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**Pressure dependent
deuterium
fractionation**

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Pressure dependent deuterium fractionation in the formation of molecular hydrogen in formaldehyde photolysis

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Abstract

The pressure dependence of the relative photolysis rates of HCHO and HCDO has been investigated using a new photochemical reactor at the University of Copenhagen. The relative photolysis rate of HCHO vs. HCDO under UVA lamp irradiation was measured at total pressures of 50, 200, 400, 600 and 1030 mbar. The relative dissociation rate $k_{\text{HCHO}}/k_{\text{HCDO}}$ was found to depend strongly on pressure, varying from 1.1 ± 0.1 at 50 mbar to 1.75 ± 0.10 at 1030 mbar. The products of formaldehyde photodissociation are either $\text{H}_2 + \text{CO}$ (molecular channel) or $\text{HCO} + \text{H}$ (radical channel). The partitioning between the channels has been estimated using available values for the absorption cross section and quantum yield. As a result of the change in pressure with altitude the isotope effect for production of molecular hydrogen is found to change from a value of $k_{\text{H}}/k_{\text{D}} = 1.8 \pm 0.2$ at the surface to unity at 50 km. The relative importance of the two product channels changes with altitude as a result of changes in both pressure and actinic flux. The study concludes that the δD of photochemical hydrogen produced in situ will increase substantially with altitude.

1 Introduction

Formaldehyde, HCHO, is a key intermediate in the atmospheric carbon cycle and is important to the atmosphere's oxidative capacity. HCHO is a product of the oxidation of methane and virtually all non-methane hydrocarbons, and is a precursor of atmospheric CO and H_2 . Over half of atmospheric H_2 is produced from the photolysis of formaldehyde (Novelli et al., 1999; Ehhalt and Rohrer, 2009; Rhee et al., 2006a). Molecular hydrogen is the reduced gas in the atmosphere with the largest turnover in moles and acts as an indirect greenhouse gas (Forster et al., 2007). The reaction with OH removes ca. 20% of H_2 , the rest is removed by soil bacteria (Rhee et al., 2006b). Replacing some or all of carbon based fuels with hydrogen would change air pollution patterns and affect climate (Rahn et al., 2003).

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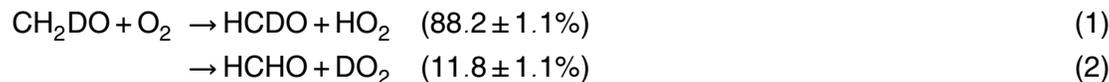
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Inverse modeling of the deuterium budget of tropospheric hydrogen provides an independent check of bottom-up budgets relying on estimates of individual source and sink terms (Ehhalt and Rohrer, 2009). Gerst and Quay's analysis of the isotope budget concludes that the photochemical source of H₂ must be highly enriched in deuterium (Gerst and Quay, 2001). They estimate that photochemical H₂ should have a δD of +130±70‰ compared to ocean water, a dramatic enrichment relative to the presumed starting material, methane, with a δD of -86±3‰. Biogenic VOC is likely to be at least this depleted in deuterium (Feilberg et al., 2007). Measurements show that tropospheric hydrogen has a δD of 120‰. The δD value for stratospheric hydrogen ranges from close to the tropospheric value to above 400‰ in the upper stratosphere; a substantial enrichment must take place (Rahn et al., 2003; Röckmann et al., 2003). In their efforts to model observed δD values both Mar et al. and Röckmann et al. varied the fractionation factor in the photolytic molecular hydrogen source (Mar et al., 2007; Röckmann et al., 2003). In addition Mar et al. investigated a number of factors that could result in variation with altitude and conclude that while there appear to be such variations it cannot be known with certainty due to the lack of experimental evidence.

Due to ongoing interest in modeling the molecular hydrogen and hydrocarbon budgets, establishing the kinetic isotope effects involved in the atmospheric oxidation of methane and non-methane volatile organic carbon species is important (see for example Feilberg et al., 2007; Pieterse et al., 2009; Ehhalt and Rohrer, 2009). It is known that CH₃D reacts more slowly than CH₄, resulting in methyl, methyl peroxy and methoxy radicals that are enriched in deuterium. Furthermore, a recent study showed that there is a great deuterium enrichment in the formaldehyde produced by the reaction of the methoxy radical with oxygen (Nilsson et al., 2007):



The enrichment of deuterium in these initial steps is only partially counteracted by a depletion observed in the photolysis of formaldehyde.

The photolysis of formaldehyde has two product channels, the radical channel producing H and HCO and the molecular channel producing H₂ and CO.



