	0.92	8.3
HMVKAO2.hmtp	1.71	3.72
HMVKAO2.hmmm	1.16	3.69
HMVKAO2.mmtt	1.44	3.41
HMVKAO2.mmtm	1.57	3.21
HMVKAO2.mmpm	1.50	2.98
HMVKAO2.mmtm	1.92	2.55
HMVKAO2.hpmm	1.35	1.86
HMVKAO2.http	2.42	1.43
HMVKAO2.mttm	2.91	1.13
HMVKAO2.htmm	2.64	1.05
HMVKAO2.mttt	2.39	1
HMVKAO2.mptt	3.01	0.394
HMVKAO2.tmtm	4.17	0.127
HMVKAO2.htmp	4.16	0.0736
HMVKAO2.hpmt	3.66	0.0597
HMVKAO2.hpmp	3.50	0.0553
HMVKAO2.httm	4.88	0.0445
HMVKAO2.htmt	4.38	0.0366
HMVKAO2.tppp	4.82	0.0153
HMVKAO2.hmmt	4.87	0.0114
HMVKAO2.pmpt	5.19	0.00546
HMVKAO2.pppt	5.65	0.00484
HMVKAO2.ptpt	6.12	0.00369
HMVKAO2.pmpp	6.11	0.00227
HMVKAO2.hppt	6.23	0.0019
HMVKAO2.mmtp	6.11	0.00189
HMVKAO2.hppp	6.20	0.00178
HMVKAO2.mptp	6.18	0.00177
HMVKAO2.ttpp	6.40	0.00177
HMVKAO2.tmpp	6.53	0.00124
HMVKAO2.ttpt	7.10	0.000732
HMVKAO2.htpp	7.30	0.000598
HMVKAO2.mtpt	7.02	0.000573
HMVKAO2.pmpm	6.85	0.000273
HMVKAO2.mppp	7.52	0.000266
HMVKAO2.hppm	7.51	0.000231
HMVKAO2.ptpm	8.17	0.000134
HMVKAO2.cpmpp	8.88	5.95e-05
HMVKAO2.mtmp	8.78	2.12e-05
HMVKAO2.mppm	8.39	1.97e-05
HMVKAO2.mtpp	8.99	1.39e-05

HMVKBO2

Conformer	Erel	%
HMVKBO2.hmmt	0.00	52.5
HMVKBO2.pppp	1.38	6.02
HMVKBO2.ptmp	0.97	5.81
HMVKBO2.ptmm	1.38	4.12
HMVKBO2.pppt	1.39	3.99
HMVKBO2.ptmt	0.85	3.98
HMVKBO2.pmmp	1.28	3.87
HMVKBO2.pttp	1.46	3.6
HMVKBO2.hmmm	1.36	2.72
HMVKBO2.htpm	1.56	2.65
HMVKBO2.pppm	2.07	2.43
HMVKBO2.ptpp	1.55	2.2
HMVKBO2.pptt	2.32	1.38
HMVKBO2.pttm	2.02	1.09
HMVKBO2.ltmmt	1.57	0.931
HMVKBO2.htpt	1.97	0.671
HMVKBO2.pptp	2.88	0.658
HMVKBO2.pppp	3.01	0.328
HMVKBO2.pppm	3.21	0.177
HMVKBO2.pppm	3.68	0.126
HMVKBO2.ltmp	3.14	0.125
HMVKBO2.ltmmt	3.29	0.112
HMVKBO2.tppp	4.07	0.0611
HMVKBO2.pttt	3.98	0.0578
HMVKBO2.lppp	4.12	0.0529
HMVKBO2.tppm	4.07	0.0446
HMVKBO2.lppm	4.40	0.0426
HMVKBO2.lppt	4.21	0.0331
HMVKBO2.tmtp	4.67	0.0219
HMVKBO2.hmpm	5.92	0.0211
HMVKBO2.tmtm	4.74	0.0163
HMVKBO2.tmpm	5.21	0.0127
HMVKBO2.ttpm	4.95	0.0115
HMVKBO2.cmtp	5.39	0.00984
HMVKBO2.pmtp	5.50	0.00842
HMVKBO2.tmtt	5.43	0.00784
HMVKBO2.tptp	5.65	0.007
HMVKBO2.lttm	5.06	0.00699
HMVKBO2.lttp	5.17	0.00604
HMVKBO2.hmpt	5.60	0.00585
HMVKBO2.tmpp	5.70	0.0042
HMVKBO2.cmtm	5.52	0.00418
HMVKBO2.cmtt	5.54	0.00349
HMVKBO2.lmtt	5.48	0.00321
HMVKBO2.lmpt	5.82	0.0031
HMVKBO2.lptp	6.19	0.00168
HMVKBO2.tppm	6.61	0.000895
HMVKBO2.lpmt	7.21	0.000188

TS.HMVKA02.14HshiftCH2OH

Conformer	Erel	%
TS.HMVKA02.14HshiftCH2OH.dtS1	0.00	94.9
TS.HMVKA02.14HshiftCH2OH.utS1	1.79	4.93
TS.HMVKA02.14HshiftCH2OH.umSc	4.38	0.119
TS.HMVKA02.14HshiftCH2OH.dmSc	6.47	0.00315
TS.HMVKA02.14HshiftCH2OH.umS1	7.81	0.000285
TS.HMVKA02.14HshiftCH2OH.dmS1	8.06	0.000178
TS.HMVKA02.14HshiftCH2OH.dtSc	8.33	0.000139

TS.HMVKA02.14HshiftCH2OH.utSc 8.65 0.000139
TS.HMVKA02.14HshiftCH2OH.upSc 9.08 5.71e-05

TS.HMVKA02.15HshiftOH

Conformer	Erel	%
TS.HMVKA02.15HshiftOH.md	0.05	50.1
TS.HMVKA02.15HshiftOH.mu	0.00	49.9
TS.HMVKA02.15HshiftOH.pd	5.66	0.00606

TS.HMVKA02.16HshiftCH3

Conformer	Erel	%
TS.HMVKA02.16HshiftCH3.a.Sp	0.00	97.9
TS.HMVKA02.16HshiftCH3.b.Sp	2.45	1.76
TS.HMVKA02.16HshiftCH3.a.Rm	3.52	0.237
TS.HMVKA02.16HshiftCH3.a.Rt	4.53	0.0631
TS.HMVKA02.16HshiftCH3.b.Rm	4.27	0.0517
TS.HMVKA02.16HshiftCH3.b.Rt	6.17	0.00335
TS.HMVKA02.16HshiftCH3.a.Sm	7.07	0.0011
TS.HMVKA02.16HshiftCH3.b.Sm	9.61	1.33e-05

TS.HMVKB02.14HshiftCH2OH

Conformer	Erel	%
TS.HMVKB02.14HshiftCH2OH.umRlp	0.00	99.4
TS.HMVKB02.14HshiftCH2OH.mmSht	3.58	0.482
TS.HMVKB02.14HshiftCH2OH.umSlp	5.24	0.0493
TS.HMVKB02.14HshiftCH2OH.mtShp	5.27	0.0324
TS.HMVKB02.14HshiftCH2OH.mmRmp	5.50	0.0235
TS.HMVKB02.14HshiftCH2OH.mmRlp	5.77	0.0217
TS.HMVKB02.14HshiftCH2OH.mmRhm	5.65	0.0205
TS.HMVKB02.14HshiftCH2OH.mtRhm	6.20	0.00761
TS.HMVKB02.14HshiftCH2OH.utRhm	7.11	0.00238
TS.HMVKB02.14HshiftCH2OH.mtShm	8.00	0.000734
TS.HMVKB02.14HshiftCH2OH.umScm	8.10	0.000502
TS.HMVKB02.14HshiftCH2OH.utScm	8.05	0.000494
TS.HMVKB02.14HshiftCH2OH.mmScm	9.25	0.000384
TS.HMVKB02.14HshiftCH2OH.mpSlp	10.27	2.29e-05
TS.HMVKB02.14HshiftCH2OH.mtRct	9.96	2.03e-05
TS.HMVKB02.14HshiftCH2OH.mpRhm	10.65	1.32e-05
TS.HMVKB02.14HshiftCH2OH.utRct	10.53	7.49e-06

TS.HMVKB02.15HshiftOH

Conformer	Erel	%
TS.HMVKB02.15HshiftOH.t	0.00	56.5
TS.HMVKB02.15HshiftOH.bis.t	0.46	43.4
TS.HMVKB02.15HshiftOH.bis.c	4.10	0.15

TS.HMVKB02.15HshiftCH3

Conformer	Erel	%
TS.HMVKB02.15HshiftCH3.bis.pm	0.00	24.5
TS.HMVKB02.15HshiftCH3.mp	0.34	20.2
TS.HMVKB02.15HshiftCH3.tm	0.36	12.2
TS.HMVKB02.15HshiftCH3.bis.mp	0.78	11.3
TS.HMVKB02.15HshiftCH3.bis.pp	0.82	10.4
TS.HMVKB02.15HshiftCH3.bis.pt	1.02	6.47
TS.HMVKB02.15HshiftCH3.bis.tm	0.82	6.38
TS.HMVKB02.15HshiftCH3.pm	0.96	5.97
TS.HMVKB02.15HshiftCH3.mt	2.34	0.717
TS.HMVKB02.15HshiftCH3.pp	2.40	0.626

TS.HMVKBO2.15HshiftCH3.bis.mm	2.63	0.614
TS.HMVKBO2.15HshiftCH3.bis.mt	2.74	0.466
TS.HMVKBO2.15HshiftCH3.mm	3.00	0.208
TS.HMVKBO2.15HshiftCH3.tp	4.81	0.0165
TS.HMVKBO2.15HshiftCH3.tt	5.65	0.00444

TS.HMVKBO2.HO2elim

Conformer	Erel %	

TS.HMVKBO2.HO2elim.cZm	0.00	95.1
TS.HMVKBO2.HO2elim.mEc	2.23	3.24
TS.HMVKBO2.HO2elim.cEc	3.29	0.723
TS.HMVKBO2.HO2elim.mEt	3.81	0.362
TS.HMVKBO2.HO2elim.mZt	4.12	0.19
TS.HMVKBO2.HO2elim.cEt	4.30	0.181
TS.HMVKBO2.HO2elim.pEt	4.50	0.101
TS.HMVKBO2.HO2elim.pZl	4.88	0.0572
TS.HMVKBO2.HO2elim.pZt	5.15	0.0356
TS.HMVKBO2.HO2elim.mZh	7.44	0.000766
TS.HMVKBO2.HO2elim.mZc	7.86	0.000462

b. Selected energetic and rovibrational data on M06-2X/aug-cc-pVTZ geometries

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HMVKAO2.mpm
-----
E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.36512897
E (CCSD/Aug-CC-pVDZ) (Hartree): -456.31464640
  T1 diagnostic: 0.022666
E (MP2/Aug-CC-pVDZ) (Hartree): -456.25443317
E (MP3/Aug-CC-pVDZ) (Hartree): -456.29038221
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.25740556
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.29218027
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.93913768
E (UHF/Aug-CC-pVDZ) (Hartree): -454.93431610
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.75629660
E (CCSD/Aug-CC-pVTZ) (Hartree): -456.68407033
  T1 diagnostic: 0.021789
E (MP2/Aug-CC-pVTZ) (Hartree): -456.64334697
E (MP3/Aug-CC-pVTZ) (Hartree): -456.66793458
E (PMP2/Aug-CC-pVTZ) (Hartree): -456.64653130
E (PMP3/Aug-CC-pVTZ) (Hartree): -456.66981848
E (PUHF/Aug-CC-pVTZ) (Hartree): -455.04635905
E (UHF/Aug-CC-pVTZ) (Hartree): -455.04118977
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.39156917
Electronic state : 2-A
Cartesian coordinates (Angs):
  O      -1.094970      -1.312715      -0.935448
  O      -1.841554      -0.447335      -0.322886
  C      -1.230065      -0.002509      0.901537
  C       0.032742       0.803278      0.636344
  C       1.152820      -0.008357      -0.018623
  C       1.645135      -1.240473      0.684559
  H      -1.980220      0.635139      1.362652
  H      -1.035318      -0.876978      1.522377
  O      -0.266653      1.932801      -0.117518
  H       0.416194      1.093642      1.625733
  H       0.301111      1.900456      -0.902046
  O       1.631720      0.401010      -1.045504
  H       2.661406      -1.455052      0.366931
  H       1.603372      -1.124521      1.767264
  H       1.001325      -2.074415      0.405041
Rotational constants (GHz):      2.5687900      1.9095300      1.5178200
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  66.0531      93.3947      108.0521
  148.4992      219.8635      234.7154
  329.5622      406.3559      432.1195
  452.3623      523.9337      596.3041
  702.1359      769.9792      897.3103
  912.7623      963.8776      1019.8574
  1058.5634      1143.6388      1184.2557
  1204.1422      1258.8232      1268.9397
  1322.9307      1350.5397      1357.4521
  1399.3340      1427.6173      1437.4639
  1441.8474      1790.7276      2910.6599
  2987.7133      3008.6247      3055.8498
  3075.9330      3087.8866      3635.1552
Zero-point correction (Hartree): 0.115633

