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**Isotope effect in the
formation of H₂ from
H₂CO**

T. Röckmann et al.

Isotope effect in the formation of H₂ from H₂CO studied at the atmospheric simulation chamber SAPHIR

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Received: 4 November 2009 – Accepted: 16 November 2009 – Published: 25 November 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Formaldehyde of known, near-natural isotopic composition was photolyzed in a large photochemical reactor under ambient conditions. The isotopic composition of the product H_2 was used to determine the isotope effects in formaldehyde photolysis. The experiments are sensitive to the molecular photolysis channel, and the radical channel has only a second order effect and can thus not be derived with high precision. The molecular channel kinetic isotope effect (KIE_{mol}), the ratio of photolysis frequencies $j(\text{HCHO} \rightarrow \text{CO} + \text{H}_2) / j(\text{HCDO} \rightarrow \text{CO} + \text{HD})$ under tropospheric conditions is determined to be $\text{KIE}_{\text{mol}} = 1.63 \pm 0.03$. Combining this result with the total KIE from a recent relative rate experiment, it is likely that KIE_{mol} and KIE_{rad} are not as different as described previously in the literature.

1 Introduction

Molecular hydrogen (H_2) is the second most abundant reduced gas in the atmosphere after methane (CH_4) with a global average mixing ratio of roughly 500 ppb. Interest in its atmospheric cycle has strongly increased in the past years because of its potential future large-scale use as energy carrier. Since H_2 production only produces H_2O , a future hydrogen economy is expected to ameliorate many of the present climate and air quality related problems (Schultz et al., 2003). However, it is expected that unavoidable leaks in the production, storage, transport and use of H_2 would considerably increase the atmospheric content of H_2 . Although H_2 is not a greenhouse gas, it affects the concentration of the greenhouse gas methane and many other species via a feedback from its removal reaction with the hydroxyl (OH) radical (Schultz et al., 2003). In the stratosphere, increased levels of H_2 will lead to higher levels of stratospheric water vapour and thus to an increase in the occurrence of polar stratospheric clouds (PSC) in the polar winter periods (Warwick et al., 2004; Schultz et al., 2003; Tromp et al., 2003; Feck et al., 2008). These PSC play a key role in the halogen-catalyzed destruc-

Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tion of ozone (the ozone hole), and thus increased H_2 levels are expected to delay the recovery of the polar ozone hole.

H_2 has a peculiar latitudinal distribution in the atmosphere with higher mixing ratios in the Southern Hemisphere (SH) compared to the Northern Hemisphere (NH) (Steele et al., 1996; Novelli et al., 1999; Ehhalt and Rohrer, 2009). This is because the main H_2 removal process is deposition to soils, and there is much more soil surface in the NH. The second important removal process is oxidation by the OH radical. H_2 is produced mainly by three classes of processes: 1) combustion processes (fossil fuel burning and biomass burning) 2) atmospheric oxidation reactions (CH_4 oxidation and oxidation of non-methane hydrocarbons, NMHC) and 3) biological processes in the soil or the ocean. The third group is likely of minor importance, but there are still large error bars on the quantitative estimates of all sources and sinks of H_2 .

Isotope studies can yield valuable insight into the relative strengths of sources and sinks of atmospheric trace gases, since gases emitted from different sources usually carry a distinct isotope composition or incur an isotope fractionation, which is characteristic for that source or sink, respectively (Gerst and Quay, 2000, 2001; Rahn et al., 2003, 2002a, 2002b; Rhee et al., 2005, 2008; Brenninkmeijer et al., 2003; Röckmann et al., 2003). In the case of hydrogen the isotope effects are particularly large due to the 100% relative mass difference between 1H and 2H (deuterium, in the following denoted D). The isotope ratio is measured as a ratio of the rare isotope D to the abundant isotope H and expressed as difference to the isotope ratio of Standard Mean Ocean Water ($VSMOW$, $(D/H)_{VSMOW} = 1.56 \times 10^{-4}$) given in per mil units ($\delta D = [(D/H)_{Sa} / (D/H)_{VSMOW} - 1]$). The average isotopic composition of atmospheric H_2 is roughly +130‰. Emissions from the ocean and nitrogen fixation in soils are expected to have the lowest D content ($\delta D \sim -700$ ‰), the equilibrium fractionation between water and H_2 (Bottinga, 1968). δD values between -200 and -300‰ have been determined for H_2 from biomass and fossil fuel burning (Rahn et al., 2002b; Gerst and Quay, 2001; Rhee et al., 2005). Atmospheric oxidation processes must have an enriched isotope signature to balance the isotope budget, as first postulated by Gerst and Quay (2001).

Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Recent investigations have confirmed this on samples from the stratosphere, where CH₄ oxidation is the only significant in-situ source and can be studied without interference from the surface sources (Rhee et al., 2006; Röckmann et al., 2003; Rahn et al., 2003). Nevertheless, it is not straightforward to apply those stratospheric results to the troposphere. Basically no information is available on isotope effects for H₂ formation from the oxidation of non-methane hydrocarbons.

