Comparative Study of the Reactions of ^{16}OH and ^{18}OH with $H^{16}O_2$.

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The gas phase reactions

$$^{18}OH + H^{16}O_2 \rightarrow H_2{}^{18}O + {}^{16}O_2 \qquad (1\,a)$$
$$^{18}OH + H^{16}O_2 \rightarrow {}^{16}OH + H^{18}O^{16}O \qquad (1\,b)$$

were studied at room temperature in a discharge flow reactor with far infrared laser magnetic resonance (LMR) detection of ^{16}OH, ^{18}OH and $H^{16}O^{16}O$. The formation of ^{16}OH in the course of the reaction was observed. The absolute rate constant for the overall removal of ^{18}OH in excess of $H^{16}O^{16}O$ was determined. Each run was accompanied by a control experiment replacing the initial ^{18}OH by the same amount of ^{16}OH. From these experiments a branching ratio is obtained of

$$k_{1a}/(k_{1a} + k_{1b}) = 0.52 \pm 0.08\,,$$

Introduction

The termination reaction

$$OH + HO_2 \overset{k(1)}{\rightarrow} H_2O + O_2 \qquad (1)$$
$$\Delta_R H^{298} = -\,291\ \text{kJ/mol}$$

is an important sink for HO_x radicals in the stratosphere as well as in combustion processes under lean conditions. For a long time the rate constants reported for this reaction spread over one order of magnitude. This situation changed in recent years, when direct measurements of the rate constant became available. At present, the reported rate coefficients are distributed around two values depending on the pressure chosen in the experiment. At low pressures (~ 3 mbar) three recently published studies [1, 2, 3] yielded in good agreement values of $3.8 \cdot 10^{13} \leqq k(1)/\text{cm}^3/\text{mol} \cdot \text{s} \leqq 4.3 \cdot 10^{13}$. At atmospheric pressure, higher values were obtained settling around $7 \cdot 10^{13}\,\text{cm}^3/\text{mol} \cdot \text{s}$ ([4], [5] and other references quoted in [5]).

This difference gave rise to speculations about a pressure dependence of the reaction under consideration and stimulated measurements of the temperature dependence of $k(1)$ [6] as well as mechanistic investigations employing end-product analysis [7] of the reaction $^{18}OH + HO_2$.

On the basis of the observed slightly negative temperature dependence ($k(1) \propto T^{-1.3}$) it has been argued [6] that the formation of a bound H_2O_3 intermediate is indicated rather than a direct H atom transfer. This intermediate might be stabilized at elevated pressures, thus explaining the larger values of $k(1)$ at atmospheric pressure.

As pointed out in [6, 7] this simple explanation has to be considered with caution, since a noticeable collisional stabilization of the H_2O_3 intermediate at pressures around one atmosphere necessarily requires lifetimes of about 10^{-9} s for the H_2O_3 adduct, whereas theory [8] predicts lifetimes of $10^{-10} - 10^{-12}$ s. In addition an end-product analysis of the reaction $^{18}OH + H^{16}O_2$ has shown that no substantial isotopic mixing occurs within the molecular oxygen produced. Thus the formation of at least a linear H–O–O–O–H intermediate has been excluded by [7], for this structure should finally yield $^{18}O^{16}O$ and $^{16}O^{16}O$ with equal probability.

In order to obtain additional information about this reaction we studied the isotope exchange process

$$^{18}OH + H^{16}O_2 \rightarrow {}^{16}OH + H^{18}O^{16}O \qquad (1\,b)$$
$$\rightarrow H_2{}^{18}O + {}^{16}O_2 \qquad (1\,a)$$

by means of sensitive laser magnetic resonance (LMR) detection of ^{18}OH, ^{16}OH as well as $H^{16}O^{16}O$.

Experimental

The reaction was studied in a discharge flow reactor coupled to a far infrared laser magnetic

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resonance detection system, combined with an EPR spectrometer, thus enabling a sensitive detection of ^{18}OH, ^{16}OH, HO_2 as well as of H, O and several other atoms. Details of the apparatus are given elsewhere [9].

All gases were of maximum commercially available purity. Helium as the main carrier gas was fed through liquid N_2 cooled traps. Known mixtures of F_2 in Helium (typically about 1%) were passed over sodium fluoride to remove HF.

Gas flows were controlled either by calibrated flow controllers (TYLAN) or were regulated by needle valves and metered by the pressure rise in a known volume. The pressure inside the flow tube was monitored by a capacitance gauge (MKS-BARATRON).