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HMVKAO2.hmm
-----
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38937903
Electronic state : 2-A
Cartesian coordinates (Angs):
  O      -1.937322      0.479021      -0.948134
  O      -1.432342      -0.701723      -0.751454
  C      -1.029459      -0.894725      0.624528
  C       0.131024      0.021538      0.981549
  C       1.274788      -0.216706      -0.019865
  C       1.691597      0.932166      -0.886584
  H      -1.893796      -0.697577      1.256253
  H      -0.723319      -1.935917      0.672723
  O      -0.241271      1.366752      1.115166
  H       0.506687      -0.311824      1.951697
  H      -0.911090      1.572476      0.452642
  O       1.772065      -1.311961      -0.071687
  H       2.502471      0.621653      -1.537597
  H       0.835456      1.263416      -1.478979
  H       1.986861      1.777429      -0.265645
Rotational constants (GHz):      2.7989200      1.6528800      1.5300100
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  44.3212      49.6524      150.6729
  178.3463      207.0611      257.3070
  332.0887      399.5535      424.3418
  484.2938      509.5258      532.2280
  677.8098      755.8077      849.4299
  945.7859      958.9797      1005.3203
  1038.2026      1138.4951      1203.0695
  1220.2100      1233.0585      1260.3784
  1314.9898      1343.8977      1351.6106

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1380.0436	1418.5389	1427.3745
1432.2132	1794.9309	2977.1398
2994.1644	3019.4504	3041.2628
3093.6439	3097.0517	3701.3854

Zero-point correction (Hartree): 0.115536

HMVKAO2.hmmt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38309537

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.436332	0.067965	0.784395
O	1.390100	-0.681042	0.601019
C	0.957413	-0.697036	-0.773050
C	-0.230137	0.233500	-0.938782
C	-1.341734	-0.216472	0.021769
C	-1.610676	0.633321	1.228201
H	1.794119	-0.378143	-1.389220
H	0.657294	-1.720906	-0.985679
O	0.222075	1.547232	-0.722541
H	-0.611216	0.088007	-1.954665
H	-0.449608	2.176615	-0.994268
O	-1.927902	-1.239882	-0.219428
H	-2.332254	0.134458	1.867296
H	-0.675338	0.818451	1.757035
H	-1.997035	1.607455	0.923124

Rotational constants (GHz): 2.9984100 1.4860700 1.4078800

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

41.6720	62.2229	78.1180
152.3784	185.1956	247.0477
257.0986	313.2798	433.9886
490.2720	507.7232	533.0408
655.6971	767.4048	861.9043
953.3239	954.1866	1000.3775
1042.3627	1140.7029	1171.5548
1199.6747	1227.4004	1270.5995
1313.4194	1344.5411	1349.8786
1358.5040	1416.4038	1422.6419
1428.1287	1796.2399	2967.5207
2979.9307	3020.0025	3040.9201
3089.1008	3095.9500	3775.0823

Zero-point correction (Hartree): 0.114836

HMVKAO2.hmtp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38822723

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.689267	-0.141984	-0.768238
O	2.235471	-0.003363	0.441306
C	0.920311	-0.584796	0.581250
C	-0.077453	0.232779	-0.215723
C	-1.468041	-0.387781	-0.106411
C	-2.636174	0.552191	-0.120812
H	0.953936	-1.614788	0.238335
H	0.707677	-0.531944	1.647059
O	-0.132845	1.571269	0.220522
H	0.204850	0.178166	-1.274819
O	0.723804	1.983445	0.075796
O	-1.579245	-1.585526	-0.038075
H	-3.558222	-0.019550	-0.148424
H	-2.600275	1.185039	0.766028
H	-2.564809	1.222109	-0.977914

Rotational constants (GHz): 4.0708900 1.2399700 1.0458300

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

33.1847	61.5060	114.4529
162.7090	185.0760	263.9730
300.5009	336.2959	405.8084
457.8591	511.5307	568.7287
599.3044	793.8402	886.3408
914.4605	967.1365	1006.7507
1095.1418	1145.4205	1179.5804
1190.9687	1213.9713	1257.7062
1293.6214	1350.9393	1357.0994
1390.8257	1420.8311	1426.0005
1434.8168	1792.0838	2942.9012
2987.1132	3026.4237	3048.5223
3095.9960	3098.1367	3754.3004

Zero-point correction (Hartree): 0.115133

HMVKAO2.hpmm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38912749

Electronic state : 2-A

Cartesian coordinates (Angs):

O	1.070887	-0.172680	1.441916
O	1.912846	-0.371452	0.478247
C	1.287710	-0.418494	-0.832484
C	0.003316	0.385640	-0.880161
C	-1.139945	-0.359259	-0.175454
C	-2.060063	0.440764	0.699298

H	2.042801	-0.009065	-1.498897
H	1.089488	-1.464560	-1.061345
O	0.176201	1.716971	-0.473664
H	-0.290569	0.421520	-1.933015
H	0.444119	1.721515	0.451223
O	-1.286545	-1.534508	-0.393279
H	-2.880346	-0.190035	1.026687
H	-1.509923	0.810724	1.565163
H	-2.428790	1.311359	0.157231
Rotational constants (GHz):	2.8090900	1.7425700	1.5973700
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)		
	55.3243	93.6720	112.4145
	167.5204	213.5378	254.6567
	321.6953	398.5843	415.4629
	463.4280	512.8632	560.2389
	716.6765	764.9209	853.2719
	906.7812	957.6689	1002.6551
	1050.5814	1123.0351	1189.1198
	1209.2447	1238.6997	1268.4701
	1292.6619	1351.2038	1361.6327
	1374.5378	1419.7543	1434.8696
	1441.1957	1792.1344	2985.4445
	2986.8555	3017.5826	3049.7165
	3078.8609	3095.4665	3736.1443
Zero-point correction (Hartree):	0.115594		

HMVKAO2.hpmp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38552622
Electronic state : 2-A
Cartesian coordinates (Angs):

O	1.059916	-1.078945	1.111721
O	1.893560	-0.429269	0.360708
C	1.288262	-0.028536	-0.884049
C	-0.005551	0.739309	-0.662202
C	-1.149157	-0.213793	-0.291927
C	-1.913281	0.060526	0.965879
H	2.049716	0.590442	-1.356737
H	1.092226	-0.915910	-1.485133
O	0.111159	1.747414	0.311050
H	-0.290009	1.151837	-1.637835
H	0.824110	2.348586	0.081311
O	-1.405935	-1.107461	-1.056323
H	-2.671586	-0.704590	1.098082
H	-1.225801	0.081545	1.810464
H	-2.369896	1.049140	0.906394

Rotational constants (GHz):	2.7161900	1.7574900	1.6038000
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)		
	66.0101	101.0653	117.4223
	173.0801	184.6929	221.3036
	246.5522	306.4058	415.9394
	468.4214	511.0148	548.6454
	714.9243	756.6897	873.2843
	915.0342	961.4854	1017.7253
	1046.4212	1138.2614	1164.0215
	1207.1803	1221.4494	1253.2902
	1304.6069	1351.4107	1356.3746
	1383.4674	1419.8776	1428.5781
	1443.7143	1795.9519	2940.7250
	2987.8783	3004.8792	3052.7252
	3062.7606	3097.4692	3765.8756
Zero-point correction (Hartree):	0.115027		

HMVKAO2.hpmt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38501930
Electronic state : 2-A
Cartesian coordinates (Angs):

O	-1.037225	-1.240566	-0.944952
O	-1.875425	-0.462590	-0.336476
C	-1.306495	0.102169	0.862666
C	-0.000372	0.817976	0.583209
C	1.131540	-0.186907	0.311012
C	1.845849	-0.110581	-1.006992
H	-2.064260	0.799602	1.210344
H	-1.146444	-0.699378	1.582094
O	-0.230169	1.747866	-0.447059
H	0.274379	1.312042	1.522459
H	0.519914	2.340822	-0.528612
O	1.433032	-0.951761	1.189803
H	2.519214	-0.957164	-1.097153
H	1.126977	-0.090444	-1.823813
H	2.425384	0.814989	-1.055212

Rotational constants (GHz):	2.6665500	1.7800900	1.6071900
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)		
	47.0286	106.0288	119.0716
	174.4696	191.6539	214.1697
	238.8637	298.4593	415.0036
	478.4024	512.8252	542.1990
	705.3374	753.2893	876.1455
	917.5224	963.1422	1010.7247

1054.9147	1137.3928	1169.1519
1202.5621	1229.8541	1267.2414
1314.5091	1345.4941	1359.7238
1369.4588	1421.6331	1431.9671
1437.7506	1795.0989	2951.3054
2973.4202	3017.6621	3047.0486
3082.0968	3097.7616	3779.6146

Zero-point correction (Hartree): 0.115081

HMVKAO2.hptp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38999356

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.699607	0.512275	-0.036585
O	2.210113	-0.684949	-0.144115
C	0.879355	-0.779969	0.408919
C	-0.078411	0.148458	-0.314103
C	-1.521643	-0.313024	-0.083523
C	-2.556930	0.757192	0.087451
H	0.591189	-1.817234	0.266537
H	0.938316	-0.528310	1.467751
O	0.045036	1.490240	0.084297
H	0.097733	0.040478	-1.394058
H	0.981541	1.718469	0.063581
O	-1.775231	-1.490456	-0.077619
H	-3.540531	0.301642	0.138511
H	-2.343354	1.323748	0.993759
H	-2.495319	1.468390	-0.736368

Rotational constants (GHz): 4.2678100 1.2729400 1.0187700

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

38.9724	53.4639	150.1838
163.8450	205.0663	281.8801
310.9090	395.0146	442.9044
453.2489	519.5213	555.0789
601.7913	796.5157	886.0312
951.2771	961.9388	1003.8463
1069.5111	1153.0967	1193.4934
1202.6976	1217.5372	1260.5183
1307.8089	1350.9797	1352.1497
1391.1871	1420.0396	1425.0613
1439.3784	1792.9337	2918.1379
2988.5289	3010.3327	3049.6105
3094.2506	3099.5669	3713.9030

Zero-point correction (Hartree): 0.115486

HMVKAO2.htmm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38653665

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.739667	-0.501148	0.645118
O	1.487379	-0.177987	0.544921
C	1.061438	-0.068166	-0.832814
C	-0.320307	0.549531	-0.775552
C	-1.298264	-0.431433	-0.106692
C	-2.067269	0.047283	1.088378
H	1.770834	0.575101	-1.348711
H	1.035974	-1.065885	-1.265300
O	-0.302071	1.829644	-0.194543
H	-0.673514	0.670971	-1.801138
H	0.201690	1.799237	0.625009
O	-1.408505	-1.536307	-0.571137
H	-2.758459	-0.726245	1.407234
H	-1.369517	0.277856	1.896404
H	-2.592356	0.972059	0.851711

Rotational constants (GHz): 2.9987400 1.4181000 1.2484800

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

38.7405	53.7813	110.4226
175.7166	185.8578	250.5812
319.1218	330.4689	400.8328
465.7606	507.9985	529.7145
679.3516	736.2681	895.4801
929.2844	960.3914	1028.4491
1042.7013	1122.9171	1187.6321
1214.9293	1248.2141	1260.3485
1293.2981	1340.5126	1351.8391
1370.2210	1420.6334	1430.4574
1442.6362	1796.4649	2979.0797
3007.2382	3018.8053	3042.7534
3083.7883	3097.3238	3740.2881

Zero-point correction (Hartree): 0.115176

HMVKAO2.htmp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38441394

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.721512	-0.585591	0.569285
O	1.462073	-0.280977	0.522404
C	1.067055	0.124200	-0.802731

C	-0.346301	0.663454	-0.706114
C	-1.264377	-0.436870	-0.158634
C	-1.938856	-0.197437	1.155835
H	1.774066	0.880735	-1.143447
H	1.100314	-0.749551	-1.451644
O	-0.441093	1.804800	0.112712
H	-0.690759	0.865103	-1.725873
H	0.124918	2.501165	-0.229306
O	-1.385337	-1.444419	-0.805559
H	-2.534644	-1.065626	1.418431
H	-1.179431	-0.000743	1.913648
H	-2.556821	0.698332	1.097318
Rotational constants (GHz):	2.9134900	1.4499700	1.2755500
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)		
44.4456	52.6062		102.5225
161.9025	175.1203		231.0717
255.8608	316.6670		390.6067
476.7800	498.6264		532.1321
681.8647	753.0173		888.8975
936.1481	963.8890		1023.2228
1052.1217	1133.7905		1161.1244
1209.0530	1224.5081		1260.4553
1309.7224	1346.7688		1350.9645
1378.1331	1419.0953		1423.3386
1443.2917	1798.2646		2960.0752
2986.0737	2998.6409		3048.3240
3061.8767	3099.1163		3767.1540
Zero-point correction (Hartree):	0.114770		