In addition to the stratospheric studies, also laboratory studies have investigated the isotope effects in the oxidation chain from CH₄ to H₂ (Nilsson et al., 2007; Feilberg et al., 2007a, 2005b, 2007b, 2004; Rhee et al., 2008; Gierzak et al., 1997). As usual for isotope effects, the most important fractionations occur where there are branching steps in the reaction mechanism. The series of rate constants of methane and deuterated methanes with OH determined by Gierzak et al. (1997) indicates that the abstraction probability for H and D in CH₃D are 96% and 4%, respectively, so D abstraction is much less than the statistically expected value of 25%. Recent measurements have shown that in the second abstraction step (CH₂DO+O₂), the abstraction probability of D is 11%, again much less than the statistically expected 33% (Nilsson et al., 2007). As D abstraction is much slower than H abstraction, most of the D from the original CH₄ stays in the oxidation chain, whereas the total number of H atoms is reduced by a factor of 2 from CH₄ to H₂. This leads to a strong enrichment in the D/H ratio, and thus the δD value.

The third step where branching occurs is production of H₂ from formaldehyde. Reactions (1–3) remove formaldehyde, two photolysis channels and the reaction with OH. Only the so-called molecular photolysis channel (1) produces H₂. Therefore, the fractionation between HCHO and H₂ in the atmosphere depends on the fractionation constant of (1) relative to the flux-weighted fractionation in the total removal of HCHO.



Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The fractionation constant in reaction (1) was determined in a laboratory experiment (Feilberg et al., 2004) to be $KIE_{OH} = 1.28$, where KIE is the ratio of rate constants of the non-deuterated and deuterated molecules $KIE = k_H/k_D$. For HCHO photolysis, different studies have reported differing values. Feilberg et al. (2007b) carried out measurements at the European Photoreactor Facility EUPHORE in Valencia, Spain, and found KIEs for the molecular (1) and radical (2) channel of $KIE_{mol} = 1.82$ and $KIE_{rad} = 1.1$. Rhee et al. (2008) carried out photolysis experiments in a glass bulb under natural insolation and found $KIE_{mol} = 2.0$ and $KIE_{rad} = 4.5$. Whereas KIE_{mol} values are in reasonable agreement, the values for KIE_{rad} disagree strongly. However, in none of the experiments this KIE was measured directly, only inferred. In the case of Feilberg et al. (2007b), the combined KIE_{tot} was determined directly by absorption spectroscopy using D-labeled reaction mixtures. Furthermore, δD of the (extremely enriched, because of the labeled H₂CO precursor) H₂ product was measured by isotope ratio mass spectrometry, and these results were used in a photochemical model to determine KIE_{mol} , and balance KIE_{rad} . Rhee et al. (2008) derived KIE_{mol} from the $\delta D(H_2)$ at small reaction yields, where the second order effect of the radical channel is negligible. They determined KIE_{rad} by total conversion of HCHO and mass balance considerations.

Here we report an independent study of the hydrogen isotope effect in the production of H₂ from HCHO. The experiments were carried out in the SAPHIR reactor at Forschungszentrum Jülich under almost ambient conditions and using natural isotope abundance HCHO reactant.

2 Experimental

The experiments were carried out in the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich, Germany. SAPHIR is a large (5 m diameter, 18 m length, $270 \pm 10 \text{ m}^3$ volume) cylindrical chamber made of double-walled Teflon suspended in a steel frame that allows studying atmospheric reactions under ambient radiation conditions. At the same time, the gas mixture in the SAPHIR chamber can be carefully

Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

selected to study only the reactions of interest. A mixture of N₂ and O₂ (>99.9999% purity) is used as ultra-clean matrix. The space between the two Teflon walls of the reactor is constantly flushed with the clean O₂-N₂ mixture, thus H₂ cannot leak in from outside. Air losses due to consumption by the analytical instruments small leaks are compensated by automatically adding an air flux of 3–4 m³ h⁻¹ into the chamber to maintain the pressure in the chamber almost constant. The dilution rate is derived from the replenishing flow.

In our experiments, approximately 500 ppb HCHO, produced by complete evaporation of typically 200 mg paraformaldehyde into the chamber, was used. Since the isotope monitoring mass spectrometry technique for the HD measurement (see below, Rhee et al., 2004) requires a minimum of 2.5 nmole H₂ for high-quality analysis, 200–400 ppb background H₂ were added at the beginning of the experiment. We used two different H₂ reference gases with very different isotope composition as background, $\delta D_{bg}=(-177\pm 5)\text{‰}$ and $\delta D_{bg}=(-680\pm 20)\text{‰}$, respectively.

Two control experiments with different gas mixtures were carried out, in which the chamber was not opened to sunlight (Table 1). These control experiments served to confirm that no outside H₂ can enter the chamber through the Teflon foil and to assure stability of the δD value of the background H₂. In the first control experiment (exp. 2), 1200 ppb of H₂ were added to the N₂/O₂ bath gas in the chamber. The mixture was sampled every hour for 7 h, then left standing overnight, and sampled again two times on the following day. Samples were taken at the start and after 2, 4 and 6 h. In the second control experiment (exp. 8), 350 ppb H₂, 500 ppb HCHO and 500 ppm CO as OH quencher were admitted, thus simulating a real experiment, but without sunlight. Samples were collected at the start and after 2, 4 and 6 h.

In the HCHO photolysis experiments, 500 ppm of CO were added as OH quencher in order to suppress the HCHO+OH reaction. Experiments 1 and 5 were similar experiments with different background mixing ratios of H₂. Exp. 3 was similar to exp. 5, but the background H₂ was provided from a different supply and had a very depleted isotopic composition of $\delta D\sim -680\text{‰}$ (see below).

Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Experiments usually started at ~10:00 LT and ended at ~17:00 LT, after which the chamber was flushed for the experiment on the following day. During the experiment, the analytics of Forschungszentrum Jülich that are operated at the SAPHIR chamber provided an extensive characterization of the photochemical conditions. Temperature, humidity, pressure, photolysis frequencies, ozone, nitrogen oxides, carbon monoxide, hydrocarbons, including several oxygenated species, and of course formaldehyde were measured (Brauers et al., 2007; Apel et al., 2008; Bohn et al., 2005; Rohrer et al., 2005; Wisthaler et al., 2008). The H₂ concentration and isotopic composition were measured on flask samples taken at 30–120 min intervals during the experiments. A total of 60 samples were taken by filling 2 l glass flasks (Normag AG) equipped with Kel-F stopcock seats to ~1.9 bar absolute pressure with a KNF Neuberger membrane pump. Flasks were flushed 3 min before sampling. The samples were analyzed within 4 weeks at the isotope laboratory of the Institute for Marine and Atmospheric research Utrecht.

The isotopic composition and concentration of H₂ in the air samples was determined by an isotope monitoring mass spectrometry technique based on Rhee et al. (2004) but modified to allow slightly larger samples to be analyzed. The analytical system has been improved such that all valve switching, heating and cooling steps and the flow rate change are automated. An air sample of ~350 ml is first admitted from the sample flask to a ~500 ml sample volume of the analytical system. The air is then connected for 10 min to a 6 cm³ stainless steel volume attached to a liquid Helium cold head at ~30 K where the bulk air and most other air constituents condense. The H₂ remains in the gas phase and is subsequently flushed with ultra-clean Helium (20 ml/min) to a 1/8' diameter stainless steel pre-concentration trap. This trap is filled with molecular sieve 5A and immersed into a liquid nitrogen bath, which has been cooled down to the triple point of N₂ (63 K) by continuously pumping on the gas phase above the N₂. Pre-concentration takes 20 min, and then the sample is transferred by a 1 ml/min flow of He into a focus trap held at liquid nitrogen temperature. When the sample has been transferred to the focus trap, the flow rate is reduced to 250 μl/min, the trap is released from the IN₂ bath and the H₂ peak is admitted to an additional Nafion drying unit, the

Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

open split interface and finally the isotope ratio mass spectrometer. Ion currents of $m/z=2$ and $m/z=3$ are monitored as voltages across $10^9\Omega$ and $10^{12}\Omega$ resistors on a ThermoFinnigan Delta plus XL isotope ratio mass spectrometer. The sample peak is bracketed by 6 square peaks of the MS running gas (3 before, 3 after the peak) and the running gas peak before the sample peak is assigned as internal reference peak. For referencing we use a stainless steel cylinder filled with whole air by the University of Heidelberg, which is measured routinely at least once per day in the same way as the sample air. The isotopic composition of this air has been calibrated against mixtures of two pure H₂ gases of certified isotopic composition ($\delta D=+200.5\%$ and $\delta D=9.0\%$ vs. VSMOW, respectively, Messer Griesheim), which were diluted in H₂-free air and analyzed the same way as the reference air.

Quantification of the $m/z=2$ peak from a known amount of air allows the mixing ratio to be determined with a reproducibility of 1–2%, which is similar to state-of the art H₂ analyzers. The typical error of the analytical system based on repetitions of reference air measurements is 2–5%. The isotopic composition (δD) of the paraformaldehyde stock used for the experiments was determined by Agrosolab, Jülich, Germany to be $(+70.0\pm 1.4)\%$ versus VSMOW.

2.1 Photochemical modeling

The research center Jülich operates an advanced photochemical model specifically designed for evaluation and interpretation of SAPHIR experiments. The isotopically substituted species HDCO and HD have been added to this model and were initialized according to the δD values measured at the beginning of each experiment. The Isotope fractionation factor for reaction of HCHO with OH $KIE_{OH}=k_{HCHO+OH}/k_{HDCO+OH}=1.28$ is available from the literature (Feilberg et al., 2004) and isotope fractionation factors in the molecular and radical channels of H₂CO photolysis were adjusted to match the experimental results.



3 Measurements and modeling

3.1 Control experiments

The drop of the H₂ concentration in the two control experiments, where the cover of the chamber is not opened (not shown), is in accordance with the dilution derived from the replenishing flow, which is approximately 3.7%/h. The important result from the control experiments is that the isotopic composition does not exhibit a significant change over a period of several hours, which excludes artifacts from fractionation by dilution or possible wall effects. Furthermore, the experiment where HCHO is added shows the same dilution rate for H₂ and HCHO, thus HCHO is stable in the reaction chamber.

3.2 Photolysis experiments

In the photolysis experiments, HCHO removal starts immediately after the chamber is exposed to sunlight. In the experiments, 30 to 40% of the initial HCHO is removed during the course of the experiment. The molecular photolysis channel produces H₂, whose concentration increases accordingly, despite the continuous dilution. At the same time, the isotopic composition of H₂ changes significantly. It should be noted that what is measured is not the isotopic composition of the freshly formed H₂, but the mixture of the background reservoir plus the freshly formed fraction. This background reservoir, which is necessary to provide sufficient material for isotope analysis, impedes the direct identification of the freshly produced H₂. Therefore, not the absolute δD values, but the changes in δD have to be evaluated to derive the isotopic composition of the H₂ produced. When the background reservoir is larger (exp. 1, [H₂]_{BG}=400 ppb) the isotopic composition changes more slowly than for a smaller background reservoir (exp. 5, [H₂]_{BG}=200 ppb).