Radical Sources

Among the various sources for HO_2 radicals the preparation of HO_2 by the reaction $H + O_2 + M \rightarrow HO_2 + M$ at pressures of ca. 50 mbar offers one of the "cleanest" approaches to this radical [3]. H atoms were obtained from microwave dissociation of H_2-He mixtures. After a reaction time sufficiently long for completion of the H atom consumption the mixture was expanded through a short capillary into the reactor. The concentration of the H atoms left was below the detection limit of the EPR ($1 \cdot 10^{-14}$ mol/cm^3), but may be estimated from the measured amount of OH ($\leqq 1 \cdot 10^{-15}$ mol/cm^3), present with the HO_2.

Inside the HO_2 supplying inlet the HO_2 concentration typically reaches values of 10^{-11} mol/cm^3 during a residence time of about 20 ms. At these conditions the variation of the OH concentration in the inlet is goverened essentially by the reactions (1) and

$$H + HO_2 \rightarrow 2\,OH\,. \qquad (2)$$

Other reactions, e.g. heterogeneous losses play a minor role only. Impurities like O atoms coming with the discharged H_2-He mixtures are effectively removed by the reaction with HO_2.

The assumption that [OH] has reached its steady state then leads to an upper limit for the H atom concentration left in the HO_2 inlet of

$$[H] \leqq k_1[OH]_{ss}/2\,k_2\,.$$

Due to the expansion of the HO_2 reaction mixture into the reactor and because of the addition by the carrier gas from the OH source the amounts of these H and OH impurities in the flow tube are reduced by the same proportion to $[H]_0$ and $[OH]_0$.

The HO_2 inlet is fixed. Thus OH associated with HO_2 is monitored by LMR in the flow tube 80 cm downstream from the expansion point of the HO_2-He mixture. Along this distance consumption and reproduction of OH by the reactions (1) and (2) continues. Therefore, an estimate of $[H]_0$ at the probe exit requires an extrapolation of the measured $[OH]_t$ back to $[OH]_0$. From direct measurements of the wall rate constant (see below) the wall depletion of OH is known to be of minor importance, the temporal decay of OH along the tube still being sufficiently described by the reactions (1) and (2). As the rate constants k_1 and k_2 are nearly equal, the initially expected H atom impurities from the HO_2 source can be approximated by the expression

$$H_0 \leqq k_1[OH]_0/2\,k_2$$
$$\leqq [OH]_t/2\,(1 + k_1[HO_2]\,t)\,\exp - (k_1[HO_2]\,t)\,.$$

At the experimental conditions chosen in this study, $[H]_0$ is expected to be a factor of 2–3 larger than the measured [OH] impurities of the HO_2 source; thus $[H]_0$ should be below $5 \cdot 10^{-15}$ mol/cm^3 throughout.

^{18}OH was produced by the reaction of F atoms with excess $H_2{}^{18}O$ of 98% isotopic purity and entered the teflon coated flow system through a moveable inlet. ^{16}OH was generated in the same way replacing ^{18}O-water by ^{16}O-water. The F atoms were obtained from microwave dissociation of carefully dried F_2-He mixtures leaving less than 3% F_2 undissociated.

Due to the alternating use of $H_2{}^{18}O$ and $H_2{}^{16}O$ the isotopic purity of the ^{18}OH produced did not reach the limit given by the manufacturers stated purity for $H_2{}^{18}O$. The amount of ^{16}OH accompanying the ^{18}OH radicals was typically 10%. Rigorous flushing with large amounts of ^{18}O-water reduces the observed impurities below 5%. To a minor extent an exchange of ^{18}OH with ^{16}OH on the reactor wall could be observed (see below). O atom or H atom impurities were not found by EPR but may be estimated from the manufacturers stated purity of Helium ($H_2 \leqq 0.5$ ppm, $O_2 \leqq 0.5$ ppm) not to exceed 10^{-14} moles/cm^3, because the He carrier gas flow discharged with the F_2 accounted to less than 20% of the total carrier gas flow only.

Calibrations

Absolute sensitivities for ^{16}OH and ^{18}OH as well as HO_2 were obtained by titrating known amounts of F atoms with the respective H_2O or H_2O_2 parent molecules in excess. These calibrations were supplemented by the common calibration routes employing nitrogen oxides. Relative sensitivities of ^{16}OH and ^{18}OH were obtained by conversion of ^{18}OH with NO or NO_2 [10].