HMVKAO2.html

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38381153

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.701373	-0.656466	0.469981
O	1.454874	-0.300516	0.478134
C	1.056499	0.243363	-0.797035
C	-0.366605	0.735364	-0.650406
C	-1.248065	-0.433165	-0.179926
C	-1.768594	-0.398828	1.226334
H	1.732197	1.060620	-1.039683
H	1.115319	-0.553397	-1.535871
O	-0.355156	1.840455	0.222587
H	-0.714710	1.006524	-1.651548
H	-1.191249	2.308736	0.171664
O	-1.464178	-1.330739	-0.951850
H	-2.280190	-1.331079	1.443518
H	-0.940123	-0.233202	1.915036
H	-2.455957	0.439529	1.352268
Rotational constants (GHz):	2.8243500	1.4707200	1.2985900
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)		
52.1938	62.7039		107.5678
157.4896	165.9704		225.3072
248.2663	308.4853		386.4867
474.5078	504.3817		530.8604
668.9022	758.2235		896.5823
932.5623	963.8940		1021.4739
1044.7157	1131.7217		1190.7293
1204.1415	1231.0694		1261.0120
1301.7642	1342.6621		1352.9531
1370.8932	1417.2942		1428.4291
1437.7623	1796.9992		2971.8308
2981.0543	3014.9580		3043.2169
3078.9689	3096.8454		3777.5855
Zero-point correction (Hartree):	0.114829		

HMVKAO2.htm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38266297

Electronic state : 2-A

Cartesian coordinates (Angs):

O	3.219527	-0.288710	0.231858
O	2.152491	0.163439	-0.350869
C	0.964239	-0.436054	0.197581
C	-0.222826	0.314435	-0.361520
C	-1.521877	-0.446386	-0.058657
C	-2.761562	0.382039	0.121080
H	0.935249	-1.484162	-0.089481
H	1.020378	-0.357190	1.285109
O	-0.271128	1.661713	0.045799
H	-0.136010	0.337627	-1.452756
H	-0.050674	1.729702	0.979118
O	-1.519919	-1.649571	-0.005717
H	-3.628007	-0.270885	0.150772
H	-2.691033	0.951059	1.048904
H	-2.845521	1.114684	-0.681145
Rotational constants (GHz):	4.3537400	1.1208100	0.9288800
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)		
19.0722	50.0898		84.4035
152.2733	158.1273		212.7663
261.8703	312.2695		391.9313

398.3336	516.4385	551.5671
608.6673	790.1938	883.2225
939.5702	984.8704	1033.5761
1044.6022	1156.1051	1169.0321
1190.4175	1254.8563	1267.2915
1284.5482	1348.2583	1355.5589
1377.1209	1417.4589	1428.4307
1452.3995	1792.1516	2970.4463
2986.0995	2991.6522	3046.5927
3072.1493	3096.6880	3750.5292

Zero-point correction (Hartree): 0.114499

HMVKAO2.http

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38707391

Electronic state : 2-A

Cartesian coordinates (Angs):

O	3.194829	-0.281486	0.314191
O	2.131532	0.141518	-0.297241
C	0.934262	-0.494408	0.198889
C	-0.219022	0.268103	-0.416096
C	-1.539285	-0.420504	-0.069197
C	-2.696588	0.458513	0.297133
H	0.935982	-1.537154	-0.108351
H	0.936476	-0.409161	1.284570
O	-0.257439	1.606023	0.022483
H	-0.128234	0.219653	-1.509184
H	0.565605	2.038055	-0.224116
O	-1.605195	-1.621778	-0.123115
H	-3.580925	-0.153413	0.442468
H	-2.456403	1.015304	1.203005
H	-2.858518	1.202273	-0.483306

Rotational constants (GHz): 4.3828500 1.1309400 0.9418900

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

23.5481	56.1398	101.3017
146.1245	167.1784	265.1543
308.7196	343.2977	397.4449
420.2489	511.1563	551.9320
601.5554	788.8277	888.2451
945.3259	975.8449	1021.8631
1077.2863	1152.8319	1179.2898
1193.0603	1216.5560	1256.3249
1291.8255	1352.4573	1358.1275
1387.5093	1419.6446	1425.2936
1445.6919	1794.0651	2933.0239
2987.2803	3013.2904	3047.7659
3083.2144	3099.3731	3753.0309

Zero-point correction (Hartree): 0.114919

HMVKAO2.mmmt

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38884339

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-2.456112	-0.245068	-0.784754
O	-1.366082	-0.833298	-0.390233
C	-0.947786	-0.406692	0.918375
C	0.220457	0.559815	0.786758
C	1.305353	-0.002494	-0.132746
C	1.826302	-1.381718	0.150072
H	-1.791016	0.082406	1.398825
H	-0.660752	-1.310683	1.455014
O	-0.218583	1.797020	0.331383
H	0.671196	0.653785	1.785604
O	0.294461	2.004830	-0.463148
O	1.696346	0.674040	-1.048704
H	2.780116	-1.521966	-0.349335
H	1.925472	-1.557448	1.220930
H	1.110024	-2.105936	-0.244178

Rotational constants (GHz): 2.9169000 1.5753800 1.3408700

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

18.8404	74.9240	87.6395
158.1056	188.4142	260.3961
336.8073	402.6684	430.5932
469.7190	511.2312	578.8863
676.5003	770.3057	872.9785
949.1313	965.8152	1015.7850
1042.1477	1146.1248	1174.8874
1201.1619	1240.0734	1287.8877
1319.1635	1344.6046	1353.7789
1387.3394	1419.9918	1435.6573
1440.3832	1795.9622	2912.3961
2977.9095	3009.4804	3043.2612
3080.8192	3091.0123	3644.0730

Zero-point correction (Hartree): 0.115238

HMVKAO2.mmpm

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38911290

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.068339	0.577820	-0.577347
O	1.927989	-0.438918	0.221202
C	0.775860	-1.222851	-0.124517
C	-0.515412	-0.692072	0.511517
C	-0.866244	0.701149	-0.014617
C	-0.262737	1.903472	0.646867
H	0.681535	-1.236357	-1.208878
H	0.970225	-2.221929	0.257788
O	-1.524004	-1.601567	0.180929
H	-0.397280	-0.648354	1.597459
H	-2.047407	-1.186089	-0.520463
O	-1.668411	0.779647	-0.912419
H	-0.112083	2.690533	-0.086971
H	-0.983270	2.255499	1.389260
H	0.668165	1.672647	1.157391

Rotational constants (GHz): 2.6359600 1.8528400 1.2856600
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

38.1236	67.0561	94.2133
162.1301	210.6093	285.9233
314.5478	349.1289	429.4013
461.1153	549.8518	597.6666
634.2725	756.4624	931.3650
962.4828	994.0660	1019.0486
1077.8145	1115.5951	1172.4412
1198.5848	1254.7533	1269.3855
1305.9176	1341.6692	1354.7727
1398.8560	1431.1245	1436.6890
1442.3620	1786.1864	2978.4616
2981.9621	3015.9064	3055.7621
3084.0487	3097.1041	3639.4080

Zero-point correction (Hartree): 0.115659

HMVKAO2.mmp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38954508

Electronic state : 2-A

Cartesian coordinates (Angs):

O	2.533484	0.419224	-0.416863
O	1.880747	-0.380553	0.370813
C	0.782242	-1.042780	-0.283808
C	-0.533653	-0.693923	0.415262
C	-1.045974	0.694930	0.037005
C	-0.168921	1.880684	0.302244
H	0.791553	-0.759197	-1.334095
H	0.946468	-2.113515	-0.177538
O	-1.468982	-1.668053	0.070066
H	-0.351218	-0.693791	1.497601
H	-2.231592	-1.198774	-0.300362
O	-2.137741	0.783278	-0.469301
H	-0.767245	2.786531	0.279407
H	0.355981	1.780636	1.251060
H	0.593828	1.933478	-0.478020

Rotational constants (GHz): 3.0248900 1.5914300 1.1301200

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

47.2227	81.7230	111.8291
176.3485	212.9832	291.7050
306.0841	357.5337	435.4580
475.1429	524.9477	578.5752
636.8265	747.0483	928.0651
965.4282	973.5848	1023.3643
1088.3998	1137.7454	1180.1716
1189.8514	1261.9081	1278.5302
1293.0466	1349.6656	1361.4048
1397.8028	1426.4253	1436.1664
1448.3632	1784.2316	2935.4829
2980.5208	3011.3493	3046.3715
3076.7360	3092.9530	3631.0164

Zero-point correction (Hartree): 0.115626

HMVKAO2.mmtm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38932208

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-2.588263	0.630343	-0.635974
O	-2.235831	-0.076676	0.392311
C	-0.871638	0.200058	0.764915
C	0.081702	-0.378876	-0.269571
C	1.494266	0.158953	-0.069042
C	1.700706	1.646863	-0.098639
H	-0.778171	1.280818	0.856919
H	-0.734733	-0.292725	1.725260
O	0.065178	-1.769791	-0.221795
H	-0.256946	-0.020200	-1.251541
H	0.981753	-2.056794	-0.099272
O	2.396164	-0.623351	0.097473
H	1.557471	2.040339	0.909986
H	2.718752	1.864652	-0.408459
H	0.983671	2.137712	-0.754991

Rotational constants (GHz): 3.5968600 1.3035900 1.0560700

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

51.1625	71.8067	120.6617
154.8383	196.1412	262.0396
325.3506	389.0274	411.4303
456.7741	547.2398	561.4819
629.1568	820.1374	900.2869
931.2981	967.4570	1006.7449
1089.0421	1141.3179	1188.0387
1211.0296	1236.9668	1279.2870
1311.7761	1351.4861	1362.5997
1393.7405	1427.5288	1429.1911
1441.7931	1788.4735	2932.5124
2979.0855	3011.2719	3045.6536
3077.3424	3088.6399	3646.5822

Zero-point correction (Hartree): 0.115519

HMVKA02.mppt

E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.36447322
E (CCSD/Aug-CC-pVDZ) (Hartree): -456.31424675
T1 diagnostic: 0.022692
E (MP2/Aug-CC-pVDZ) (Hartree): -456.25346708
E (MP3/Aug-CC-pVDZ) (Hartree): -456.28996447
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.25635073
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.29171757
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.94047181
E (UHF/Aug-CC-pVDZ) (Hartree): -454.93576234
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.75578191
E (CCSD/Aug-CC-pVTZ) (Hartree): -456.68380725
T1 diagnostic: 0.021786
E (MP2/Aug-CC-pVTZ) (Hartree): -456.64247456
E (MP3/Aug-CC-pVTZ) (Hartree): -456.66766572
E (PMP2/Aug-CC-pVTZ) (Hartree): -456.64556846
E (PMP3/Aug-CC-pVTZ) (Hartree): -456.66950140
E (PUHF/Aug-CC-pVTZ) (Hartree): -455.04765520
E (UHF/Aug-CC-pVTZ) (Hartree): -455.04259446
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.39079856

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-2.479236	0.197130	-0.617633
O	-1.836708	0.286801	0.508534
C	-0.884596	-0.780459	0.655683
C	0.269752	-0.660900	-0.342642
C	1.170590	0.537294	-0.053252
C	0.576553	1.913568	-0.096861
H	-0.532419	-0.713799	1.683858
H	-1.394939	-1.726306	0.489516
O	0.999855	-1.846522	-0.277705
H	-0.166209	-0.523355	-1.339123
H	1.911742	-1.597793	-0.064533
O	2.332366	0.332388	0.202292
H	1.372194	2.648671	-0.172810
H	-0.128484	2.011438	-0.921142
H	0.014111	2.085756	0.822761

Rotational constants (GHz): 3.0574000 1.5833300 1.1646600

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

45.9000	73.9665	141.8265
159.7013	201.3066	287.2900
308.9659	353.8382	431.4591
457.1968	551.6724	592.1856
634.0541	745.4390	925.2148
957.2824	973.8735	1022.3296
1093.1384	1136.5243	1189.0421
1195.2579	1246.2433	1275.9191
1294.5337	1351.1883	1360.9925
1399.3596	1422.9120	1436.0124
1447.9794	1782.3110	2953.1140
2983.4728	3013.6931	3047.7724
3077.7398	3091.9292	3630.6979

Zero-point correction (Hartree): 0.115652

HMVKA02.mptt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38762419

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-3.144348	-0.488120	-0.272461
O	-2.127133	0.057597	0.317698
C	-0.893057	-0.330687	-0.315086
C	0.224059	0.402889	0.403039
C	1.586505	-0.158762	0.001837
C	1.841048	-1.626968	0.191780
H	-0.810644	-1.413404	-0.224296
H	-0.943005	-0.035090	-1.362175
O	0.154896	1.768709	0.146112
H	0.111497	0.211371	1.479980
H	1.021647	2.034511	-0.194117
O	2.412790	0.594642	-0.446872
H	2.909591	-1.800777	0.278495
H	1.316088	-2.015525	1.063179
H	1.473875	-2.162536	-0.686293

Rotational constants (GHz): 3.9321700 1.1593600 0.9482900

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

54.9632	76.9741	96.3934
156.8415	162.1109	256.3337
335.1344	367.8861	407.2047
444.2978	467.8995	589.6304
631.8637	820.4356	897.0323
952.7943	971.5637	1033.0031
1078.9590	1145.1832	1181.4230
1223.9606	1238.3767	1256.6885
1314.3277	1350.6375	1364.0348
1395.2613	1426.9265	1435.1303
1444.4384	1791.4260	2919.3429
2979.5858	2999.3969	3045.8763
3061.5053	3090.4310	3644.4143