Qualitatively, in experiment 1 and 5, $\delta D(\text{H}_2)$ decreases with time, which shows that the freshly produced fraction is isotopically lighter than the background reservoir. In exp. 3 with the strongly depleted background reservoir, $\delta D(\text{H}_2)$ increases during the

Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



experiment, because the freshly produced H_2 is enriched relative to the reservoir. In principle, it should be possible to determine the source signature from those experiments by triangulation, but this is not straightforward. Due to the kinetic fractionation, the isotopic composition of HCHO also changes strongly with increasing degree of removal and we do not have an isotopically constant substrate. Data interpretation was therefore made using the SAPHIR photochemical model.

3.3 Model results

Figure 1 compares the measurements to values modeled with the SAPHIR model for HCHO mixing ratio, H_2 mixing ratio and $\delta\text{D}(\text{H}_2)$ for the photolysis experiments 1, 3 and 5 (Table 1). In all cases the model captures the evolution of the mixing ratios very well, which is expected since formaldehyde photolysis is well understood as regards changes in concentration. The new feature in this work is the incorporation of isotope information. HCHO and HCDO are modeled as separate species and the kinetic isotope effects KIE_{mol} and KIE_{rad} in the two photolysis channels of HCHO and HCDO (1 and 2) are included and can be adjusted to match the observations. It should be noted that the system is underdetermined, since we only have one measurable, $\delta\text{D}(\text{H}_2)$ but two unknowns, KIE_{mol} and KIE_{rad} . Therefore, we can in principle only determine pairs of KIE_{mol} and KIE_{rad} .

As first attempt, we choose $\text{KIE}_{\text{mol}} = \text{KIE}_{\text{rad}} = \text{KIE}$, although recent publications indicate possible strong (but not consistent among publications) differences between KIE_{mol} and KIE_{rad} . The value of KIE is then optimized by minimizing the square root of the squared sum of model-data differences, χ^2 . Ideally, χ^2 should be of the same order as σ^2 , where σ is the typical measurement uncertainty, since it describes the random fluctuations of the measurements around the model results. Table 2 shows that the best fit to the results of the three photolysis experiments is achieved for $\text{KIE}_{\text{mol}} = \text{KIE}_{\text{rad}} = 1.63$, which is displayed as the red solid line in Fig. 1. For this value, $\chi^2 = 34.3$, i.e., the typical difference between the measurements and the model is slightly larger than the

Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



estimated analytical uncertainty in δD of $\sim 5\%$. Based on 26 individual measurements, χ^2 has a statistical error of $\chi^2/26=1.3$. Consequently, KIE values that produce χ^2 values up to 35.6 still fall in the range of valid scenarios. Table 2 shows that this leads to a result of $KIE=1.63\pm 0.02$ for the case $KIE_{mol}=KIE_{rad}$.

Figure 1 also shows the different sensitivity of the model results to changes in KIE_{mol} and KIE_{rad} . The cyan area depicts the range of model results when KIE_{mol} is changed by ± 0.1 while KIE_{rad} remains unchanged, the grey area the range of model results when KIE_{rad} is changed by ± 0.5 while KIE_{mol} remains unchanged. The 5 times larger change of KIE_{rad} compared to KIE_{mol} is reflected in the modeled changes of the isotopic composition of HCHO. This is because both channels remove HCHO at roughly comparable rates (60%:40%). For the H_2 production, however, the resulting change in $\delta D(H_2)$ caused by the modeled change in KIE_{rad} is 5 times larger compared to the change caused by a modeled change in KIE_{mol} , although the change in KIE_{rad} is 5 times smaller than the change in KIE_{mol} . This is due to the fact that KIE_{mol} has a direct effect on $\delta D(H_2)$, whereas KIE_{rad} only changes $\delta D(H_2)$ through a feedback via $\delta D(HCHO)$ as discussed below in more detail. The poor sensitivity to KIE_{rad} means that it is not possible to strongly constrain KIE_{rad} by our measurements. On the other hand, it means that the fact that the system is underdetermined does not pose a strong restriction on deriving precise values for KIE_{mol} . Even when KIE_{rad} is varied over a wide range, this has only a minute effect on the value of KIE_{mol} that is needed to obtain best agreement with the data for a particular KIE_{rad} . Therefore, the insensitivity to KIE_{rad} actually means that we can derive tight constraints on KIE_{mol} .

In retrospect, it is unfortunate that not more samples were taken before starting and after finishing the photolysis period. Determining those points with a higher precision may have enabled an even more precise determination of the total isotope change, and thus KIE_{mol} . Nevertheless, the error estimates are sufficiently low to conclude that for the assumption $KIE_{mol}=KIE_{rad}$ the derived $KIE=1.63\pm 0.02$, which is significantly lower than the values reported by Feilberg et al. (2007b) and Rhee et al. (2008). As mentioned above, although the results from these two publications do not agree on the

Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

magnitude or even the direction of the effect, they both indicated that there may be large differences between KIE_{mol} and KIE_{rad} . Therefore, in the second step, we investigate whether the comparatively low value for KIE_{mol} can be due to the assumption $KIE_{mol}=KIE_{rad}$.

When both KIE values are optimized simultaneously, KIE_{rad} yields values <1 , which is physically unlikely, given the lower zero point energies of HCDO compared to HCHO. We therefore constrain KIE_{rad} to be ≥ 1 , and the best fit is obtained for $KIE_{rad}=1$ and $KIE_{mol}=1.60$. The χ^2 value for this scenario is the lowest with $\chi^2=31.8$. This scenario is also shown in Fig. 1 as dashed black line, which is very similar and in some cases virtually indistinguishable to the optimal solution for $KIE_{mol}=KIE_{rad}$. $KIE_{mol}=1.60$ is the minimum that can be achieved for $KIE_{rad}\geq 1$. We therefore extend our error estimate to the final value of $KIE_{mol}=1.63\pm 0.03$ to account for possible differences between KIE_{mol} and KIE_{rad} .