Results

The measurements of the reactions

$$^{18}OH + H^{16}O_2 \rightarrow H_2{}^{18}O + {}^{16}O_2\,, \tag{1 a}$$

$$^{18}OH + H^{16}O_2 \rightarrow {}^{16}OH + H^{18}O^{16}O \tag{1 b}$$

have been carried out at room temperature under pseudo-first-order conditions with $H^{16}O_2$ in excess over ^{18}OH. The experimental conditions and the results obtained are collected in Table 1. Each run was supplemented with a control experiment using ^{16}OH instead of ^{18}OH. For this purpose the $H_2{}^{18}O$ flow was replaced by $H_2{}^{16}O$ only, leaving all other conditions unchanged.

The HO_2 concentration given in Table 1 are mean values taking the average of the measured HO_2 concentrations with and without ^{16}OH present. The concentrations of $H_2{}^{18}O$ and $H_2{}^{16}O$ in Table 1 refer to the conditions inside the OH supplying probe.

The concentrations of ^{18}OH and ^{16}OH were monitored at different reaction times with the H atom discharge on and off, i. e. with and without $H^{16}O_2$.

Figure 1 shows a typical example of the concentration profiles observed. The decay rate (ca. 10/s) of ^{18}OH in the absence of HO_2 generally was found to be slightly higher than the measured wall rate constant (ca. 5/s) for ^{16}OH in the corresponding control experiment. On the other hand with no

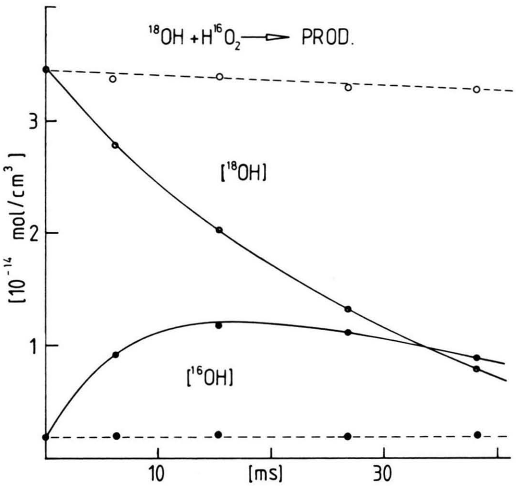

Fig. 1. Concentration profiles of ^{18}OH and ^{16}OH during the course of the reaction $^{18}OH + H^{16}O_2 \rightarrow$ prod. $[HO_2] = 4.8 \cdot 10^{-13}$ mol/cm^3. Concentration profiles of ^{18}OH and ^{16}OH measured under the same conditions but in the absence of HO_2 are shown by dotted lines.

Table 1. Experimental results for the reaction $^{18}OH + H^{16}O^{16}O \rightarrow$ prod. and for the control reaction $^{16}OH + H^{16}O^{16}O \rightarrow$ prod.

p mbar	v m/s	$[HO_2]$ $\cdot 10^{13}$ mol/cm^3	$[^{18/16}OH]_0$ $\cdot 10^{14}$ mol/cm^3	$[H_2{}^{18/16}O]$ $\cdot 10^{10}$ mol/cm^3	$k_1[^{18}OH]$ 1/s	$k_1[^{16}OH]$ 1/s	$k(^{18}OH + H^{16}O_2)$ $\cdot 10^{-13}$ cm^3/mol s	$k(^{16}OH + H^{16}O_2)$ $\cdot 10^{-13}$ cm^3/mol s
3.19	34.7	4.0	3.4	2.5	23	–	5.7	–
3.26	34.3	2.8	3.8	2.5	26	14	9.3	5.2
4.16	17.6	4.8	3.4	4.3	36	19	7.6	4.0
3.36	26.4	6.9	1.5	5.0	43	19	6.2	2.8
3.36	26.4	7.2	4.9	5.0	41	22	5.7	3.1
11.50	15.7	14.5	7.8	16	84	61	5.8	4.2
12.44	13.9	10.2	7.7	16	78	34	7.7	3.3
6.23	26.2	6.8	8.2	3.6	41	20	6.0	2.9
							6.8 ± 1.3	3.6 ± 0.9

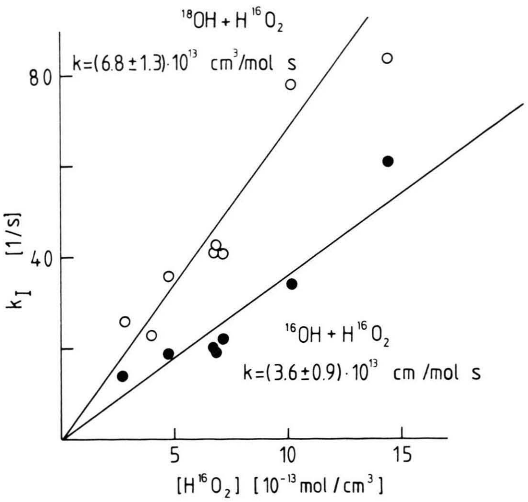

Fig. 2. Plot of the pseudo first order rate constants – corrected for wall losses – vs. the [HO$_2$] concentration. *Open circles:* ^{18}OH + H^{16}O$_2$ → Prod. *Full circles:* control experiment ^{16}OH + H^{16}O$_2$ → Prod.