Zero-point correction (Hartree): 0.115222

HMVKA02.mtmt

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.39003314

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-2.707871	-0.523962	-0.501435
O	-1.465855	-0.151371	-0.520940
C	-1.027157	0.285862	0.780955
C	0.423568	0.707970	0.655123
C	1.260279	-0.354197	-0.061256
C	1.176509	-1.767572	0.436125
H	-1.643247	1.130710	1.080873
H	-1.160366	-0.545366	1.472864
O	0.524466	1.935852	0.007600
H	0.822941	0.777680	1.677235
H	1.146766	1.816629	-0.724720
O	1.951516	-0.018254	-0.987895
H	2.010470	-2.343407	0.046846
H	1.163929	-1.801914	1.525399
H	0.242269	-2.204831	0.077175

Rotational constants (GHz): 2.8513500 1.5466700 1.2359000

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

50.4405	80.2300	120.4407
159.9724	170.6262	262.6058
341.1771	387.3799	407.5405
435.8850	487.8237	600.4469
689.1991	764.2914	902.7885
933.9365	959.7116	1037.9678
1054.9706	1142.3648	1181.8151
1203.8190	1256.6117	1262.0736
1331.4079	1351.3732	1357.5931
1391.7556	1424.5184	1439.3132
1444.4454	1796.9812	2916.3570
2978.3086	3005.6891	3042.8044
3067.3373	3091.1395	3645.8175

Zero-point correction (Hartree): 0.115384

HMVKA02.mttm

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38673248

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-3.144129	-0.502243	-0.322911
O	-2.128337	-0.030725	0.330159
C	-0.895000	-0.307117	-0.360201
C	0.216531	0.353676	0.440943
C	1.573758	-0.141430	-0.056466
C	1.993232	-1.542935	0.280632
H	-0.795885	-1.390094	-0.423165
H	-0.959427	0.128384	-1.356310
O	0.130415	1.740880	0.342431
H	0.107103	0.050416	1.489222
H	0.891818	2.032726	-0.179391
O	2.279066	0.622653	-0.665568
H	2.761257	-1.876111	-0.411092
H	2.412973	-1.526665	1.288892
H	1.154921	-2.236339	0.289517

Rotational constants (GHz): 3.8806600 1.1428900 0.9614600

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

52.2819	57.6277	74.2192
102.2574	167.4903	253.2880
321.0248	376.0466	395.0560
436.0323	489.9314	610.5484
614.8621	833.0515	894.2333
945.7864	974.6595	1030.8643
1075.6596	1136.5001	1174.7851
1213.0947	1244.7064	1259.1878
1304.2716	1355.5133	1365.4888
1391.0496	1426.7108	1433.5427
1443.8018	1791.2480	2950.3555
2982.3242	3001.1129	3050.2723
3062.8517	3093.4871	3649.4865

Zero-point correction (Hartree): 0.115046

HMVKA02.tmtm

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E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38379567
Electronic state : 2-A
Cartesian coordinates (Angs):
O      -2.666954      -0.102077      0.857345
O      -2.274104      -0.017583      -0.376299
C      -0.958721      -0.578199      -0.543268
C       0.077851       0.273951       0.159714
C       1.454004      -0.395731       0.094149
C       2.641221       0.498390       0.316980
H      -0.957023      -1.592004      -0.152803
H      -0.797879      -0.597724      -1.621660
O       0.109501       1.606086      -0.299998
H      -0.194575       0.332863       1.217811
H       0.133733       1.619336      -1.261244
O       1.551260      -1.579487      -0.109703
H       3.527303      -0.110256       0.467540
H       2.778478       1.143227      -0.551776
H       2.466215       1.158581       1.165922
Rotational constants (GHz):   3.9592800   1.2274900   1.0474300
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  33.4619      59.7255      113.0360
 134.9421     188.9764     244.2672
 265.6634     303.4995     378.7914
 467.1706     512.8112     572.3056
 605.9303     800.4753     884.0376
 918.2081     975.5425    1019.0587
1055.3383    1146.8642    1180.4708
1186.9668    1241.7074    1276.1955
1296.4107    1352.8056    1362.9387
1374.0704    1418.7859    1428.9692
1441.4032    1789.5760    2982.9262
2986.7212    3009.0926    3047.2028
3082.6137    3096.1299    3746.6155
Zero-point correction (Hartree): 0.114921

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HMVKA02.tppp

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E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38340412
Electronic state : 2-A
Cartesian coordinates (Angs):
O      -2.554109      -0.057422      0.892221
O      -1.973085      -0.647658      -0.107147
C      -1.076508       0.251333      -0.785972
C       0.130674       0.564326       0.088331
C       1.190318      -0.535292       0.009956
C       2.551975      -0.188004       0.538301
H      -0.791613      -0.265963      -1.698109
H      -1.628278       1.163712      -1.006347
O       0.744095       1.780082      -0.284017
H      -0.210825       0.598416       1.130411
H       0.205097       2.515991       0.016354
O       0.908420      -1.613721      -0.441945
H       3.154607      -1.087911       0.610457
H       3.020477       0.527825      -0.137235
H       2.469217       0.303509       1.507886
Rotational constants (GHz):   3.3000500   1.3937300   1.1388600
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  44.2196      63.3972      118.3372
 145.1153     202.1860     278.1230
 287.1753     329.4333     385.0060
 447.5637     514.7723     586.8065
 612.4401     736.6090     911.8375
 953.4319     977.9932    1025.0465
1069.0636    1134.5136    1176.2887
1189.2965    1211.7459    1264.9204
1300.7930    1350.5097    1370.3267
1394.5539    1423.9446    1430.3500
1434.1345    1802.6620    2944.7735
2986.5210    3012.3735    3048.9798
3085.9154    3095.5167    3766.7338
Zero-point correction (Hartree): 0.115230

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HMVKBO2.hmmm

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E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38601666
Electronic state : 2-A
Cartesian coordinates (Angs):
C      -0.295418      -0.120935      -0.248545
H      -0.490830      -0.161200      -1.323563
C       1.196278       0.116204      -0.031796
C      -1.167808       0.954802       0.390267
O      -0.609874      -1.413645       0.305360
O       1.594738       1.242253       0.137986
C       2.103906      -1.076294      -0.070026
H       1.880463      -1.692818      -0.941269
H       1.917746      -1.696427       0.807906
H       3.137692      -0.746005      -0.082562
O      -1.042387       2.169040      -0.299866
H      -2.205925       0.634769       0.316643
H      -0.904645       1.052851       1.447916

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H -0.132920 2.468388 -0.189225
O -1.720393 -1.885426 -0.177886
Rotational constants (GHz): 2.2424400 2.0326600 1.1226800
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
41.8211 86.1842 143.7879
153.2770 205.7749 241.4123
285.0609 370.9473 441.0036
463.5506 512.4466 562.2539
614.9058 762.9668 923.7757
947.3793 1009.6484 1056.5799
1077.7947 1100.7797 1167.4701
1205.8266 1244.4364 1259.2896
1321.6536 1350.1286 1360.2928
1391.1680 1420.2299 1429.7315
1468.9250 1786.7622 2959.9654
2983.2563 2990.8611 3043.0634
3044.3387 3097.4613 3721.6557
Zero-point correction (Hartree): 0.115546

HMVKBO2.hmmt

E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.36228035
E (CCSD/Aug-CC-pVDZ) (Hartree): -456.31196852
T1 diagnostic: 0.022819
E (MP2/Aug-CC-pVDZ) (Hartree): -456.25052340
E (MP3/Aug-CC-pVDZ) (Hartree): -456.28759527
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.25339001
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.28934166
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.93781106
E (UHF/Aug-CC-pVDZ) (Hartree): -454.93312479
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.75274738
E (CCSD/Aug-CC-pVTZ) (Hartree): -456.68071667
T1 diagnostic: 0.021933
E (MP2/Aug-CC-pVTZ) (Hartree): -456.63873437
E (MP3/Aug-CC-pVTZ) (Hartree): -456.66445591
E (PMP2/Aug-CC-pVTZ) (Hartree): -456.64181153
E (PMP3/Aug-CC-pVTZ) (Hartree): -456.66628735
E (PUHF/Aug-CC-pVTZ) (Hartree): -455.04444045
E (UHF/Aug-CC-pVTZ) (Hartree): -455.03940173
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38774592
Electronic state : 2-A

Cartesian coordinates (Angs):

C	0.168693	-0.338645	0.542811
H	0.360975	-0.216773	1.611565
C	-0.489529	0.940519	0.022094
C	1.475992	-0.664231	-0.175101
O	-0.744416	-1.445959	0.462108
O	0.193985	1.772848	-0.519474
C	-1.961836	1.114568	0.253029
H	-2.234430	0.784923	1.255645
H	-2.507838	0.486219	-0.451389
H	-2.229110	2.155266	0.098726
O	2.473257	0.254985	0.183371
H	1.806863	-1.653116	0.139046
H	1.295747	-0.682355	-1.252650
H	2.210769	1.111088	-0.173205
O	-1.155687	-1.619189	-0.761596

Rotational constants (GHz): 2.5812600 1.9422000 1.2647800
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
54.8136 107.9351 145.0558
150.4859 188.8972 254.3537
272.1788 384.2404 430.9141
471.0983 507.3485 578.8845
664.9822 755.6207 920.2916
957.3054 985.7546 1033.3337
1076.4458 1105.8887 1168.0677
1202.6481 1205.0512 1289.8933
1328.0027 1348.4916 1355.8334
1390.9839 1422.9861 1431.3208
1470.1653 1788.6138 2976.1864
2985.8059 3001.7244 3041.9637
3049.5521 3095.8439 3721.0237
Zero-point correction (Hartree): 0.115715

HMVKBO2.htpm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38560665
Electronic state : 2-A

Cartesian coordinates (Angs):

C	-0.275109	-0.109746	-0.528328
H	-0.399952	-0.490528	-1.546293
C	1.211314	-0.142509	-0.182253
C	-0.871287	1.283166	-0.413569
O	-0.942266	-1.042076	0.349854
O	1.869319	0.852689	-0.355233
C	1.780734	-1.428402	0.335177
H	1.458985	-2.265591	-0.284680
H	1.386182	-1.610637	1.336022
H	2.863504	-1.359672	0.366106
O	-0.583336	1.891866	0.818869
H	-0.507891	1.876765	-1.255370

H	-1.953552	1.193118	-0.493222	
H	0.341637	2.156634	0.808521	
O	-2.126569	-1.341872	-0.088145	
Rotational constants (GHz):	2.4594600	1.9322500	1.2338200	
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)			
47.6130	82.9656		133.6649	
166.0596	209.1338		215.3120	
303.6500	385.5156		428.6993	
454.8453	502.8540		560.3778	
684.9740	796.1875		850.5170	
928.0016	964.2144		1023.8657	
1066.3216	1113.7771		1174.4969	
1206.0177	1249.6644		1284.1323	
1311.1610	1358.2685		1361.5554	
1378.6846	1420.7760		1429.8616	
1451.6729	1790.1856		2977.8438	
2982.3002	2988.3199		3043.5675	
3046.4503	3096.4365		3747.7734	

Zero-point correction (Hartree): 0.115475

HMVKBO2.htpt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38498868
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-0.171767	0.165805	0.811420	
H	0.068122	0.186162	1.878527	
C	0.893460	-0.672283	0.098911	
C	-1.583189	-0.372196	0.625790	
O	-0.079354	1.542545	0.405251	
O	0.601198	-1.763722	-0.318896	
C	2.279332	-0.102224	0.002396	
H	2.532115	0.470517	0.893913	
H	2.315447	0.581064	-0.846252	
H	2.987617	-0.910137	-0.155453	
O	-1.972216	-0.465036	-0.714856	
H	-1.630121	-1.340199	1.133847	
H	-2.278560	0.307714	1.116393	
H	-1.415644	-1.126532	-1.138910	
O	0.064623	1.650813	-0.885645	
Rotational constants (GHz):	2.6133200	2.0378500	1.4509700	
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)			
59.9358	93.2346		120.3062	
175.3317	204.4379		218.0102	
317.3178	330.7297		441.4846	
473.3125	520.8014		577.3602	
686.6530	800.8391		868.3274	
934.6709	971.1242		1021.0531	
1041.4595	1125.4804		1160.3434	
1201.6176	1210.9168		1302.9794	
1331.7900	1357.8512		1360.1541	
1391.4469	1425.9508		1434.6136	
1448.6704	1792.1918		2963.1050	
2987.1661	2989.7979		3035.6634	
3055.3390	3091.6888		3739.4762	

Zero-point correction (Hartree): 0.115580

HMVKBO2.ltm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38275007
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-0.269109	-0.146356	-0.529960	
H	-0.389395	-0.448199	-1.572907	
C	1.087726	-0.605771	-0.005250	
C	-0.453455	1.357343	-0.387441	
O	-1.285093	-0.821704	0.238438	
O	1.176661	-1.457377	0.833906	
C	2.277097	0.096883	-0.601614	
H	2.347484	1.088259	-0.149427	
H	2.167601	0.225106	-1.678768	
H	3.176979	-0.466802	-0.375799	
O	-0.092650	1.804752	0.897798	
H	0.196410	1.870111	-1.095085	
H	-1.489478	1.599818	-0.634808	
H	-0.678965	1.407467	1.549005	
O	-2.446943	-0.711715	-0.332219	
Rotational constants (GHz):	2.7045200	1.7251000	1.2996300	
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)			
57.3966	91.4060		113.8358	
170.7709	193.3369		209.9038	
316.1493	361.6076		374.3667	
462.3873	477.4024		574.2544	
679.5297	812.0626		853.6056	
935.6415	953.2807		1038.9404	
1056.2030	1108.0326		1157.2511	
1192.8550	1247.2049		1250.0158	
1312.8826	1346.8165		1362.6181	
1376.0668	1426.7965		1438.3994	
1464.9343	1816.0856		2977.3779	
2983.4431	2999.8109		3042.4519	