It is interesting, and maybe counterintuitive, that both KIEs are shifted in the same direction when adjusted independently. KIE_{mol} directly influences the isotopic composition of the product H₂, and when KIE_{mol} is decreased, $\delta D(H_2)$ increases accordingly. KIE_{rad} , on the other hand, has only an indirect effect by changing the isotopic composition of the formaldehyde reservoir that remains for H₂ formation. At the start of the experiment changing KIE_{rad} has no effect at all. In the course of the experiment, smaller values of KIE_{rad} (i.e., relatively faster HCDO removal via the radical channel) lead to a depletion of $\delta D(HCHO)$ in the remaining formaldehyde reservoir. To make up for the lower $\delta D(HCHO)$ value, KIE_{mol} also has to be decreased in the model to still explain the same $\delta D(H_2)$ value. This explains the fact that only changing both KIE's in the same direction can describe the observed $\delta D(H_2)$ value.

Based on these theoretical considerations, it can already be deduced that it is impossible to quantitatively reconcile the results of Feilberg et al. (2007b) with the new dataset, as KIE_{mol} from Feilberg et al. (2007b) is significantly larger and KIE_{rad} significantly smaller than the new values derived for $KIE_{mol}=KIE_{rad}$. The lower KIE_{rad} derived in Feilberg et al. (2007b) would lead to an even lower value of KIE_{mol} for

Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

our experiments, even increasing the discrepancy to KIE_{mol} determined in Feilberg et al. (2007b). Concerning the results by Rhee et al. (2008) KIE_{rad} and KIE_{mol} deviate in the same direction, but the differences are also much larger. Apparently, even the extreme value of $KIE_{rad}=4.5$ is not sufficient to compensate for the only slightly higher value of $KIE_{mol}=2.0$ because of the lack in sensitivity to KIE_{rad} . Figure 1 also shows model results obtained with the parameters from these publications, and it is clear that they do not yield satisfactory agreement with the observations.

In order to further explore the sensitivity to KIE_{rad} for one example, we investigated whether the effect of a potential value of $KIE_{mol}=1.75$ can be compensated by higher KIE_{rad} values. $KIE_{mol}=1.75$ is an arbitrary choice between the present results and the result from Feilberg et al. (2007b). Figure 2 shows the model-measurement differences χ^2 for model runs in which $KIE_{mol}=1.75$ was kept constant and KIE_{rad} was varied over a very wide range. Clearly, χ^2 is higher for these runs, and it is not possible to compensate for the higher value of KIE_{mol} by choosing even higher values of KIE_{rad} . Above a threshold of 5–10 for KIE_{rad} , there is no significant improvement in χ^2 , even when extreme values up to 2000 are used. In absolute terms, already a $KIE=5$ means that H reactions are favored by a factor of 5 compared to D reactions, and any further reduction of the D reaction paths only has a minor effect.

The model also calculates $\delta D(HCHO)$, which could not be determined experimentally. $\delta D(HCHO)$ values increase by ~ 100 to 200‰ in the model, depending on the relative removal fraction. These are large changes and although it appears to be very difficult to obtain high precision in isotope measurements on HCHO, the precision achieved in the only publication that is available to date ($\pm 50\%$) (Rice and Quay, 2006) would be sufficient to detect changes of this magnitude.

4 Discussion

It is intriguing that three different studies of the KIEs in the photolysis of formaldehyde yield three different results. Therefore, in the following we attempt to explain the dif-

Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

ferences. As noted already in (Pieterse et al., 2009), the values of KIE_{mol} , KIE_{rad} and KIE_{tot} reported in Feilberg et al. (2007b) are not consistent with the recommended relative photolysis yields of the molecular channel and radical channel. In the following, we define β_{mol} and β_{rad} as the relative photolysis yields of the molecular and radical channel, respectively. For near-natural isotope abundance, when β_{mol} and β_{rad} are very close to the branching ratios for the non-deuterated HHCO molecules, KIE_{tot}^{-1} is the flux weighted average of KIE_{mol}^{-1} and KIE_{rad}^{-1} :

$$\begin{aligned} \frac{1}{KIE_{tot}} &= \frac{J_{HDCO}}{J_{HHCO}} = \frac{J_{HDCO \rightarrow HD+CO} + J_{HDCO \rightarrow H+DCO} + J_{HDCO \rightarrow D+HCO}}{J_{HHCO \rightarrow HH+CO} + J_{HHCO \rightarrow H+HCO}} \\ &= \frac{J_{HDCO \rightarrow HD+CO}}{J_{HHCO \rightarrow HH+CO} + J_{HHCO \rightarrow H+HCO}} + \frac{J_{HDCO \rightarrow H+DCO} + J_{HDCO \rightarrow D+HCO}}{J_{HHCO \rightarrow HH+CO} + J_{HHCO \rightarrow H+HCO}} \\ &= \frac{J_{HDCO \rightarrow HD+CO}}{J_{HHCO \rightarrow HH+CO}} * \frac{J_{HHCO \rightarrow HH+CO}}{J_{HHCO \rightarrow HH+CO} + J_{HHCO \rightarrow H+HCO}} + \frac{J_{HDCO \rightarrow H+DCO} + J_{HDCO \rightarrow D+HCO}}{J_{HHCO \rightarrow H+HCO}} * \frac{J_{HHCO \rightarrow H+HCO}}{J_{HHCO \rightarrow HH+CO} + J_{HHCO \rightarrow H+HCO}} \\ &= \frac{1}{KIE_{mol}} \beta_{mol} + \frac{1}{KIE_{rad}} \beta_{rad} \\ &= \frac{1}{KIE_{mol}} \beta_{mol} + \frac{1}{KIE_{rad}} (1 - \beta_{mol}) \end{aligned}$$