5 The molecular channel includes a contribution from:



The threshold energy for Eq. (3) corresponds to a wavelength of about 330 nm, possibly extending as far as 340 nm. In this range thermal excitation of the molecule is necessary to produce radical products (Troe, 2007). The production of H₂ and CO via
10 Eq. (4) has a threshold energy of ca. 360 nm (Troe, 2007). In addition a fraction of the radical dissociations produce molecular products via the “roaming atom” pathway Eq. (5) (Bowman and Zhang, 2006; Townsend et al., 2004).

Quantum yields for the two product channels have been evaluated and parameterized by Sander et al. (2006). While the pressure dependence of the molecular channel quantum yield is significant, no pressure dependence is observed in the radical channel. The quantum yield recommended by JPL (Sander et al., 2006) is a parameterization based on diverse experimental data; IUPAC recommends a more structured quantum yield (Atkinson et al., 2005). A theoretical paper by Troe discusses the possibility that the radical channel quantum yield is lower at higher wavelengths (330–340 nm)
15 than the current recommendations (Troe, 2007). The IUPAC, JPL and Troe quantum yields for the radical channel and the yield in the molecular channel at 1030 mbar total pressure are shown in Fig. 1. The group of Orr-Ewing also reports a more structured quantum yield that is higher for the radical channel than previous results (Gorrotxategi Carbajo et al., 2008).

25 Table 1 summarizes the available experimental results for the isotope effects in the photolysis of formaldehyde. The results for the molecular channel are similar, even though they are statistically distinct, while the results for the radical channel differ significantly. In all studies the results for the radical channel have been inferred indirectly

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using the results for the molecular channel. Previous studies have been conducted under ambient conditions; the present study is the first one where the pressure dependence in the isotope effect is investigated. Pieterse et al. have used a model to investigate the whole oxidation scheme from methane to molecular hydrogen (Pieterse et al., 2009). They identify the isotope effects in formaldehyde photolysis as “by far the most critical parameters in the H₂ isotope scheme”.

We have undertaken the present study to investigate the effect of pressure on the relative rate $k_{\text{HCHO}}/k_{\text{HCDO}}$ of formaldehyde photodissociation. We have used a photolysis lamp that mainly dissociates formaldehyde into molecular products, since this is where pressure dependence is expected.

2 Experimental

2.1 Experimental setup

The photolysis experiments were carried out in a photochemical reactor at the University of Copenhagen. The reaction chamber is a 2 m quartz tube with stainless steel end flanges and a volume of 101.4 L. The chamber is inside an insulated housing with temperature control. The output beam from a Bruker IFS66v/s FTIR spectrometer is coupled to the White type optics of the reaction chamber and used to monitor changes in reactant concentrations. The absorption path length in the cell was 72 m and a liquid nitrogen cooled InSb detector was used. The experimental setup is described in detail in Nilsson et al. (2009).

2.2 Photolysis of HCHO/HCDO

The two formaldehyde isotopologues in the form of paraformaldehyde were carefully heated and introduced into the chamber via a heated inlet. The chamber was then filled to the target pressure with synthetic air. Experiments were conducted with samples of

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formaldehyde having a series of HCDO to HCHO ratios, see Table 2, and formaldehyde partial pressures from 0.09 to 4.5 μ bar. Total pressures in the cell were 50, 200, 400, 600 and 1030 mbar. Photolysis was performed in 8 to 20 steps of increasing duration giving a total photolysis time of 6 to 35 h, using 8 UV-A lamps. The lamps used have the emission maximum at 350 nm, see Fig. 1.

2.3 Reference spectra and analysis of FTIR data

FTIR spectra were analyzed using a spectral fitting program that generates a synthetic spectrum which is compared to the experimental result (Griffith, 1996). The program uses either high quality line parameters from the HITRAN data base (Rothman et al., 2005) or high resolution reference spectra.

For spectra taken at total pressures of 400, 600 and 1030 mbar, the absorption cross sections published by Gratien et al. (2007) were used as reference spectra. Spectra recorded at 50 and 200 mbar were analyzed using high resolution reference spectra obtained using a Bruker HR-120 FTIR spectrometer. Three spectra were recorded for each isotopologue, at a resolution of 0.05 cm^{-1} , each spectrum consisting of 64 co-added interferograms. The three spectra were averaged to obtain the final spectrum used for the analysis.

The photolytic kinetic isotope effect was determined from the slope of the relative rate plot which shows the natural logarithm of the relative concentrations of the two species HCHO and HCDO.

