Atmos. Chem. Phys. Discuss., 10, C6746–C6753, 2010
www.atmos-chem-phys-discuss.net/10/C6746/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Does acetone react with HO₂ in the upper-troposphere?" *by* T. J. Dillon et al.

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Received and published: 23 August 2010

Referee Comments on ACPD manuscript acp-2010-442 by T. J. Dillon et al.

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General Comments

The authors have performed an experimental investigation of the reaction between HO2 radicals and acetone at low temperatures of 207 - 228 K and reduced pressures of 25 - 85 Torr, essentially based on measuring the OH resulting from the competition between (i) the sequence HO2 + CH3C(O)CH3 ↔ (CH3)2C(OH)OO (R1, reversible; k1 and k-1) followed by (CH3)2C(OH)OO + NO → products (k2), and (ii) the well known reaction HO_2 + NO → OH + NO_2 (k8). The OH was monitored by LIF and calibration was achieved on basis of the kinetically well characterized reaction system in absence of acetone. The experimental results, obtained using proven methodologies, are of high quality, and the lower-limit k1 data that could be derived directly are by themselves of much value, showing that the reaction does indeed occur at these low temperatures at rates of at least 1 x 10(-12) cm3 s-1 at T $\leq$ 210 K and 25 Torr. However, the more involved interpretation of the experimental data in terms of both k1 and k-1 (or K1) is not straightforward (see Specific Comments, below), and more importantly, two aspects of reaction (R1), with a large impact on the chemistry as detailed in the Specific Comments below, were not taken into account. Thus, though the paper shows convincingly that reaction (R1) does occur, the derived k-1(T) and equilibrium constant K1(T) data are both questionable, and the conclusion of the authors that the HO2 initiated oxidation of acetone and formation of acetic acid thereby is not significant in the tropopause appears therefore insufficiently substantiated. The interpretation of the data should therefore be re-addressed, in the light of the particular aspects of reaction (R1) detailed below.

Specific Comments

1. First, it should be noted that the k-1(T) and equilibrium constant K1(T) results obtained by the authors appear rather unusual in the light of the experimental data for the analogous reactions of HO2 with HCHO and CH3CHO and the reverse reactions. The reported k-1(T) for (CH3)2C(OH)OO decomposition imply a very high k-1(300 K) of around 2x10(6) s-1. When comparing this result to the experimental values of 175 s-1 for H2C(OH)OO (Veyret et al., 1989) and 1900 s-1 for CH3CH(OH)OO (Tomas et al., 2001), the carbonyl-stabilizing inductive effect of the second CH3 group seems a hundred times stronger than that of the first CH3 substituent, which is definitely not in keeping with group additivity concepts. Further, from the reported K1(T) results, the stability of (CH3)2C(OH)OO with respect to the reactants appears to be 11 kJ mol-1 less than the 59 ± 2 kJ mol-1 computed at various high-levels of theory by Hermans

et al., 2005, whereas the stabilities computed in that same paper at the same levels of theory for the two analogous α-OH-peroxys CH3CH(OH)OO and H2C(OH)OO were shown to agree with experiment within 2 kJ mol-1. This gives reason to question the more involved interpretation of the [OH] data in presence/absence of acetone in terms of both k1 and k-1.

2. The apparent rate constant that can be derived from the measured reduction of [OH] upon acetone addition is essentially k1/(1 + k-1/k2[NO]), or K1/(1/k-1 + 1/k2[NO]), and hence k1 and k-1 (or k1 and K1) could not be obtained independently from these experiments. The authors opted for adopting the theoretically predicted k1 of Hermans et al. 2004, and so deriving k-1 (and hence K1) from the observed [OH] reduction upon acetone addition. This by itself was not the best choice, since the theoretical k1 of Hermans et al. 2004 (as all the k in that paper and likewise in Hermans et al. 2005) are TST-based and therefore by definition high-pressure limit values, whereas the reaction in question, through a stable pre-reactive complex (PRC) and over a submerged barrier, will necessarily show pressure-dependence, while the experimental pressures are quite low. Moreover, equilibrium constants, besides being independent of pressure, can in general be predicted (much) more accurately than rate coefficients; therefore, a better choice would have been to adopt the theoretical K1 of Hermans et al. 2005, in which paper the stability of the α-OH-peroxy at hand was verified at higher levels of theory compared to the 2004 paper, and the rate coefficients at issue here were accordingly upgraded.