Solving for β_{mol} with the KIE values from Feilberg et al. (2007) returns $\beta_{mol}=0.77$. Whereas there are still considerable uncertainties in radical and molecular channel quantum yields between the IUPAC and JPL recommendations (IUPAC: $\beta_{mol} \approx 0.56$, JPL: $\beta_{mol} \approx 0.63$ for typical atmospheric conditions) (Sander et al., 2006; Atkinson et al., 2006) both values imply a considerable lower value for the molecular channel. This indicates an overestimate of the molecular photolysis channel in Feilberg et al. (2007). Whereas the origin of the different photolysis yields from Feilberg et al. (2007) still needs to be resolved (M.S. Johnson, personal communication), the implications for the determination of KIE_{mol} and KIE_{rad} can be qualitatively assessed. The experiments of Feilberg et al. (2007) were carried out with strongly labeled formaldehyde. Therefore, the overestimate of the molecular photolysis channel means effectively that HD production is overestimated compared to the present study. To compensate for the higher flux into the molecular channel, KIE_{mol} needs to be increased and KIE_{rad} decreased. The result is that relatively less D is directed into the molecular channel, which coun-



teracts the higher $\beta_{\text{mol}}=0.77$. Note that due to analytical problems, no concentration data were available for the Feilberg et al. experiments, so that the overestimated flux into the molecular channel could not be detected by H_2 measurements. The reevaluation of the Feilberg et al., 2007 data is not yet complete, but the effect outlined here is expected to resolve at least part of the deviations between Feilberg et al. (2007) and the present study.

Table 2 also lists the results of the present experiments when instead of the IUPAC recommendations for the branching ratio between the molecular and radical channels, the JPL recommendations are used. The results only change by 0.01 and a sensitivity analysis showed that this is largely due to the “triangulation” approach in the experiments. Since the H_2 formed is isotopically between the light and heavy reservoirs, it can be constrained very robustly. Changes that would tend to make the model results either heavier or lighter for a single reservoir gas (by compensation of e.g. branching ratio and KIE as explained above) now result in large discrepancies for the experiment with the other H_2 reservoir. Even a change in the initial H_2CO concentration by a factor of 2 deteriorates the fit quality (χ^2) tremendously, but still returns 1.64 for the free fit with the condition $\text{KIE}_{\text{mol}}=\text{KIE}_{\text{rad}}$. The freshly produced H_2 has to have a well-defined isotopic composition in between the two reservoirs. Finally, the higher values of χ^2 for the optimizations using the branching ratios from JPL indicate that the IUPAC values are in slightly better agreement with our experimental results, but the experiments are not really designed to distinguish these differences.

Rhee et al. (2008) conducted formaldehyde photolysis experiments in 0.1 to 3 l glass or quartz photochemical reactors, employing HCHO mixing ratios between 0.4 and 3 ppm and photolysis times between 1 h and 17 d. Although stability was verified in one experiment for 2 d, the affinity of formaldehyde to stick to surfaces constitutes a potential source of error in these experiments. Furthermore, no radical quencher was used, and the interference from radical reactions was only determined using a model, but without direct supporting measurements of fast photochemistry. A third important uncertainty is that the isotopic composition of the original HCHO was not determined

Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

independently. Rather, it was inferred from the H₂ product after complete photolysis of pure HCHO to H₂ with a mercury photolysis lamp, under the assumption that the HCHO is quantitatively converted to H₂. This means that in the absence of other reactants, also the products from the radical channel H and HCO recombine to form H₂. This was postulated by (Atkinson et al., 2006; McQuigg and Calvert, 1969), but it is possible that radical reactions with molecules adsorbed at the reactor surface constitute another loss process.

Whereas the partitioning between KIE_{mol} and KIE_{rad} in Feilberg et al. (2007) may be erroneous, the value of KIE_{tot} itself was directly measured by FTIR spectroscopy in a relative rate experiment using highly enriched HCHO-HCDO mixtures and is considered a robust measurement result. The value of 1.63±0.03 derived above for the condition KIE_{mol}=KIE_{rad} trivially leads to KIE_{tot}=1.63±0.03, which agrees within the combined error bars with the value of 1.58±0.03 from Feilberg et al. (2007b). Although the experiments were done under different photochemical and experimental conditions (the Feilberg et al. (2007b) experiments were carried out at the photochemical reactor EUPHORE in Valencia, Spain, in late spring, and with isotopically labeled material) it is not expected that this should lead to strongly different KIEs. Therefore, we may derive independent estimates from combining the KIE_{mol}=1.63±0.03 derived here with the KIE_{tot}=1.58±0.03 from Feilberg et al. (2007b). In our study, optimizing both KIEs independently leads to slightly lower values for KIE_{mol} but much lower values for KIE_{rad}. Although this provides an even better fit to the data, the 60:40 weighted average of these values (line 8 in Table 2), KIE_{tot}=1.29 is in clear disagreement with the measured value of 1.58±0.03 from Feilberg et al. (2007). Exploring the best estimates and combined error ranges of KIE_{tot} from Feilberg et al. (2007b) and KIE_{mol} from the present study leads to a value of KIE_{rad}=1.51(−0.10, +0.12). Thus, the combined evidence from both studies indicates that the difference between KIE_{mol} and KIE_{rad} is much smaller than derived by Feilberg et al. (2007).