3 Results and discussion

Figure 2 shows an example of a relative rate plot where the slope is $k_{\text{HCHO}}/k_{\text{HCDO}}$. This plot includes data from three independent experiments conducted at 1030 mbar total pressure and $293 \pm 0.5 \text{K}$. Similar plots were constructed at each pressure. The relative rates for the individual experiments are summarized in column 2 of Table 2.

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The results are also plotted in Fig. 3, where significant pressure dependence is seen. Error bars are based on the uncertainty in the determination of the slope of the relative rate plot with an additional 3% error to account for possible uncertainties in reference spectra.

The relative rates obtained from the experiments rely on the loss of formaldehyde and do not distinguish between the product channels. As seen in Fig. 1 while the emission spectrum of the lamps will mainly give molecular products, a tail is present at wavelengths that activate the radical channel. The relative importance of the two product channels can be estimated using Eq. (6) where the subscript i distinguishes the radical channel (1) from the molecular channel (2).

$$j_i = \int \sigma(\lambda) \phi_i(\lambda) I(\lambda) d\lambda \quad (6)$$

The absorption cross section, $\sigma(\lambda)$, has recently been determined with high accuracy by Gratien et al. (2007). $I(\lambda)$ is the emission spectra of the photolysis lamps. Quantum yields for the molecular channel, $\phi(\lambda)$, are, as mentioned, pressure dependent. Figure 4 shows quantum yields scaled to the lamp spectrum, $\phi(\lambda)I(\lambda)$, for the radical channel, and for the molecular channel at two different pressures, 50 and 1030 mbar. Recommended quantum yields for the radical channel by IUPAC (Atkinson et al., 2005) and JPL (Sander et al., 2006) are shown in Fig. 1, together with a theoretically determined yield published by Troe (2007). The most recent experimental study reports radical channel quantum yields that are larger than the previous recommendations (Gorrotxategi Carbajo et al., 2008).

For the data analysis we chose the quantum yields recommended by JPL, since these are the most commonly used parameterizations. Use of one of the other available quantum yields would change the partitioning between molecular and radical channels slightly. After convoluting with the photolysis lamp spectrum, recent work by Troe (2007) shows that the radical channel contribution may be up to 30% smaller than we have calculated using the JPL recommendation, whereas the IUPAC recommendation (Atkinson et al., 2005) says that it may be 5% larger.

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The relative photolysis rate $k_{\text{HCHO}}/k_{\text{HCDO}}$ can be divided into molecular and radical contributions according to the first step of Eq. (7). In Eq. (7) H and D distinguish between normal hydrogen (^1H) and deuterium (^2H). Capital letters are used for the rates of production of molecular products, while lower case represent the radical production.

$$\frac{k_{\text{HCHO}}}{k_{\text{HCDO}}} = \frac{k_{\text{H}} + k_{\text{h}}}{k_{\text{D}} + k_{\text{d}}} = \frac{k_{\text{H}} + c k_{\text{H}}}{k_{\text{D}} + \frac{c}{r} k_{\text{H}}} \quad (7)$$

In Eq. (7) the factor $c = k_{\text{h}}/k_{\text{H}}$, the ratio between photolysis rates in the radical and molecular channels, is calculated for different pressures using Eq. (6). The factor $r = k_{\text{h}}/k_{\text{d}}$ is the isotope effect in the radical channel, previously determined by two groups, see Table 1.

From Eq. (7) we can derive an expression for the relative rate in the molecular channel:

$$\frac{k_{\text{H}}}{k_{\text{D}}} = \left(\frac{k_{\text{HCDO}}}{k_{\text{HCHO}}} + \frac{c}{k_{\text{HCHO}}/k_{\text{HCDO}}} - \frac{c}{r} \right)^{-1} \quad (8)$$

The $k_{\text{HCHO}}/k_{\text{HCDO}}$ ratios are the direct result of our experimental study. The resulting relative rate for the molecular channel, $k_{\text{H}}/k_{\text{D}}$, is sensitive to the values of c and r . The ratio c varies with pressure since it contains the pressure dependent photolysis rate for the molecular channel. As discussed previously different quantum yields are found in the literature, that have a varying ratio between the molecular and radical channels, and thus c will vary depending on the choice of quantum yield. While different quantum yields give c values that vary by a few percent, the parameter r has highly differing values, as listed in Table 1. Figure 5 shows $k_{\text{H}}/k_{\text{D}}$ ratios where different values for r have been inserted in Eq. (8).