3. As to the pressure-dependence of reaction (R1), the rate of prompt redissociation of the nascent chemically activated PRC† formed at 210-230 K can be estimated at roughly kred(Eav = 8 kJ/mol) $\approx$ 3x10(9) s-1, such that at 25 and 85 Torr, collisional stabilization, with βscZLJ[M] of $\approx$5x10(7) s-1 and $\approx$1.5x10(8) s-1, respectively, is too slow and hence product formation occurs mainly through the nascent, activated PRC†, meaning that the reaction is in its low-P limit. The forward kf(Eav = 8 kJ/mol) rate to form the product is estimated at about 2x10(7) s-1, i.e. 100 times slower than redis-

sociation; both these rates are estimated here from the data in Hermans et al. 2005 and their available Supporting Information. (See Note on rates estimated in these comments , below). That higher pressures should increase the product formation rate (i.e. the effective k1) substantially, is readily seen: PRC(†) that are brought just below the reactants level by collisions can no longer redissociate promptly, but still promptly yield the product as the submerged transition state lies 11 kJ mol-1 below the reactants (see Hermans et al. 2005 for the energetics). The pressure effect at these low T should be pronounced; assuming an HO2-acetone capture rate kcapt = 10(-10) cm3 s-1, the low-P k1 is estimated at barely 10(-12) cm3 s-1, i.e. substantially lower than the upgraded high-P limit k1,∞(207 K) = 5.8x10(-12) cm3 s-1 and k1,∞(228 K) = 3.0x10(-12) cm3 s-1 predicted by Hermans et al. 2005.

4. Equally important, but not considered by the authors, is that at these low T and high [acetone] around 10(15) cm-3, the bulk of the HO2 can be expected to be sequestered in the very stable H-bonded OOH—O=C(CH3)2 PRC complex, in thermal equilibrium with acetone and free HO2. The HO2 + CH3C(O)CH3 $\leftrightarrow$ OOH—O=C(CH3)2 complexation (Kcompl) was first described by Aloisio and Francisco 2000 at B3LYP level, while Hermans et al. 2005 computed an even slightly higher complex stability of 41$\pm$4 kJ mol-1 at several higher levels of theory, giving also the vibration/rotation parameters in Supporting Information (SI). Of much impact on the issue at hand are the magnitude of Kcompl(T) and the timescale to attain the equilibrium. Kcompl(200-230 K) is large because the complex is stable but at the same time quite "loose" and hence exhibits a high density of states and high partition function on account of the quasi-free internal rotation of the terminal hydroperoxy-O about the O-H—O= axis. The harmonic-oscillation-approximation of Gaussian attributes a "vibration frequency" of 60 cm-1 to this mode (see SI Hermans et al. 2005), but this results merely from a small dip in the (otherwise flat) V(θ) internal rotation potential, at a dihedral angle where the terminal hydroperoxy-O is close to the nearest methyl-H (but still 2.6 A distant); the 207 K partition function for this quasi-free internal rotation mode is estimated at about 20, i.e. much higher than the HOA value of 2.9. As earlier reported by Aloisio and Fran-

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cisco, two other new modes of the complex (Gaussian "frequencies 83 and 157 cm-1" of Hermans et al.) are hindered internal rotations, which together can put the partition function another factor of $\approx$3 above the HOA approximation. Thus, Kcompl(T) is roughly estimated at about 3x10(-14) cm3 at 207 K and 5x10(-15) cm3 at 228 K, with a probable error of a factor of 10. Given the experimental [acetone] of order 10(15) cm-3, this implies that at equilibrium the bulk of the HO2 (some 80% to well over 90%) can be tied up in the thermal OOH—O=C(CH3)2 complex. As the terminal O is quasi-free, this complex should still react with NO, to yield an OH that is more weakly H-bonded to the carbonyl-O (see Aloisio and Francisco, 2000) and thus easily released. On the other hand, reaction of the complex with another acetone to form the α-OH-peroxy is not expected to contribute, as it is both energetically (by 41 kJ mol-1) and entropically strongly disfavored compared to (R1). Besides thermal redissociation, the complex can thermally convert, about 20 times slower, to the α-OH-peroxy, which brings the effective k1 somewhat above the low-P limit. The rate of approach to the equilibrium can be approximated as kcapt x [acetone] x βscZLJ[M]/(kred(Eav) + βscZLJ[M]) (given that the term for the thermal redissociation is sizably smaller, at least at 207 K and 25 Torr). This gives an equilibration time constant of roughly 1000 μs (with a large uncertainty) for the 207 K, 25 Torr, 7.5x10(14) cm-3 acetone experiments, such that at [NO] = 1.5x10(14) cm-3 much of the HO2 will already have reacted before the complex attains equilibrium. At 228 K, 85 Torr and 1.7x10(15) cm-3 acetone however, where also the thermal redissociation term becomes important, the time constant is nearer 50 μs, such that HO2 complexation is quasi-immediate. It should be stressed however that the Kcompl estimates above may be off by a factor of 10, given the $\pm$4 kJ mol-1 uncertainty on the complex stability, as stated for most relative energies in the Hermans et al. 2005 paper.