A precise determination of the KIEs in both photolysis channels is very important for the evaluation of the global isotope budget of molecular hydrogen (Gerst and Quay,

2001; Röckmann et al., 2003; Rhee et al., 2008; Feilberg et al., 2007b, 2005a, 2007a; Price et al., 2007). Even disregarding the feedback via the radical channel, a change of KIE_{mol} from 1.82 to 1.63 implies that the isotopic composition of H_2 from HCHO photolysis decreases by 117‰ ($1.63^{-1}/1.82^{-1} - 1$). This is a huge change, given that photochemistry via HCHO constitutes about 50% of the global H_2 source. Pieterse et al. (2009) already noted that in a simple box model of the isotopic composition of atmospheric H_2 , it was difficult to close the isotope budget with the original values from Feilberg et al. (2007b). Given the inconsistency of the values as described above, they recommended using the value of KIE_{tot} for both photolysis channels, which then led to reasonable values for the global isotope budget. The new results in general confirm this recommendation, since KIE_{rad} and KIE_{mol} turn out not to be statistically different within the errors.

In summary, the present study presents a well-constrained value for KIE_{mol} , which, together with KIE_{tot} from Feilberg et al. (2007b), implies a rather small difference between KIE_{mol} and KIE_{rad} , confirming the suggestion by Pieterse et al. (2009). The model calculations show that direct determination of $\delta D(HCHO)$ would help constraining both fractionation factors from a single photolysis experiment with non-labeled formaldehyde. However, δD measurements on formaldehyde are difficult, and the only published technique for atmospheric $\delta D(HCHO)$ reached a precision of $\pm 50\%$ only (Rice and Quay, 2006), which is of the order of the modeled differences between the scenarios in Fig. 2. Thus, at this precision, such an experiment may not allow a very precise quantification.

5 Conclusions

Formaldehyde photolysis experiments have been carried out in the SAPHIR photochemical reactor to determine the associated isotope effects. This was the first study where both, large reactor volumes and near-natural isotope abundance were employed. Similar results are obtained when using two isotopically different H_2 gases

Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



as background. The results allow to closely constrain the kinetic isotope effect in the molecular photolysis channel to be $KIE_{mol} = 1.63 \pm 0.03$. The KIE in the radical channel KIE_{rad} cannot be constrained precisely with the present experiments, because it has an indirect effect only on the photolysis product H_2 . When combining our value for KIE_{mol} with the total kinetic isotope effect $KIE_{tot} = 1.58$ from Feilberg et al. (2007b), this indicates that KIE_{rad} and KIE_{mol} are not as different as postulated in Feilberg et al. (2007b) and Rhee et al. (2008).

Acknowledgements. We thank C. Richter for initial model studies to determine the most suitable conditions in the SAPHIR chamber. This work was funded by the Dutch science foundation NWO, project 816.01.001, H_2 budget.

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Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Isotope effect in the formation of H_2 from H_2CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Isotope effect in the formation of H₂ from H₂COT. Röckmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Wisthaler, A., Apel, E. C., Bossmeyer, J., Hansel, A., Junkermann, W., Koppmann, R., Meier, R., Müller, K., Solomon, S. J., Steinbrecher, R., Tillmann, R., and Brauers, T.: Technical Note: Intercomparison of formaldehyde measurements at the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys., 8, 2189–2200, 2008, <http://www.atmos-chem-phys.net/8/2189/2008/>.

5

ACPD

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Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

Table 1. List of gas mixtures used in the control and HCHO photolysis experiments.

#	date	[H ₂]/ppb	$\delta D(H_2)_{bg}/\text{‰}$	[HCHO]/ppb	[CO]/ppm	type
1	16.10.	400	-177±5	500	500	photolysis
2	17/18.10.	1200	-177±5	0	0	control
3	19.10.	200	-680±5	500	500	photolysis
5	22.10.	200	-177±5	500	500	photolysis
8	25.10.	350	-177±5	500	500	control

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

Table 2. χ^2 values for a range of KIE_{mol}–KIE_{rad} pairs.

Constraint	IUPAC			JPL		
	KIE _{mol}	KIE _{rad}	χ^2	KIE _{mol}	KIE _{rad}	χ^2
KIE _{mol} =KIE _{rad}	1.63	1.63	34.3	1.64	1.64	42.6
KIE _{mol} =1.64, KIE _{rad} =1.63	1.64	1.63	34.7	1.64	1.63	42.6
KIE _{mol} =1.65, KIE _{rad} =1.63	1.65	1.63	35.9	1.65	1.63	43.2
KIE _{mol} =1.66, KIE _{rad} =1.63	1.66	1.63	37.7	1.66	1.63	44.6
KIE _{mol} =1.62, KIE _{rad} =1.63	1.62	1.63	34.6	1.62	1.63	44.4
KIE _{mol} =1.61, KIE _{rad} =1.63	1.61	1.63	35.7	1.61	1.63	46.7
KIE _{mol} =1.60, KIE _{rad} =1.63	1.60	1.63	37.6	1.60	1.63	50.2
KIE _{rad} ≥1	1.60	1.00	31.8	1.60	1.00	43.4
Feilberg et al. (2007b)	1.82	1.10	170	1.82	1.10	204
Rhee et al. (2008)	2.00	4.50	321	2.00	4.50	403