As listed in Table 1 previous determinations of $k_{\text{H}}/k_{\text{D}}$ at atmospheric pressure are in the range from 1.6 to 2. The uppermost line in Fig. 5 represents $k_{\text{H}}/k_{\text{D}}$ in the present experiments when $r = k_{\text{h}}/k_{\text{d}}$ is set to 1.1 (Feilberg et al., 2007). This gives a relative rate in the molecular channel that is about 3 at atmospheric pressure, which

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clearly disagrees with the experimental results (Feilberg et al., 2007; Rhee et al., 2007; Röckmann et al., 2009). The other extreme is when $r=4.5$ (Rhee et al., 2007), giving unacceptably low values for k_H/k_D , less than unity at the lower pressures. The extreme values of r give results that are not consistent with field studies, models and experiments. If $r=1.6$, as suggested by Röckmann et al. (2009), the k_H/k_D value becomes a little higher than derived in that work, while $r=2$ is able to reproduce their value for k_H/k_D at atmospheric pressure.

Assuming steady state conditions for the excited formaldehyde intermediate, the rate of absorption is equal to the rates of collisional quenching, k_q , and dissociation into the molecular, k_{mol} , and radical, k_{rad} , channels, $j=k_q+k_{\text{mol}}+k_{\text{rad}}$. Assuming that $k_{\text{rad}} \ll k_{\text{mol}}$ the following expression is valid, where k_u is the (molecular channel) unimolecular dissociation rate for formaldehyde (Troe, 2007):

$$\phi(k_{\text{mol}}^{\text{H}}) = \frac{k_u^{\text{H}}}{k_u^{\text{H}} + k_q^{\text{H}}} = \frac{k_u^{\text{H}}}{k_u^{\text{H}} + bz^{\text{H}}[M]} \quad (9)$$

Note that superscript H represents HCHO and superscript D, below, HCDO. Here z is the collision rate calculated using the hard-sphere collision model, and b is the efficiency of quenching. No rates for the unimolecular dissociation of mono-deutero formaldehyde are available in the literature; we have simply set it to be a factor f of that of the rate for normal formaldehyde:

$$\phi(k_{\text{mol}}^{\text{D}}) = \frac{k_u^{\text{D}}}{k_u^{\text{D}} + k_q^{\text{D}}} = \frac{fk_u^{\text{H}}}{fk_u^{\text{H}} + bz^{\text{D}}[M]} \quad (10)$$

The experimentally derived k_H/k_D values were used to determine the ratio of ϕ 's in Eqs. (9) and (10) and were fit by varying the values of b and f for the results as a function of pressure. The line in Fig. 6 is the best fit to the experimental data points and has values $b=0.005$ and $f=0.45$, which gives:

$$k_H/k_D = (500 + 2.5 \cdot P)/(500 + 1.15 \cdot P) \quad (11)$$

where P is total pressure. The value of b obtained using this simple model falls in the range of measurements of collisional quenching rates for other molecules (Moore, 2007).

4 Atmospheric implications

The effect of pressure on the kinetic isotope effect in the photolysis of formaldehyde has been investigated for the first time. We observed a significant pressure dependence. The fractionation effects obtained from measurements corresponding to the surface can apparently not be used throughout the atmosphere.

We conclude that the fractionation factor for formaldehyde photolysis shows a significant variation with altitude. This has previously been suggested by analysis of field measurements and modeling of δD_{H_2} values in the atmosphere (Mar et al., 2007; Röckmann et al., 2003), although it was not clear from these studies if the effect arose from the variation of temperature, actinic flux spectrum or pressure with altitude. In 2001 Gerst and Quay presented a mechanism that could explain deuterium enrichment in molecular hydrogen originating from atmospheric methane. They estimated that the overall fractionation in methane oxidation must be about 1.3 to explain the measured data (Gerst and Quay, 2001). Since 2001, the knowledge of the fractionation factors and branching ratios in the oxidation chain has increased and been incorporated in modeling of recent field measurements. Rahn et al. assume stratospheric conditions at 30 km altitude and report an overall fractionation of $1.33(+0.29/-0.25)$ (Rahn et al., 2003). Rhee et al. use average stratospheric conditions when deriving the overall fractionation factor from field data; $\alpha_{CH_4 \rightarrow H_2} = 1.43 \pm 0.06$ (Rhee et al., 2006a). Although several studies indicate altitude dependence in the fractionation, lack of experimental evidence and estimates of the magnitude of the altitude dependence make it problematic to incorporate in models. In the present work we identify the pressure dependence of the photolysis of formaldehyde as the cause for the variation in α with altitude. The consequences of this mechanism must be investigated using stratospheric models.