Items 3 and 4 above can explain the strong apparent disagreement between the k-1 and K1 data derived in this manuscript and the predictions of Hermans et al. For instance, at 207 K, 25 Torr: a same effective k1/(1 + k-1/k2[NO]) rate as concluded to in the paper is obtained with k-1 negligible and k1 = 1.6x10(–12) cm3 s-1 (i.e. 0.27

times the k1,∞ prediction of Hermans et al. 2005); and at 228 K, 85 Torr: likewise, with k-1 negligible and k1 ≈ 1x10(–12) cm3 s–1 (i.e. 0.33 x k1,∞) but with 80-90% of the HO2 quickly complexed.

5. According to the authors' interpretation of the observed [OH] behavior in Fig. 2, with a large k-1 of 30000 s-1 at T = 228 K, the second term in the denominator of the apparent rate for HO2 removal by acetone, k1[acetone]/(1 + k-1/k2[NO]) (see sub 1., above), would be much larger than 1, such that the apparent rate would simplify to K1k2[acetone][NO], and thus show the same dependence on [NO] as the rate k8[NO] of the competing HO2 + NO → OH + NO2 reaction. As a result, the competition between HO2 removal by acetone and by NO to yield OH would be independent of [NO]. If on the other hand k-1 is negligible at these T as predicted by Hermans et al., the apparent rate of HO2 removal by NO is independent of [NO], very different from the linear [NO]-dependence of the competing HO2 + NO reaction. This might have been easily checked by the authors. However, the tell-tale dependence of the competition at issue on [NO] was not investigated, all experiments at given T having having been conducted at a single [NO].

6. In the light of the above, the section on atmospheric modelling in the manuscript appears rather premature.

Technical and minor Comments

Page 16755, line 24: this should be : k-1 = 3x10(–12) cm3 molecule-1 s-1 (minus sign in exponent).

Table 3: the fast OH + HO2 reaction is missing as a (minor) OH sink.

Table 3: A minus sign is missing in the exponent of 10 of the second term.

Table 3: OCH2C(O)CH3† decomposes promptly into CH3CO + HCHO instead of reacting with O2 (Orlando et al., 2000).

Table 3: The expression given for k(CH3 + O2) would result at the experimental pres-

sures in values well above the high-P limit.

Table 3: The reaction of CH3CO + O2 generates about 30% OH at 207 K and 25 Torr, and about 8% at 228 K and 85 Torr.

Table 3: Equilibrium formation of the ≈68 kJ mol-1 stable HOOOOH tetroxide from HO2 + HO2 (see Denis et al., J. Phys. Chem. A, 2009, 113, 499) is missing, but is only minor at the fairly low experimental [HO2] of this work, though quite important at the much higher [HO2] in another recent study.

Page 16761, line 24: twice "in line with (the) theoretical predictions".

NOTE on rates and equilibria estimated for these comments.

Chemically activated rates estimated for these comments by the referee are generally Whitten-Rabinovitch-type RRKM-estimates, and should not be considered as rigorous RRKM derivations, from which they may deviate by a factor of 3 or more. Estimated thermal rates in these comments are likewise not rigorous MC-TST derivations and can be off by a factor of 3 to 10; similar for the thermal-equilibrium constants.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 16747, 2010.