3042.7286 3091.8938 3745.9751
Zero-point correction (Hartree): 0.115236

HMVKBO2.ltmp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38307280

Electronic state : 2-A

Cartesian coordinates (Angs):

C	-0.270934	0.219250	-0.596878
H	-0.484882	-0.017106	-1.641676
C	0.487232	-0.945161	0.051044
C	0.505774	1.519853	-0.473379
O	-1.516567	0.431270	0.074432
O	0.009667	-1.573862	0.950891
C	1.862492	-1.199592	-0.504526
H	2.538419	-0.448601	-0.090323
H	1.878962	-1.107151	-1.590587
H	2.196610	-2.187304	-0.202041
O	1.000711	1.711980	0.830849
H	1.368942	1.488245	-1.136311
H	-0.137349	2.344591	-0.790673
H	0.263629	1.747241	1.448417
O	-2.385275	-0.492640	-0.212968

Rotational constants (GHz): 2.3897800 1.9802600 1.3450600

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

65.1638	95.2324	110.8721
154.6955	162.5004	255.8422
306.0399	349.2375	384.5720
433.1074	492.8386	599.2923
663.0260	793.7187	866.5581
941.9997	955.4868	1031.1973
1062.6538	1114.3263	1159.1461
1205.0048	1241.3257	1252.4847
1309.5465	1344.9532	1355.3348
1380.7233	1426.2816	1438.2127
1461.5598	1820.2171	2974.2037
2977.1634	3001.3954	3042.1990
3042.9910	3091.6192	3744.7470

Zero-point correction (Hartree): 0.115216

HMVKBO2.lmtt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38557278

Electronic state : 2-A

Cartesian coordinates (Angs):

C	0.169954	-0.047912	0.825026
H	-0.063288	-0.120015	1.889070
C	-1.028048	-0.549641	0.008751
C	0.520989	1.390634	0.454511
O	1.287183	-0.932823	0.658548
O	-0.934365	-1.502191	-0.710401
C	-2.286135	0.259766	0.166721
H	-2.159686	1.188863	-0.392305
H	-2.467007	0.514852	1.211159
H	-3.126159	-0.295689	-0.238869
O	0.406625	1.644314	-0.922386
H	-0.178108	2.058425	0.957102
H	1.525302	1.605510	0.829999
H	1.001568	1.038186	-1.378298
O	1.891410	-0.747703	-0.476750

Rotational constants (GHz): 2.6420400 1.9810700 1.4753200

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

70.7910	112.8546	144.0210
149.7968	208.8947	248.4337
329.9750	351.7887	434.1508
500.7448	533.8174	570.1607
694.6942	798.8306	868.9105
941.2740	970.9506	1018.9021
1034.0424	1118.1087	1154.7921
1198.4145	1227.0856	1246.0614
1341.8251	1344.8153	1362.3830
1393.3283	1426.7489	1438.1171
1459.3515	1819.1844	2970.5536
2978.4292	3010.2307	3032.7122
3044.4124	3091.0465	3721.2178

Zero-point correction (Hartree): 0.115813

HMVKBO2.pmp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38605168

Electronic state : 2-A

Cartesian coordinates (Angs):

C	-0.073869	-0.446687	-0.202854
H	-0.057929	-0.673670	-1.270866
C	0.179497	1.052735	-0.018916
C	-1.401288	-0.887950	0.407452
O	0.974231	-1.208608	0.423441
O	-0.768431	1.797722	0.037018
C	1.597899	1.528172	0.063512
H	2.165790	1.158338	-0.790736
H	2.071660	1.112634	0.953949

H	1.611019	2.612649	0.099588
O	-2.477712	-0.401967	-0.348915
H	-1.446491	-1.975464	0.386771
H	-1.453029	-0.560839	1.450322
H	-2.449420	0.560556	-0.299286
O	1.990033	-1.401125	-0.364659
Rotational constants (GHz):	2.6560700	1.8096900	1.1499900
Vibrational harmonic frequencies (cm-1):	(Scaled by 0.9710)		
29.3370	92.1224		137.4153
187.4753	214.7167		245.0729
293.7142	370.1615		423.1506
471.4444	519.0918		583.6509
612.5507	739.7493		920.8275
948.6184	1026.0429		1039.0144
1085.6430	1105.1152		1177.4556
1203.9053	1244.1436		1270.4952
1305.1716	1352.0703		1358.1149
1396.0066	1421.3734		1430.6372
1472.1997	1780.4187		2960.8289
2984.3219	3004.9277		3040.6368
3044.8809	3099.0686		3712.5695

Zero-point correction (Hartree): 0.115678

HMVKBO2.ppm

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38187741
Electronic state : 2-A
Cartesian coordinates (Angs):

C	0.097276	-0.067479	-0.346786
H	0.340036	-0.085975	-1.410359
C	-1.407836	-0.224091	-0.168338
C	0.823366	-1.188121	0.396316
O	0.520501	1.206636	0.165521
O	-1.930820	-1.199964	-0.639622
C	-2.146891	0.824387	0.608695
H	-2.051220	1.788618	0.108169
H	-1.697213	0.942886	1.595539
H	-3.190543	0.539000	0.693014
O	2.217114	-1.052871	0.353571
H	0.544220	-1.162190	1.450565
H	0.473543	-2.132279	-0.029051
H	2.508035	-0.903852	-0.550590
O	1.552912	1.664402	-0.479047

Rotational constants (GHz): 2.9281300 1.5704400 1.1531500
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

34.7856	85.6573		127.4500
171.2138	178.3183		214.2633
236.7573	311.2924		386.9152
449.0142	478.8825		547.0694
586.3216	842.7041		868.2483
946.1716	984.5389		1039.9110
1078.1989	1115.8314		1165.5931
1216.6648	1248.2188		1274.4499
1308.9865	1325.6860		1357.2191
1385.3495	1419.4563		1429.1750
1464.1188	1796.1878		2972.5498
2982.3487	3007.1971		3027.8095
3042.8095	3096.9468		3754.2843

Zero-point correction (Hartree): 0.114867

HMVKBO2.pmp

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38305263
Electronic state : 2-A
Cartesian coordinates (Angs):

C	0.276412	-0.005210	-0.301158
H	0.487136	0.079292	-1.368019
C	-1.085935	-0.682748	-0.130555
C	1.359138	-0.800129	0.414484
O	0.283971	1.321998	0.250801
O	-1.233335	-1.766873	-0.630847
C	-2.143160	0.017827	0.668947
H	-2.438840	0.935469	0.158798
H	-1.743008	0.316392	1.638959
H	-2.996600	-0.641770	0.787719
O	2.649939	-0.312474	0.147852
H	1.210455	-0.711510	1.491437
H	1.239456	-1.848335	0.135132
H	2.907420	-0.554989	-0.744926
O	-0.338668	2.163226	-0.518982

Rotational constants (GHz): 2.5086700 1.7359400 1.1607800
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

38.8721	95.2404		113.0322
175.9211	189.9353		236.5696
264.5373	291.5241		346.3134
462.7306	520.5808		574.3105
579.5246	799.9983		850.2093
952.6980	990.9950		1043.6508
1073.1789	1106.2352		1179.6281
1219.6558	1239.0379		1254.3435
1303.5145	1352.7399		1354.7301

1378.7326	1421.2466	1430.2613
1458.0333	1795.3886	2981.4968
2985.5546	3013.2393	3036.2376
3042.2121	3097.8618	3766.7791

Zero-point correction (Hartree): 0.115003

HMVKBO2.ppmt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38262265

Electronic state : 2-A

Cartesian coordinates (Angs):

C	-0.225815	-0.115045	0.472810
H	-0.385538	-0.402480	1.515320
C	1.162333	-0.622168	0.064912
C	-1.333634	-0.678229	-0.404522
O	-0.272365	1.325929	0.515148
O	1.279001	-1.782171	-0.232602
C	2.318824	0.333939	0.114285
H	2.302871	0.903734	1.043655
H	2.230729	1.054873	-0.698712
H	3.242926	-0.226894	0.017215
O	-2.613469	-0.372861	0.097112
H	-1.259218	-0.220592	-1.389447
H	-1.165238	-1.750148	-0.506947
H	-2.832498	-0.974145	0.812300
O	-0.101202	1.842187	-0.664445

Rotational constants (GHz): 2.8615600 1.7063400 1.1894100

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

30.6995	76.8091	127.8559
183.2377	195.9827	211.9420
260.8098	306.9296	348.0882
441.6987	496.8116	577.9107
655.9839	784.0356	859.6897
950.5229	990.8198	1019.4969
1060.4766	1097.3815	1163.0105
1190.7140	1229.6263	1259.2339
1340.1784	1350.6213	1353.0369
1369.0224	1422.4405	1430.5732
1459.5652	1793.1857	2985.8957
2992.0049	3005.2398	3049.2809
3058.1770	3096.0724	3773.8960

Zero-point correction (Hartree): 0.114962

HMVKBO2.pppm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38448356

Electronic state : 2-A

Cartesian coordinates (Angs):

C	0.085530	-0.062836	-0.322456
H	0.316099	-0.121091	-1.388410
C	-1.410292	-0.301944	-0.119614
C	0.932472	-1.069671	0.445281
O	0.382354	1.284945	0.113256
O	-1.835119	-1.411321	-0.305140
C	-2.275716	0.856590	0.281833
H	-2.166751	1.671449	-0.434673
H	-1.948934	1.246349	1.246552
H	-3.308227	0.526672	0.334194
O	2.261372	-1.120786	0.001267
H	0.867699	-0.833696	1.513885
H	0.493029	-2.051247	0.280826
H	2.622707	-0.228532	-0.007772
O	1.582944	1.654320	-0.216241

Rotational constants (GHz): 3.0053900 1.5981800 1.1042900

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

24.3305	49.4088	138.2027
187.2052	200.2285	221.0619
332.0613	395.2853	396.8329
416.5813	449.8376	544.3039
592.3846	836.3206	846.1745
944.7846	1001.9338	1049.1484
1066.2250	1101.2570	1186.8150
1204.1434	1240.6986	1261.8346
1305.8180	1346.1158	1358.2028
1388.8844	1420.7169	1431.2297
1461.0865	1800.3194	2943.3956
2983.8046	3004.1170	3044.0688
3054.9615	3098.1627	3733.2039

Zero-point correction (Hartree): 0.115108

HMVKBO2.pppp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38544420

Electronic state : 2-A

Cartesian coordinates (Angs):

C	0.261460	-0.055277	-0.333960
H	0.463923	0.020518	-1.401860
C	-1.141421	-0.625106	-0.120922
C	1.306271	-0.918781	0.353522
O	0.399179	1.263434	0.232450
O	-1.373717	-1.712171	-0.580035

C	-2.134995	0.176435	0.666144
H	-2.358418	1.104679	0.138764
H	-1.708103	0.459569	1.629440
H	-3.038134	-0.409651	0.801663
O	2.612043	-0.496609	0.054215
H	1.119794	-0.921573	1.433104
H	1.192607	-1.934947	-0.016128
H	2.754896	0.377998	0.426094
O	-0.159310	2.175318	-0.506604

Rotational constants (GHz): 2.5316200 1.7502900 1.1591400
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

33.1502	101.3747	122.0450
171.3028	186.7654	250.6214
277.7278	336.2307	351.5365
454.8613	521.0974	572.1374
578.8619	794.2581	850.5543
952.6400	994.3599	1048.9013
1077.5756	1098.4816	1190.4935
1216.6849	1232.2015	1251.8481
1300.5122	1350.4082	1354.5593
1375.7838	1421.6538	1430.2523
1459.2989	1796.8678	2949.4225
2981.7498	3030.9733	3042.4802
3063.4235	3098.3650	3759.5137

Zero-point correction (Hartree): 0.115154

HMVKBO2.pppt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38559643
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-0.201634	-0.145643	0.502130
H	-0.323498	-0.387436	1.560199
C	-1.204248	-0.562109	0.063598
C	-1.294530	-0.817259	-0.311220
O	-0.355592	1.292503	0.470732
O	1.378327	-1.694314	-0.302033
C	2.307653	0.452056	0.162748
H	2.257485	0.979166	1.115854
H	2.185135	1.199967	-0.621126
H	3.261998	-0.051807	0.047080
O	-2.572701	-0.515322	0.193207
H	-1.187685	-0.530061	-1.359475
H	-1.151974	-1.891728	-0.234975
H	-2.776891	0.405010	0.007573
O	-0.244908	1.756459	-0.739239

Rotational constants (GHz): 2.9395000 1.6979800 1.2038200
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

34.1663	84.5920	132.5795
175.2633	184.8622	256.3641
287.5115	332.9495	355.5396
447.6494	490.3882	578.4060
657.7165	776.6129	857.9300
952.3378	989.9856	1020.7370
1078.0167	1093.6517	1171.9210
1187.5010	1226.5372	1257.7610
1337.5590	1353.9156	1355.5643
1370.0442	1423.8223	1433.6211
1457.5495	1797.6352	2985.0581
2987.6623	3008.0366	3048.2969
3072.3986	3096.0977	3761.7874