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As reviewed in the introduction, the atmospheric pressure fractionation results of Rhee et al. (2007), Feilberg et al. (2007), and Röckmann et al. (2009), do not agree. Regarding the Rhee et al. study a possible source of errors may be interference from the surface of the reaction vessel, i.e. the known difficulty of maintaining a constant pressure of formaldehyde in the gas phase due to adsorption, solvation and the formation of a polymeric solid. Historically, this phenomenon has confounded efforts to measure accurate UV and IR cross sections (Gratien et al., 2007). One way to minimize the impact of surface interactions is to perform photolysis experiments in a large chamber with a low surface to volume ratio. The studies of Feilberg et al. (2007) and Röckmann et al. (2009) were both performed in large atmospheric chambers. These experiments agree with the atmospheric pressure results in the present study, which were conducted in a 100 L chamber. We do not have a good explanation for why the radical channel isotope effect of 1.1 determined by Feilberg et al. (2007) appears to be unacceptable. Much of the work that has been done, including our analysis here, assumes that k_h/k_d and k_H/k_D are independent of wavelength, however we know of no experiments to date that support this assumption.

The significant pressure dependence in the isotopic fractionation in the production of molecular hydrogen in formaldehyde photolysis must be further characterized. Ideally photolysis experiments should be performed where there is no contribution from photolysis to radical production, this is however very difficult since it would require a light source with a cutoff at 340 nm. Using sunlight or available UV lamps one must rely on experimental absorption cross sections and quantum yields to be able to estimate the relative contributions from molecular and radical channels. In this work we have analyzed the loss of reactants; an improvement of the experiments would be to also analyze the products. The molecular products H_2 and CO can be analyzed with IRMS (Isotope Ratio Mass Spectrometry) or GC (Gas Chromatography) with a HgO reduction detector and FTIR, while the radical products are difficult to detect in an accurate way.

In addition to more experimental studies a theoretical investigation would lead to a better understanding of the different timescales of HCHO and HCDO photolysis.

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Table 1. Summary of previous experimental determinations of deuterium fractionation in the molecular and radical channels and in the over all process, at atmospheric pressure.

Experimental facility and volume	$k_{\text{HCHO}}/k_{\text{HCDO}}$		Reference
	Total	Molecular	
EUPHORE, 200 m ³ chamber	1.58±0.03	1.82±0.07	Feilberg et al. 2007
Glass/quarts vessel, 1–3 L	2.5±0.03	2.0±0.02	Rhee et al. 2008
SAPHIRE, 370 m ³ chamber	1.63±0.03	1.63±0.03	Röckmann et al. 2009

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Table 2. Summary of experimental results. The first column shows the pressure in the chamber. Column 2 shows the relative rates obtained from the slopes of the plots. The last column gives the nominal ratio between the two isotopologues in each experiment.

Chamber Pressure (mbar)	$k_{\text{HCHO}}/k_{\text{HCDO}}$	HCHO:HCDO
50	1.064±0.039	95:5
50	1.207±0.040	95:5
50	1.058±0.032	35:65
50	1.076±0.036	80:20
200	1.357±0.080	95:5
200	1.205±0.037	95:5
200	1.354±0.041	60:40
400	1.621±0.056	53:47
400	1.629±0.052	60:40
600	1.792±0.055	40:60
600	1.718±0.069	80:20
1030	1.784±0.055	95:5
1030	1.718±0.069	93:7
1030	1.792±0.054	55:45