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Isotope effect in the formation of H₂ from H₂CO

T. Röckmann et al.

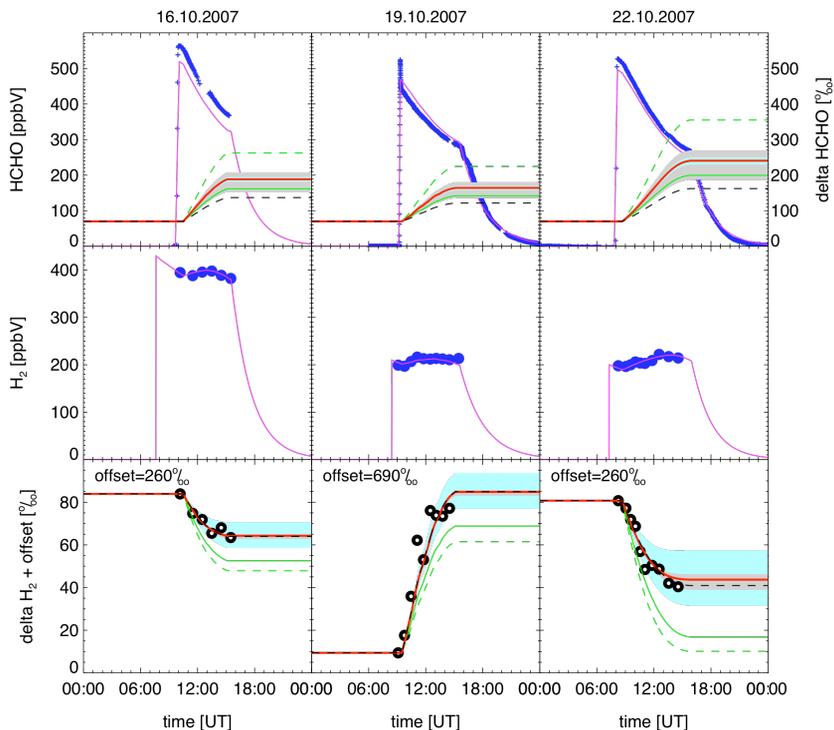


Fig. 1. Experimental and model results of the formaldehyde photolysis experiments in the SAPHIR chamber. Top panels show the concentration (left scale) and isotopic composition (right scale) of formaldehyde. Middle panels show the H₂ concentration, bottom panels show the isotopic composition of H₂, shifted in positive direction by the listed offsets in order to subtract the effect from the different bath gases used. Symbols represent measurement results (blue: concentration, black: δD). Lines represent model results as follows: pink: concentration; red: δD for $KIE_{rad}=KIE_{mol}=1.63$ (line 1 in Table 2); grey shaded area: KIE_{rad} varied by ± 0.5 ; light blue shaded area: KIE_{mol} varied by ± 0.1 ; black dashed line: $KIE_{rad}=1.00$, $KIE_{mol}=1.60$ (line 8 in Table 2); green solid line: Feilberg et al. (2007b); green dashed line: Rhee et al. (2008).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Isotope effect in the
formation of H₂ from
H₂CO**

T. Röckmann et al.

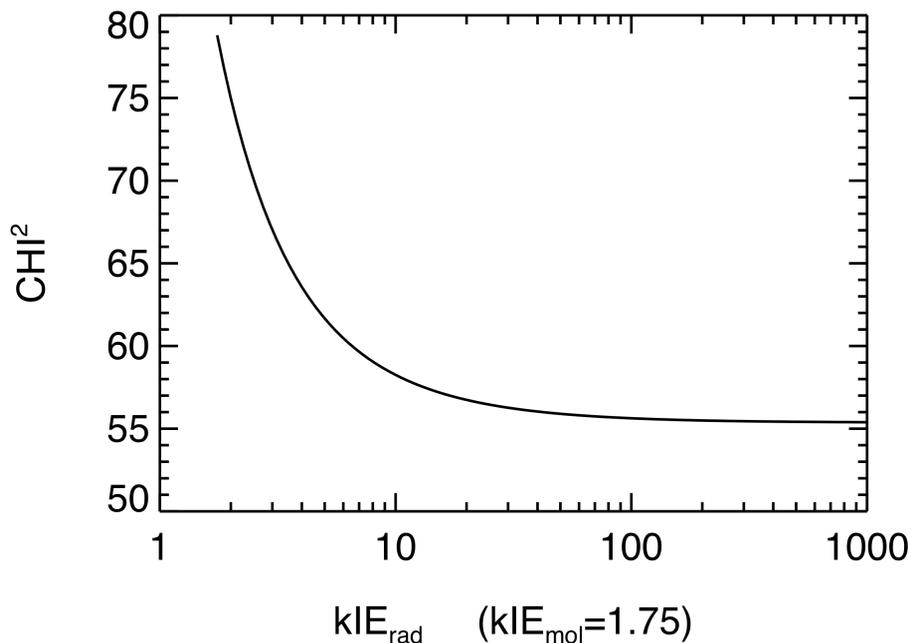


Fig. 2. Dependence of CHI^2 on KIE_{rad} for a fixed value of $\text{KIE}_{\text{mol}}=1.75$. It is obvious that there exists no value for KIE_{rad} , which would bring CHI^2 down to the best-fit values in Table 1. Thus, $\text{KIE}_{\text{mol}}=1.75$ is not compatible with the observations.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)