Zero-point correction (Hartree): 0.115246

HMVKBO2.pptp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38319855
Electronic state : 2-A
Cartesian coordinates (Angs):

C	0.269735	-0.008816	-0.281047
H	0.471285	0.114474	-1.345707
C	-1.084888	-0.706839	-0.110473
C	1.378711	-0.798241	0.375601
O	0.263680	1.302567	0.312649
O	-1.180337	-1.846608	-0.483195
C	-2.216234	0.060624	0.505783
H	-2.453677	0.926045	-0.114142
H	-1.917699	0.449885	1.479944
H	-3.078771	-0.591305	0.597504
O	2.603050	-0.251667	-0.059467
H	1.269878	-0.727200	1.463221
H	1.260768	-1.840553	0.074696
H	3.327672	-0.681338	0.399348
O	-0.306818	2.179411	-0.456743

Rotational constants (GHz): 2.5415400 1.7689900 1.1430300
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

27.9185	97.9612	116.5699
181.9591	197.7506	210.6049
270.6874	287.7640	348.1112
443.6351	517.1663	567.2144
584.7587	795.8430	866.7977
947.6971	996.4104	1053.4444

1090.3072	1108.6697	1189.6189
1211.1619	1244.5519	1254.0372
1262.0759	1309.8692	1353.8205
1416.3269	1421.9616	1429.9800
1471.6997	1795.2592	2948.9335
2983.3987	3012.7190	3023.1671
3043.7955	3098.8050	3784.2259

Zero-point correction (Hartree): 0.114886

HMVKBO2.pptt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38385697

Electronic state : 2-A

Cartesian coordinates (Angs):

C	0.227521	-0.099929	-0.475074
H	0.373600	-0.319987	-1.535478
C	-1.153923	-0.616431	-0.058753
C	1.351591	-0.707601	0.328407
O	0.267689	1.343270	-0.423402
O	-1.259147	-1.738211	0.361061
C	-2.327559	0.300353	-0.257124
H	-2.262690	0.804063	-1.221699
H	-2.312736	1.076242	0.508665
H	-3.243547	-0.276732	-0.179653
O	2.560381	-0.355475	-0.311676
H	1.300330	-0.319774	1.348737
H	1.195765	-1.786765	0.351998
H	3.300424	-0.645285	0.225064
O	0.063962	1.776652	0.783721

Rotational constants (GHz): 2.9057200 1.6946600 1.2100900

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

41.9529	87.0286	129.4222
170.2735	190.9055	213.9529
256.4142	308.1670	352.5393
454.6422	484.5264	577.2760
661.9600	779.9339	871.6284
951.1732	1004.5754	1035.3765
1074.6016	1097.0879	1169.9718
1204.6371	1212.8751	1252.0693
1279.2774	1344.0204	1355.0891
1413.9729	1423.7619	1433.0009
1474.7444	1798.8531	2976.8026
2986.1378	3000.8442	3028.3669
3049.8639	3095.8275	3787.5883

Zero-point correction (Hartree): 0.115037

HMVKBO2.ptmm

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38541874

Electronic state : 2-A

Cartesian coordinates (Angs):

C	-0.207111	-0.081349	-0.632725
H	-0.324968	-0.325954	-1.688003
C	1.264917	-0.197614	-0.246708
C	-0.721224	1.321462	-0.343717
O	-0.971672	-1.041224	0.135531
O	2.062314	0.378729	-0.938130
C	1.630587	-0.980298	0.976943
H	1.300930	-2.014478	0.875074
H	1.104427	-0.559688	1.835290
H	2.704599	-0.932635	1.126004
O	-0.578423	1.648401	1.020163
H	-0.114460	2.022249	-0.914095
H	-1.759394	1.392500	-0.673362
H	-1.253846	1.188036	1.525392
O	-2.194757	-1.128811	-0.293696

Rotational constants (GHz): 2.6449000 1.6748400 1.3717600

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

56.0002	68.9391	115.6606
163.1310	197.0979	214.3560
282.1476	344.2629	389.1909
428.8006	502.2004	567.6253
676.5713	788.4973	862.2212
924.0932	979.7005	1031.6174
1045.2235	1099.0648	1178.5429
1210.4048	1246.2574	1258.3690
1300.9182	1351.7209	1359.0597
1366.6487	1420.4869	1429.4954
1456.3396	1802.4164	2982.4722
2988.8938	3029.1413	3045.4470
3055.5251	3097.3201	3759.3561

Zero-point correction (Hartree): 0.115141

HMVKBO2.ptmp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38616208

Electronic state : 2-A

Cartesian coordinates (Angs):

C	0.200181	0.262901	-0.667408
H	-0.014395	0.434566	-1.721658
C	-0.647214	-0.918442	-0.182856

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C      1.675206      -0.018547      -0.439751
O      -0.087990      1.477394      0.051790
O      -0.617148      -1.918165      -0.849367
C      -1.417283      -0.784337      1.094848
H      -2.184234      -0.016645      0.990640
H      -0.741332      -0.463281      1.888539
H      -1.869405      -1.740140      1.339519
O      1.951595      -0.247996      0.924169
H      1.929671      -0.927794      -0.980463
H      2.268578      0.808189      -0.837427
H      1.885087      0.583573      1.401265
O      -1.263870      1.947777      -0.240269
Rotational constants (GHz):  2.1504900      2.0699500      1.4157600
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  60.3906      105.0131      112.2804
 158.9012      172.3129      247.9999
 282.1159      342.4722      368.5942
 487.2192      501.2833      553.3674
 664.8032      778.1565      875.6863
 924.3854      982.3656      1025.7450
1046.7165      1105.4728      1181.6672
1217.3587      1250.1195      1263.2864
1291.2312      1350.2354      1355.9515
1370.7613      1421.3988      1431.0105
1457.4311      1801.6516      2977.8896
2984.1615      3031.5200      3048.4822
3055.4916      3097.6252      3759.2044
Zero-point correction (Hartree): 0.115297

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HMVKBO2.ptmt

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38651897

Electronic state : 2-A

Cartesian coordinates (Angs):

```

C      -0.116533      0.131926      -0.854754
H      0.083683      0.291361      -1.913404
C      1.231199      -0.038425      -0.140910
C      -0.871311      1.321327      -0.275544
O      -0.893411      -1.088531      -0.834921
O      2.095271      0.751377      -0.409413
C      1.382883      -1.145382      0.856663
H      1.199112      -2.109077      0.380633
H      0.634143      -1.027639      1.641247
H      2.382250      -1.111053      1.278336
O      -0.889773      1.340379      1.129825
H      -0.342845      2.216959      -0.597061
H      -1.879594      1.336184      -0.699019
H      -1.418355      0.591243      1.421048
O      -1.614064      -1.228806      0.236445
Rotational constants (GHz):  2.5880700      1.8948500      1.5155800
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  65.2674      91.5164      135.3830
 168.0937      206.6647      245.0121
 298.5172      382.5474      418.6313
 483.7740      491.7933      577.0722
 696.5067      794.7127      836.7653
 945.4678      985.1181      998.9883
1028.1956      1115.4329      1186.7456
1213.9712      1229.1401      1243.3893
1338.7468      1351.6332      1355.5719
1386.3746      1420.5855      1430.9494
1448.3091      1802.7665      2970.0614
2983.7571      3035.8041      3046.5786
3048.9355      3097.4236      3745.3665
Zero-point correction (Hartree): 0.115672

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HMVKBO2.ptpp

E (UM062X/Aug-CC-pVTZ) (Hartree): -457.38573015

Electronic state : 2-A

Cartesian coordinates (Angs):

```

C      -0.019616      -0.417300      -0.534748
H      0.346524      -0.565198      -1.553350
C      0.120357      1.068906      -0.186089
C      -1.457573      -0.890457      -0.400404
O      0.811475      -1.221267      0.326352
O      -0.805901      1.799152      -0.436405
C      1.398777      1.540525      0.434325
H      2.249663      1.235741      -0.175234
H      1.524661      1.060163      1.405963
H      1.365895      2.619419      0.546353
O      -2.035848      -0.526188      0.827777
H      -2.021912      -0.494254      -1.246723
H      -1.469569      -1.977891      -0.454371
H      -2.238646      0.413685      0.792340
O      2.029239      -1.314410      -0.116910
Rotational constants (GHz):  2.4709700      1.9727300      1.2665900
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  33.3405      97.7831      112.7793
 183.8623      188.2793      257.4453
 307.6236      389.9054      414.5123

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452.7363	497.0320	555.4023
672.1927	792.7407	851.0493
932.4196	966.7542	1024.2907
1060.1629	1121.5695	1185.6749
1205.9792	1254.0582	1287.3592
1293.7897	1355.5532	1360.7531
1381.0659	1421.1339	1427.7896
1449.2558	1783.9538	2983.8085
2985.4759	3001.9224	3045.1487
3045.1918	3098.8830	3747.8877

Zero-point correction (Hartree): 0.115496

HMVKBO2.pttm

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38457772
Electronic state : 2-A

Cartesian coordinates (Angs):

C	-0.261432	-0.095853	-0.610895
H	-0.423200	-0.351396	-1.657271
C	1.216950	-0.274615	-0.267496
C	-0.682340	1.334014	-0.349547
O	-1.044600	-1.006897	0.192629
O	2.020668	0.231708	-1.005310
C	1.573487	-1.028825	0.975277
H	1.209058	-2.054253	0.907041
H	1.067120	-0.565828	1.823311
H	2.650528	-1.013536	1.108954
O	-0.333125	1.634669	0.986693
H	-0.147372	1.968062	-1.060712
H	-1.758414	1.416377	-0.517968
H	-0.603869	2.530052	1.198114
O	-2.277174	-1.051706	-0.209700

Rotational constants (GHz): 2.6356000 1.6976700 1.3813700
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

66.3023	82.6482	120.1623
167.8721	178.9902	199.7035
216.5603	303.0397	383.6611
427.0117	503.6255	567.8711
661.9545	800.9025	874.3112
933.9567	984.1521	1039.4178
1073.4055	1109.1335	1161.0414
1212.3320	1235.5293	1253.6985
1299.1084	1311.3344	1356.7202
1398.4878	1420.7526	1429.9668
1467.8101	1801.0880	2968.1492
2983.2765	3015.5040	3033.0184
3046.8383	3096.9583	3789.4607

Zero-point correction (Hartree): 0.114907

HMVKBO2.pttp

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.38522117
Electronic state : 2-A

Cartesian coordinates (Angs):

C	-0.040028	-0.395706	-0.634049
H	0.238531	-0.505859	-1.681171
C	0.184703	1.064891	-0.221122
C	-1.488721	-0.769671	-0.420453
O	0.761618	-1.311590	0.134039
O	-0.269061	1.912170	-0.943284
C	0.904178	1.344037	1.061341
H	1.942741	1.021704	0.980786
H	0.444119	0.762369	1.860866
H	0.854985	2.407392	1.273218
O	-1.812895	-0.459242	0.919744
H	-2.082638	-0.184414	-1.126157
H	-1.619443	-1.834603	-0.629256
H	-2.737631	-0.654309	1.083214
O	2.020156	-1.200537	-0.169974

Rotational constants (GHz): 2.2423500 2.0264800 1.4304800
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

70.0097	108.7506	114.6693
167.4057	175.7500	207.1586
254.2924	289.0592	353.3932
487.5893	496.8874	553.8032
653.6210	784.8339	884.9331
936.1688	983.0298	1021.3123
1092.8179	1117.3398	1172.3681
1209.6483	1237.8308	1251.5239
1296.3613	1303.7654	1351.9150
1408.6215	1424.0275	1429.9098
1465.0896	1800.2201	2963.9023
2984.1362	3010.2189	3034.0693
3049.0904	3097.0753	3787.1405

Zero-point correction (Hartree): 0.115034

TS.HMVKAO2.14HshiftCH2OH.dtS1

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.34602051
Electronic state : 2-A

Cartesian coordinates (Angs):

O	1.884171	0.188745	-1.055055
O	1.852812	0.548972	0.277798
C	1.123920	-0.489998	0.893118
C	-0.104567	-0.650375	-0.015422
H	0.648553	-0.322220	-1.015917
H	0.900320	-0.181208	1.914315
H	1.672279	-1.432968	0.878928
O	-0.593223	-1.907358	-0.057665
H	-1.546562	-1.831176	-0.241213
C	-1.193966	0.393339	-0.015825
O	-2.327034	0.006330	-0.200933
C	-0.830192	1.834260	0.159317
H	-0.071840	2.116848	-0.570816
H	-0.386807	1.988826	1.143882
H	-1.720905	2.445021	0.050537

Rotational constants (GHz): 2.9661000 1.7353800 1.3023300
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

i12103.8767	92.9891	125.7682
182.2763	218.3234	281.4142
325.3019	373.9734	405.0106
483.8817	564.7528	618.2414
652.0706	684.0746	740.0971
933.8709	963.0414	973.5332
1044.2322	1046.0252	1060.0143
1159.8413	1202.2727	1211.6371
1279.5388	1348.7362	1369.2613
1383.3540	1418.8511	1432.7145
1456.8753	1698.4056	1748.0782
2985.4161	2986.0010	3046.7891
3048.4940	3095.5150	3564.4345