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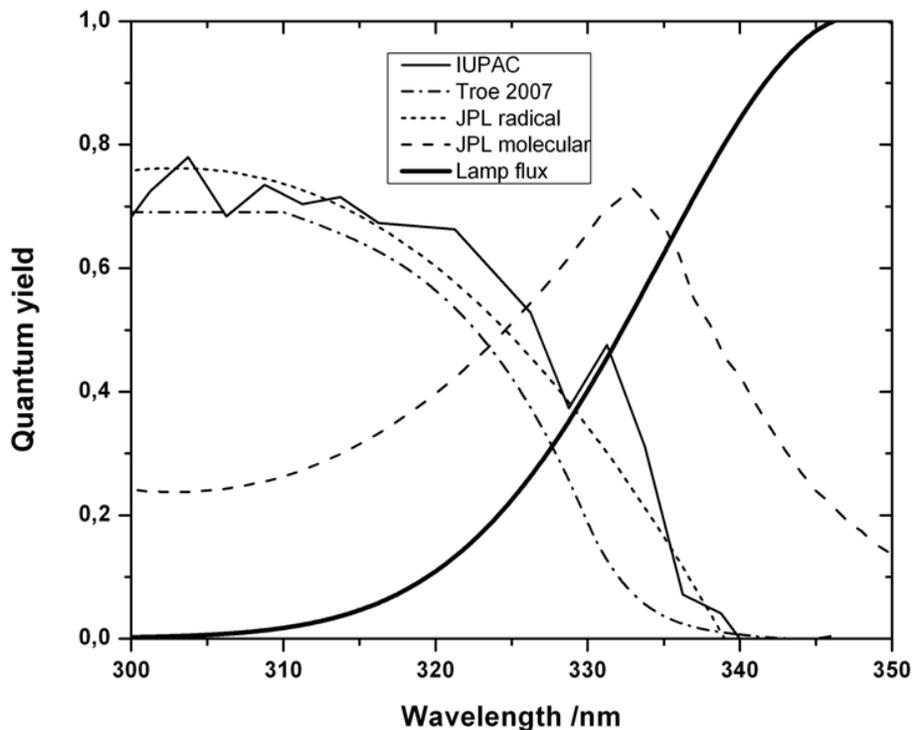


Fig. 1. Pressure independent quantum yields of radical products of formaldehyde photolysis as a function of wavelength from JPL (Sander et al., 2006), IUPAC (Atkinson et al., 2005), and the lowest estimate by Troe (Troe, 2007). Thicker full drawn line is the emission spectrum of the UV-A lamp (Osram Eversun 100W/79) used for the photolysis experiments.

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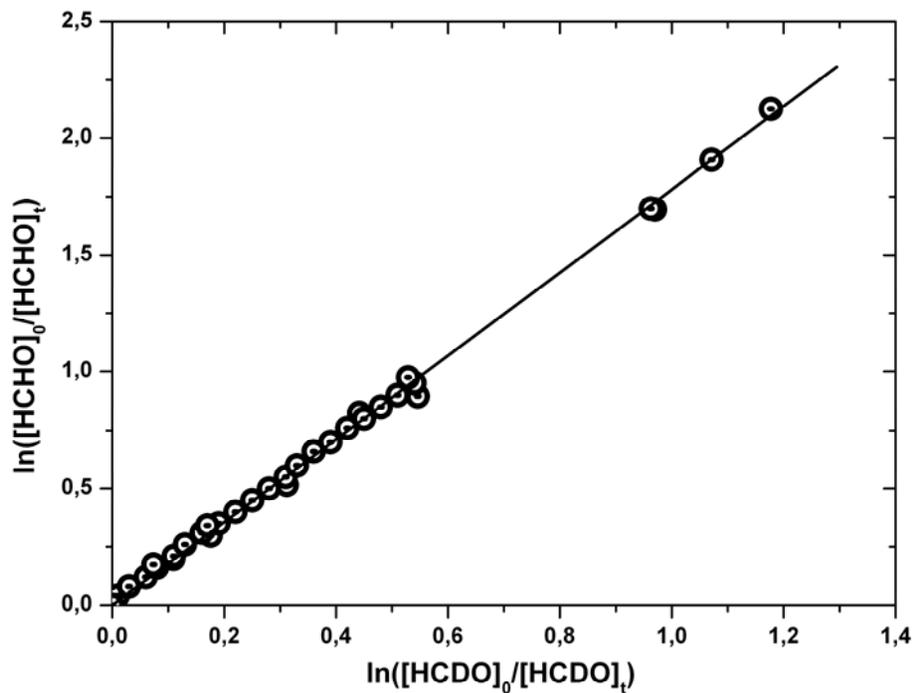


Fig. 2. Relative rate plots of HCHO versus HCDO from experiments at 293 K and total pressure of 1030 mbar, error bars within symbols.

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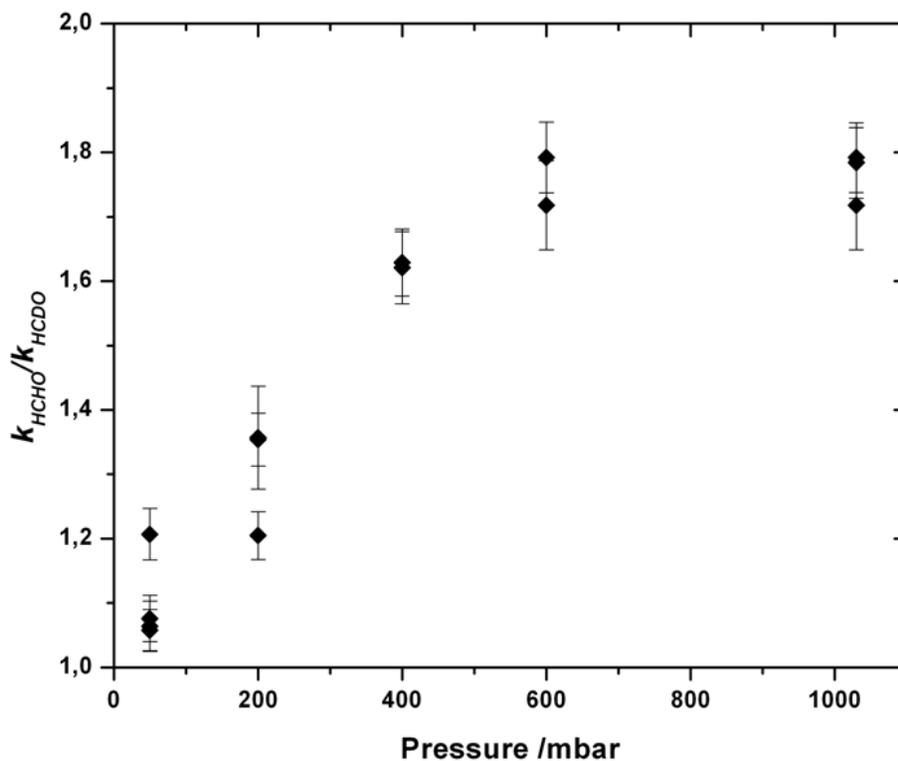


Fig. 3. Relative dissociation rate, $k_{\text{HCHO}}/k_{\text{HCDO}}$, as a function of pressure.

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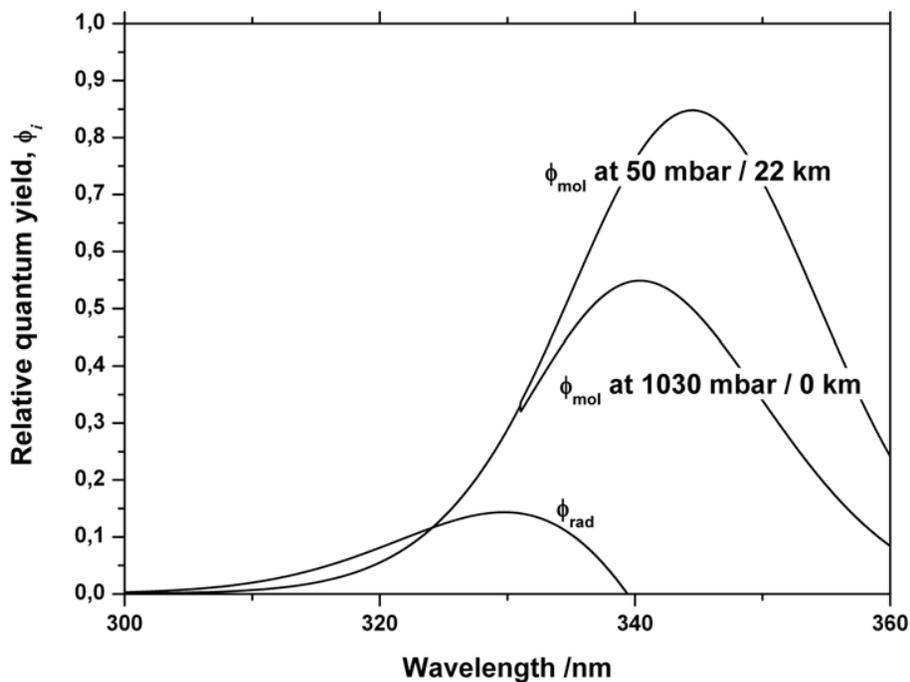


Fig. 4. Quantum yields from JPL (Sander et al., 2006) in the radical channel, and in the molecular channel at two different pressures, scaled by the photolysis lamp spectrum (Fig. 1).