Zero-point correction (Hartree): 0.110753

TS.HMVKA02.15HshiftOH.md

E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.32252047
E (CCSD/Aug-CC-pVDZ) (Hartree): -456.26584391
T1 diagnostic: 0.035376
E (MP2/Aug-CC-pVDZ) (Hartree): -456.20231883
E (MP3/Aug-CC-pVDZ) (Hartree): -456.23515652
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.20749097
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.23842643
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.86974318
E (UHF/Aug-CC-pVDZ) (Hartree): -454.86206821
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.71475739
E (CCSD/Aug-CC-pVTZ) (Hartree): -456.63566900
T1 diagnostic: 0.033944
E (MP2/Aug-CC-pVTZ) (Hartree): -456.59254836
E (MP3/Aug-CC-pVTZ) (Hartree): -456.61373848
E (PMP2/Aug-CC-pVTZ) (Hartree): -456.59792785
E (PMP3/Aug-CC-pVTZ) (Hartree): -456.61710646
E (PUHF/Aug-CC-pVTZ) (Hartree): -454.97777406
E (UHF/Aug-CC-pVTZ) (Hartree): -454.96980049
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.35092637

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-2.194552	0.560661	-0.341599
O	-1.376592	-0.347004	-0.972750
C	-0.859745	-1.192702	-0.020123
C	0.156353	-0.295562	0.879044
O	-0.490127	0.804216	1.266050
H	-1.527908	0.901480	0.464448
H	-1.631658	-1.554724	0.656101
H	-0.292442	-1.977730	-0.512487
H	0.403470	-0.986455	1.698519
C	1.400321	-0.065880	0.005497
O	2.169709	-0.977478	-0.149342
C	1.549924	1.290269	-0.610553
H	2.431720	1.312457	-1.242577
H	0.652566	1.526328	-1.185575
H	1.615637	2.038732	0.179502

Rotational constants (GHz): 3.2642900 1.5528300 1.4423400
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

i1254.5188	58.4025	86.4330
167.5849	191.7071	268.2428
386.3769	422.2017	485.1879
523.9390	555.6501	641.2558
680.5528	700.9230	774.9743
883.7553	951.0160	965.6347
986.8015	1024.1314	1082.1581
1165.3930	1204.0555	1217.2889
1241.6209	1268.4149	1315.2966
1352.4414	1416.7158	1425.6615
1438.7196	1770.9353	1796.8264
2910.7482	2980.9627	3009.3562
3041.9162	3098.5096	3101.2741

Zero-point correction (Hartree): 0.109317

TS.HMVKA02.15HshiftOH.mu

IRC pathway available

E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.32262687

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E (CCSD/Aug-CC-pVDZ) (Hartree): -456.26547103
  T1 diagnostic: 0.040391
E (MP2/Aug-CC-pVDZ) (Hartree): -456.20041131
E (MP3/Aug-CC-pVDZ) (Hartree): -456.23338339
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.20547813
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.23662340
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.86836382
E (UHF/Aug-CC-pVDZ) (Hartree): -454.86083426
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.71525572
E (CCSD/Aug-CC-pVTZ) (Hartree): -456.63558622
  T1 diagnostic: 0.038365
E (MP2/Aug-CC-pVTZ) (Hartree): -456.59115793
E (MP3/Aug-CC-pVTZ) (Hartree): -456.61244759
E (PMP2/Aug-CC-pVTZ) (Hartree): -456.59645225
E (PMP3/Aug-CC-pVTZ) (Hartree): -456.61579632
E (PUHF/Aug-CC-pVTZ) (Hartree): -454.97676820
E (UHF/Aug-CC-pVTZ) (Hartree): -454.96891190
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.35136408
Electronic state : 2-A
Cartesian coordinates (Angs):
  O      2.421102      0.568993      0.284794
  O      2.058305     -0.742989      0.096903
  C      0.738987     -0.882780      0.466299
  C     -0.101163     -0.076133     -0.647893
  O      0.381045      1.161292     -0.735574
  H      1.597110      1.080473     -0.230205
  H      0.469663     -1.934205      0.417473
  H      0.549910     -0.426079      1.438454
  H     -0.039670     -0.667377     -1.569183
  C     -1.544636     -0.169451     -0.080214
  O     -2.155652     -1.188275     -0.231977
  C     -2.051004      1.044497      0.635661
  H     -3.015634      0.831354      1.084670
  H     -1.326843      1.364928      1.384805
  H     -2.126043      1.861949     -0.082311
Rotational constants (GHz):  4.0840000  1.3513100  1.1612800
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
  i1175.4275      66.3794      100.6276
  156.0419      183.5656      269.9151
  370.4835      399.0959      512.9335
  513.7438      554.8283      578.3265
  693.6849      700.4782      772.6359
  883.6102      939.9847      975.7201
  993.5901      1048.7162      1114.4712
  1173.5535      1180.5114      1203.4188
  1268.1748      1280.3517      1321.2393
  1349.7902      1414.1226      1420.1917
  1433.8348      1775.0689      1804.2545
  2950.6215      2986.2198      2993.7107
  3046.9900      3094.5837      3101.0906
Zero-point correction (Hartree): 0.109396

TS.HMVKA02.16HshiftCH3.a.Sp
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IRC pathway available
E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.32282572
E (CCSD/Aug-CC-pVDZ) (Hartree): -456.26825438
  T1 diagnostic: 0.024330
E (MP2/Aug-CC-pVDZ) (Hartree): -456.21180407
E (MP3/Aug-CC-pVDZ) (Hartree): -456.24375974
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.22202486
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.25029721
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.88015200
E (UHF/Aug-CC-pVDZ) (Hartree): -454.86685827
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.71395585
E (CCSD/Aug-CC-pVTZ) (Hartree): -456.63705508
  T1 diagnostic: 0.023234
E (MP2/Aug-CC-pVTZ) (Hartree): -456.60076598
E (MP3/Aug-CC-pVTZ) (Hartree): -456.62086538
E (PMP2/Aug-CC-pVTZ) (Hartree): -456.61127981
E (PMP3/Aug-CC-pVTZ) (Hartree): -456.62756435
E (PUHF/Aug-CC-pVTZ) (Hartree): -454.98634600
E (UHF/Aug-CC-pVTZ) (Hartree): -454.97268688
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.34948846
Electronic state : 2-A
Cartesian coordinates (Angs):
  O      -2.034844      0.381901     -0.558831
  H     -1.343551      1.192867     -0.092088
  C     -0.284735      1.733053      0.588736
  O     -1.788701     -0.734668      0.198473
  C      0.757086      0.826163      0.089710
  C     -0.558452     -1.313862     -0.196905
  C      0.658119     -0.644102      0.479413
  H     -0.666170      1.541014      1.586562
  H     -0.189588      2.769722      0.290608
  H     -0.599297     -2.352546      0.125735
  H     -0.453846     -1.263187     -1.280849
  O      1.643684      1.179359     -0.657519
  O      1.802278     -1.333181      0.082637
  H      0.530287     -0.714396      1.564007
  H      2.310719     -0.728276     -0.477777

```

Rotational constants (GHz): 2.8338200 1.9070400 1.2979500
 Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
 i1872.5623 101.2725 119.9780
 244.3469 295.0858 324.0826
 354.7458 414.7901 441.5113
 522.3909 546.6416 600.5345
 641.4140 665.5430 759.3995
 892.8739 949.9451 976.4107
 1009.7079 1051.5321 1069.0764
 1119.1297 1136.9355 1190.5607
 1235.1835 1260.3616 1295.5344
 1334.0887 1402.7679 1408.2471
 1434.8895 1447.7660 1736.9053
 2968.1232 3000.1752 3043.4983
 3066.4384 3146.8376 3638.5821
 Zero-point correction (Hartree): 0.109914

TS.HMVKA02.16HshiftCH3.b.St

 E(UM062X/Aug-CC-pVTZ) (Hartree): -457.34542770

Electronic state : 2-A

Cartesian coordinates (Angs):

O	-2.151359	0.140081	-0.305700
H	-1.478585	1.018788	0.042125
C	-0.435404	1.698677	0.646150
O	-1.264356	-0.821926	-0.716329
C	0.651286	0.884346	0.102687
C	-0.550072	-1.313282	0.412009
C	0.781905	-0.556221	0.599827
H	-0.710163	1.531518	1.682543
H	-0.487939	2.718290	0.285309
H	-1.195990	-1.244055	1.285903
H	-0.309772	-2.353130	0.198295
O	1.393254	1.271961	-0.773465
O	1.812983	-1.197807	-0.081447
H	1.003171	-0.531457	1.675095
H	2.168811	-0.559550	-0.717779

Rotational constants (GHz): 2.7254600 2.0162200 1.4085000

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

i1862.5122	85.5569	115.6288
264.9617	279.5386	335.7266
403.8751	413.7656	446.8780
501.1056	519.5281	590.6030
614.2366	693.3021	811.5645
899.6150	928.0395	984.4128
989.2139	1039.7892	1054.5468
1101.7804	1147.2013	1169.3000
1220.6310	1285.0151	1303.0087
1337.4599	1393.4307	1410.5817
1427.1204	1440.5856	1728.6471
2927.3395	3005.1192	3046.6354
3068.5662	3148.8787	3631.4786

Zero-point correction (Hartree): 0.109720

TS.HMVKB02.14HshiftCH2OH.umRlp

 IRC pathway available

E(CCS(D)/Aug-CC-pVDZ) (Hartree): -456.31676020

E(CCS(D)/Aug-CC-pVDZ) (Hartree): -456.26121932

T1 diagnostic: 0.024454

E(MP2/Aug-CC-pVDZ) (Hartree): -456.20488418

E(MP3/Aug-CC-pVDZ) (Hartree): -456.23592090

E(PMP2/Aug-CC-pVDZ) (Hartree): -456.21278298

E(PMP3/Aug-CC-pVDZ) (Hartree): -456.24067724

E(PUHF/Aug-CC-pVDZ) (Hartree): -454.86786824

E(UHF/Aug-CC-pVDZ) (Hartree): -454.85692566

E(CCS(D)/Aug-CC-pVTZ) (Hartree): -456.70766299

E(CCS(D)/Aug-CC-pVTZ) (Hartree): -456.62976787

T1 diagnostic: 0.023693

E(MP2/Aug-CC-pVTZ) (Hartree): -456.59335513

E(MP3/Aug-CC-pVTZ) (Hartree): -456.61254242

E(PMP2/Aug-CC-pVTZ) (Hartree): -456.60152856

E(PMP3/Aug-CC-pVTZ) (Hartree): -456.61744357

E(PUHF/Aug-CC-pVTZ) (Hartree): -454.97407001

E(UHF/Aug-CC-pVTZ) (Hartree): -454.96277393

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.34102477

Electronic state : 2-A

Cartesian coordinates (Angs):

O	0.030855	1.693522	-0.905691
O	0.278002	1.581015	0.468525
C	-0.123051	0.261882	0.744546
C	-1.537333	0.238381	0.139886
H	-1.087115	0.971146	-0.829715
O	-2.123173	-0.935785	-0.159351
H	-1.423473	-1.586982	-0.350916
H	-2.225324	0.916677	0.643108
C	0.817364	-0.758675	0.102187
H	-0.105425	0.122473	1.829707
O	0.395450	-1.843896	-0.232519
C	2.247922	-0.354227	-0.051545
H	2.630568	0.036422	0.891808

```

H      2.298585      0.460911     -0.774239
H      2.833698     -1.203650     -0.387907
Rotational constants (GHz):  2.5144600  2.1689300  1.3592700
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
i1720.0102      70.0149      151.7520
176.5398      237.4238      240.8273
302.9182      431.1423      461.7598
485.3768      547.5701      625.7265
684.7628      701.5996      774.6627
906.2657      947.0595      958.4325
1013.2427     1057.1299     1066.7569
1171.9378     1193.3112     1235.1972
1250.4523     1314.0060     1334.8429
1356.5694     1418.0833     1425.5807
1429.0119     1750.9040     1768.6382
2982.7178     2985.6879     3033.2588
3048.3434     3098.4020     3501.0526
Zero-point correction (Hartree): 0.110598

```

TS.HMVKBO2.15HshiftCH3.mp

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.33644494

Electronic state : 2-A

Cartesian coordinates (Angs):

```

O      0.201107      1.711954     -0.627580
O     -0.275255      1.245265      0.585368
C     -0.271170     -0.183531      0.540160
C      1.124183     -0.664273      0.138014
C      2.140221      0.405979     -0.000860
H      1.321141      1.311043     -0.591765
H      2.319121      1.005619      0.887705
H      3.001357      0.160155     -0.608588
O      1.324777     -1.824982     -0.120056
H     -0.493634     -0.487286      1.564562
C     -1.341109     -0.718921     -0.399036
O     -2.621355     -0.316697      0.020832
H     -1.126636     -0.387852     -1.418661
H     -1.308401     -1.805569     -0.376099
H     -2.659893      0.644043      0.004656

```

Rotational constants (GHz): 2.9586100 1.7846500 1.2436200

Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)