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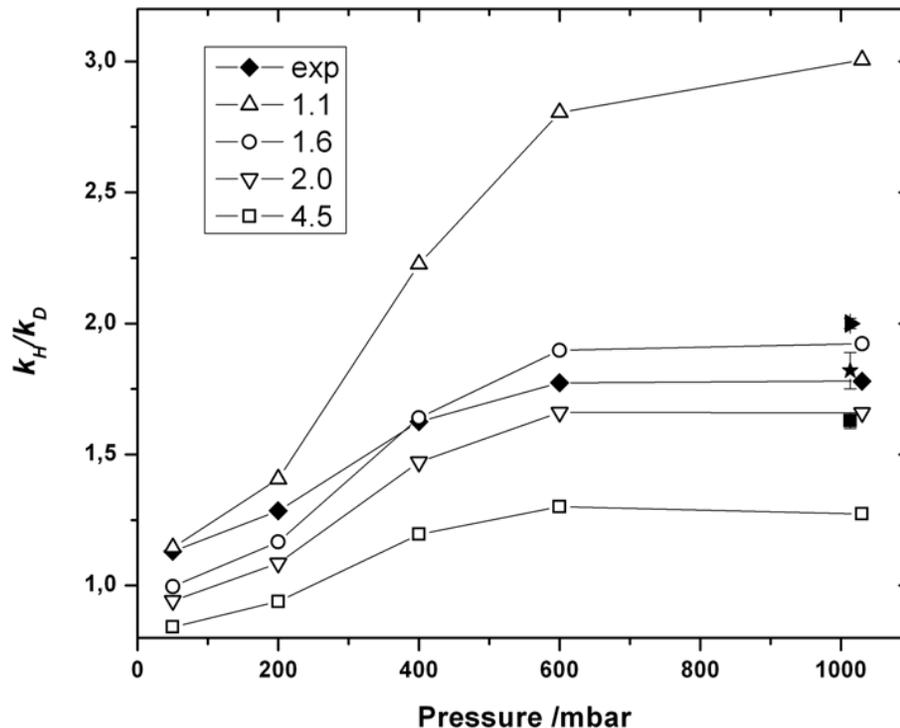


Fig. 5. The filled diamonds are averages of the experimental results for $k_{\text{HCHO}}/k_{\text{HCDO}}$ presented in Table 2 and Fig. 4. Open symbols represent $k_{\text{H}}/k_{\text{D}}$ ratios when different radical channel corrections have been applied to the experimental data. Atmospheric pressure measurements of the kinetic isotope effect in the molecular channel ($k_{\text{H}}/k_{\text{D}}$) are shown using a filled triangle (Rhee et al., 2007), a filled star (Feilberg et al., 2007) and a filled square (Röckmann et al., 2009).

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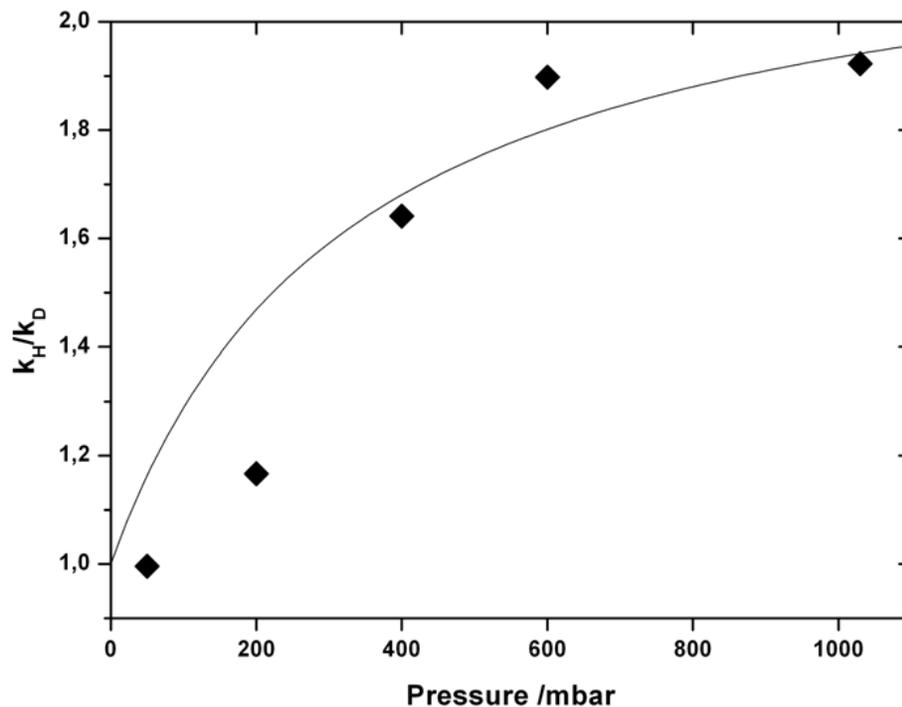


Fig. 6. Symbols represent the relative reaction rate, k_H/k_D , in the molecular channel when the parameter r is set to 1.6. The line is a fit of the ratio of Eqs. (9) and (10) to the points, with $b=0.005$ and $f=0.45$.

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