```

i1999.0682      68.7395      108.2236
174.7116      255.6608      302.2956
354.4028      367.8836      457.7299
503.5329      526.9672      573.1544
598.8990      681.7914      816.9942
883.2750      921.8354      952.0351
984.4238      1045.3135     1091.4188
1096.0339     1108.0500     1167.6634
1194.7102     1231.9245     1311.2107
1351.9559     1375.3268     1379.1848
1460.9286     1571.4736     1766.0710
2974.4332     3014.0022     3036.8963
3061.6024     3147.2530     3751.9136

```

Zero-point correction (Hartree): 0.109497

TS.HMVKBO2.15HshiftCH3.bis.pm

IRC pathway available

E(CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.31237540

E(CCSD/Aug-CC-pVDZ) (Hartree): -456.25856605

T1 diagnostic: 0.022101

E(MP2/Aug-CC-pVDZ) (Hartree): -456.20268700

E(MP3/Aug-CC-pVDZ) (Hartree): -456.23458198

E(PMP2/Aug-CC-pVDZ) (Hartree): -456.21229527

E(PMP3/Aug-CC-pVDZ) (Hartree): -456.24064295

E(PUHF/Aug-CC-pVDZ) (Hartree): -454.87136962

E(UHF/Aug-CC-pVDZ) (Hartree): -454.85871419

E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.70300785

E(CCSD/Aug-CC-pVTZ) (Hartree): -456.62694511

T1 diagnostic: 0.021103

E(MP2/Aug-CC-pVTZ) (Hartree): -456.59114466

E(MP3/Aug-CC-pVTZ) (Hartree): -456.61113840

E(PMP2/Aug-CC-pVTZ) (Hartree): -456.60107187

E(PMP3/Aug-CC-pVTZ) (Hartree): -456.61737601

E(PUHF/Aug-CC-pVTZ) (Hartree): -454.97746327

E(UHF/Aug-CC-pVTZ) (Hartree): -454.96441293

E(UM062X/Aug-CC-pVTZ) (Hartree): -457.33727492

Electronic state : 2-A

Cartesian coordinates (Angs):

```

O      1.541131     -1.501412     -0.253918
O      0.164209     -1.431274     -0.160893
C     -0.262151     -0.197213     -0.724566
C      0.530727      0.955242     -0.098392
C      1.433896      0.567494      1.007693
H      1.858203     -0.593629      0.446336
H      2.248758      1.248362      1.217172
H      0.943250      0.106213      1.860867
O      0.442557      2.065876     -0.556308
H     -0.078277     -0.184962     -1.801829
C     -1.741850     -0.070472     -0.415196

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```

O      -1.973330   -0.032670   0.975626
H      -2.094497   0.872496   -0.828591
H      -2.284359   -0.890549   -0.892147
H      -1.753343   -0.892394   1.344901
Rotational constants (GHz):  2.4049100  2.0563600  1.4501700
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
i1984.4981      82.6755      109.9682
159.5793      262.1384      291.0805
347.9969      376.4799      435.4536
504.2152      526.0002      577.8632
626.3082      689.2824      772.4624
877.3116      925.2918      944.2674
1016.7547     1036.5645     1069.8357
1104.6733     1110.0099     1161.8959
1212.2982     1275.6507     1290.1107
1353.5253     1371.8910     1376.7065
1455.3543     1569.0197     1774.7764
2973.1973     2992.0208     3035.6566
3051.3003     3146.2402     3759.0546
Zero-point correction (Hartree): 0.109439

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TS.HMVKBO2.15HshiftOH.t

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IRC pathway available
E(CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.31841429
E(CCSD/Aug-CC-pVDZ) (Hartree): -456.26241001
  T1 diagnostic: 0.035348
E(MP2/Aug-CC-pVDZ) (Hartree): -456.19762041
E(MP3/Aug-CC-pVDZ) (Hartree): -456.23292148
E(PMP2/Aug-CC-pVDZ) (Hartree): -456.20220625
E(PMP3/Aug-CC-pVDZ) (Hartree): -456.23583228
E(PUHF/Aug-CC-pVDZ) (Hartree): -454.87036633
E(UHF/Aug-CC-pVDZ) (Hartree): -454.86348135
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.70991292
E(CCSD/Aug-CC-pVTZ) (Hartree): -456.63172003
  T1 diagnostic: 0.033539
E(MP2/Aug-CC-pVTZ) (Hartree): -456.58735544
E(MP3/Aug-CC-pVTZ) (Hartree): -456.61111167
E(PMP2/Aug-CC-pVTZ) (Hartree): -456.59214593
E(PMP3/Aug-CC-pVTZ) (Hartree): -456.61411650
E(PUHF/Aug-CC-pVTZ) (Hartree): -454.97787761
E(UHF/Aug-CC-pVTZ) (Hartree): -454.97068590
E(UM062X/Aug-CC-pVTZ) (Hartree): -457.34568179
Electronic state : 2-A

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Cartesian coordinates (Angs):
O      0.745605   1.501524   -0.620875
O      0.525690   1.231735   0.715991
C      0.116002   -0.084617   0.828991
C      1.341605   -1.004066   0.389523
O      1.799705   -0.579280   -0.802316
H      1.370616   0.652473   -0.913900
H      2.086464   -0.951690   1.189223
H      0.870296   -1.994835   0.318864
H      -0.077107   -0.255372   1.890267
C      -1.154136   -0.432817   0.030386
O      -1.349639   -1.570229   -0.296362
C      -2.129430   0.685590   -0.199325
H      -3.047786   0.277482   -0.608948
H      -2.323876   1.205862   0.739379
H      -1.693744   1.411536   -0.883843

```

```

Rotational constants (GHz):  2.8483700  1.9725100  1.4629400
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
i1158.7670      54.9385      113.6510
130.0334      204.4073      270.6639
335.2259      417.8518      467.2986
518.1767      570.4574      607.4376
673.7363      775.2853      794.0243
873.4363      925.9955      964.5587
972.0458      1038.5901     1062.5708
1139.6786     1179.2062     1205.6529
1241.0571     1283.6026     1323.1509
1349.7309     1422.7638     1431.1558
1454.4978     1755.7741     1803.3453
2896.2745     2980.7331     2987.9592
3009.9441     3055.9995     3099.9579
Zero-point correction (Hartree): 0.108843

```

TS.HMVKBO2.15HshiftOH.bis.c

```

-----
E(UM062X/Aug-CC-pVTZ) (Hartree): -457.33974626
Electronic state : 2-A
Cartesian coordinates (Angs):
O      -2.043193   -1.018306   0.443766
O      -0.768707   -1.157121   -0.057623
C      -0.032754   -0.077789   0.359886
C      -0.626854   1.210855   -0.445540
O      -1.945881   1.238620   -0.249758
H      -2.277737   -0.012157   0.127477
H      -0.108463   2.056806   0.026760
H      -0.323068   1.078372   -1.491014
H      -0.196682   0.128820   1.419089

```

```

C      1.435821      -0.249294      -0.002334
O      1.802043      -1.178971      -0.663090
C      2.357317      0.838196      0.483881
H      3.378627      0.469596      0.470850
H      2.286070      1.690195      -0.195677
H      2.085969      1.182787      1.480803
Rotational constants (GHz):      3.4716400      1.5030500      1.1684700
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
i1013.8197      43.1844      119.0336
147.8901      193.0349      208.9061
340.3352      367.1566      469.6613
481.4378      530.3842      604.0190
646.9820      671.0444      879.1713
892.7017      935.8769      967.3829
1009.5274      1072.7320      1123.7730
1172.3153      1206.3595      1217.9980
1226.8518      1275.4401      1344.3337
1362.9907      1426.5258      1437.6367
1469.3026      1808.2405      1831.5482
2895.1876      2961.7268      2979.0601
3005.3212      3045.3523      3092.2116
Zero-point correction (Hartree): 0.109011

```

TS.HMVKBO2.15HshiftOH.bis.t

```

-----
E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.31690208
E (CCSD/Aug-CC-pVDZ) (Hartree): -456.26077363
T1 diagnostic: 0.037099
E (MP2/Aug-CC-pVDZ) (Hartree): -456.19580528
E (MP3/Aug-CC-pVDZ) (Hartree): -456.23028948
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.20066373
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.23344478
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.86814107
E (UHF/Aug-CC-pVDZ) (Hartree): -454.86099526
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.70918662
E (CCSD/Aug-CC-pVTZ) (Hartree): -456.63076391
T1 diagnostic: 0.035250
E (MP2/Aug-CC-pVTZ) (Hartree): -456.58628082
E (MP3/Aug-CC-pVTZ) (Hartree): -456.60915747
E (PMP2/Aug-CC-pVTZ) (Hartree): -456.59135563
E (PMP3/Aug-CC-pVTZ) (Hartree): -456.61241794
E (PUHF/Aug-CC-pVTZ) (Hartree): -454.97640047
E (UHF/Aug-CC-pVTZ) (Hartree): -454.96893868
E (UM062X/Aug-CC-pVTZ) (Hartree): -457.34522621
Electronic state : 2-A

```

Cartesian coordinates (Angs):

```

O      -1.872571      1.215932      -0.410969
O      -0.555085      1.153499      -0.021354
C      -0.038682      -0.056620      -0.434548
C      -0.771555      -1.187352      0.465574
O      -2.091096      -0.997269      0.356708
H      -2.237036      0.248610      -0.044487
H      -0.419101      -2.113343      -0.006419
H      -0.384772      -1.082437      1.486730
H      -0.292586      -0.270700      -1.472514
C      1.457171      -0.144926      -0.172208
O      2.046132      -1.103971      -0.593114
C      2.090804      0.953012      0.627682
H      3.142305      0.729862      0.776189
H      1.967556      1.902771      0.106115
H      1.578167      1.055016      1.585211

```

```

Rotational constants (GHz):      3.4397400      1.5178900      1.1907400
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
i1201.7934      45.2626      147.6267
158.5306      183.1466      212.5315
321.2716      411.0014      473.1626
486.1009      546.3366      568.8128
665.5663      681.8361      831.6410
863.2232      917.4099      982.8861
1012.1289      1069.8365      1123.7764
1189.4767      1195.1637      1204.1936
1229.2232      1276.5268      1320.4431
1357.5302      1419.0248      1426.6049
1466.8381      1778.1354      1802.4415
2903.7104      2966.9422      2983.3432
3027.4038      3044.1597      3099.6627
Zero-point correction (Hartree): 0.108847

```

TS.HMVKBO2.HO2elim.p2m

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-----
IRC pathway available
E (CCSD(T)/Aug-CC-pVDZ) (Hartree): -456.31014617
E (CCSD/Aug-CC-pVDZ) (Hartree): -456.24990038
T1 diagnostic: 0.033259
E (MP2/Aug-CC-pVDZ) (Hartree): -456.19833979
E (MP3/Aug-CC-pVDZ) (Hartree): -456.21898987
E (PMP2/Aug-CC-pVDZ) (Hartree): -456.22754672
E (PMP3/Aug-CC-pVDZ) (Hartree): -456.24442716
E (PUHF/Aug-CC-pVDZ) (Hartree): -454.87061449
E (UHF/Aug-CC-pVDZ) (Hartree): -454.83893501
E (CCSD(T)/Aug-CC-pVTZ) (Hartree): -456.69941482

```

```

E(CCS/ Aug-CC-pVTZ) (Hartree): -456.61634437
T1 diagnostic: 0.033018
E(MP2/ Aug-CC-pVTZ) (Hartree): -456.58459471
E(MP3/ Aug-CC-pVTZ) (Hartree): -456.59304969
E(PMP2/ Aug-CC-pVTZ) (Hartree): -456.61504853
E(PMP3/ Aug-CC-pVTZ) (Hartree): -456.61953681
E(PUHF/ Aug-CC-pVTZ) (Hartree): -454.97780129
E(UHF/ Aug-CC-pVTZ) (Hartree): -454.94481991
E(UM062X/ Aug-CC-pVTZ) (Hartree): -457.33102745
Electronic state : 2-A
Cartesian coordinates (Angs):
O -1.600602 1.577093 -0.473492
O -0.381432 1.683747 -0.299410
C 0.007739 -0.031122 0.846214
C -1.230978 -0.677766 0.715075
H -1.771137 0.353518 0.220605
O -1.428894 -1.718010 -0.170292
H -0.649465 -1.775960 -0.744313
H -1.816856 -0.804403 1.621860
C 1.177094 -0.322897 -0.012823
H 0.174297 0.574827 1.725566
O 1.094585 -1.112130 -0.933774
C 2.440989 0.424506 0.294026
H 3.218798 0.143151 -0.408547
H 2.245208 1.496359 0.230771
H 2.760839 0.210581 1.314851
Rotational constants (GHz): 2.4029100 1.8353600 1.2661800
Vibrational harmonic frequencies (cm-1): (Scaled by 0.9710)
i1027.9926 69.8267 111.2287
131.0264 148.6305 204.2438
249.0331 340.6202 364.4529
456.6042 517.6168 550.8328
624.2639 691.3864 715.6867
844.1860 909.3656 958.2840
1003.7957 1022.7406 1110.1159
1171.2932 1196.2076 1257.0953
1333.0390 1348.0429 1386.3677
1423.0189 1429.0542 1434.3050
1509.3672 1549.4444 1736.7490
2977.9066 3039.3516 3053.5596
3095.1894 3128.6717 3590.9805
Zero-point correction (Hartree): 0.109529

```