H^{16}O$_2$ present the amount of ^{16}OH impurities (dashed line with solid points in Fig. 1) from the ^{18}OH radical source was found to be constant in time (see Figure 1). These observations can be explained by assuming an exchange of ^{18}OH with ^{16}OH on the reactor wall due to the presence of ^{16}O-water. In the case of the control experiment with ^{16}OH a corresponding formation of ^{18}OH has not been observed, as traces of ^{18}O-water were effectively removed by flushing with large amounts of ^{16}O-water, whereas in the other case smaller amounts of ^{18}O-water had to satisfy the same purpose.

As shown in Fig. 1, the exchange on the wall was only of minor importance compared to the monitored decrease of ^{18}OH and increase of ^{16}OH when H^{16}O$_2$ was admixed.

In Fig. 2 the pseudo first order rate constants – corrected for wall losses – are plotted as a function of the H^{16}O$_2$ concentration. The rate data of the control experiments are included. The bimolecular rate constants obtained from the distinctly different data sets are

$$k^{298}(^{18}\mathrm{OH} + \mathrm{H}^{16}\mathrm{O}_2) = (6.8 \pm 1.7) \cdot 10^{13}\ \mathrm{cm}^3/\mathrm{mol} \cdot \mathrm{s}\,,$$

$$k^{298}(^{16}\mathrm{OH} + \mathrm{H}^{16}\mathrm{O}_2) = (3.6 \pm 0.9) \cdot 10^{13}\ \mathrm{cm}^3/\mathrm{mol} \cdot \mathrm{s}\,.$$

The latter value agrees well with the mean value from the three low pressure studies mentioned above. For the ratio of these rate constants an average value of

$$k(^{16}\mathrm{OH} + \mathrm{H}^{16}\mathrm{O}_2)/k(^{18}\mathrm{OH} + \mathrm{H}^{16}\mathrm{O}_2) = 0.52 \pm 0.08$$

is obtained from the data in Table 1.

Discussion

Before the present results are discussed in terms of an isotope exchange process, possible sources of error need to be mentioned. The presence of H and O atom impurities in the reaction system would cause the formation of ^{16}OH radicals by the reactions $\mathrm{H} + \mathrm{HO}_2 \rightarrow 2\mathrm{OH}$ and $\mathrm{O} + \mathrm{HO}_2 \rightarrow \mathrm{OH} + \mathrm{O}_2$. The latter reaction is known to proceed through a loose [OOOH] complex that dissociates to OH and O$_2$ by breakage of the central O–O bond [11], thus in any case – irrespective of the isotopic constitution of the O atom impurities – ^{16}OH will be formed in the reaction of O atoms with H^{16}O$_2$.

If the amount of ^{16}OH formed during the reaction of H^{16}O$_2$ with ^{18}OH were due to such impurities, the presence of similar amounts of impurities in the control reaction ^{16}OH + H^{16}O$_2$, would decrease the effective rate constant in accordance with the observed difference. In the case that the results of the present study were mainly due to impurities and not due to reaction (1 b), the difference of about 70% between the observed reaction rate for ^{18}OH + H^{16}O$_2$ and the literature value for k(1 a) would exceed the overall error of the experiment, which we estimate to 25%. We therefore feel confident that we have observed an acceleration of the decay rate for ^{18}OH due to an isotope exchange process, although we cannot exclude an artifact as the impurities required to produce the desired effect are at or below the detection limit of the EPR spectrometer.

The inconsistency between the theory predicting a short lived intermediate and the observed pressure dependence of k(1), which requires a complex sufficiently long-lived to be stabilised at elevated pressures does not arise if the reaction proceeds by two different channels that do not share a common intermediate:

$$^{18}\mathrm{OH} + \mathrm{H}^{16}\mathrm{O}_2 \xrightarrow{[\mathrm{H}^{18}\mathrm{O} \cdots \mathrm{H}\text{-}^{16}\mathrm{O}^{16}\mathrm{O}]} \mathrm{H}_2{}^{18}\mathrm{O} + {}^{16}\mathrm{O}_2 \qquad (1\,\mathrm{a})$$

$$^{18}\mathrm{OH} + \mathrm{H}^{16}\mathrm{O}_2 \underset{b'}{\overset{a}{\rightleftarrows}} [\mathrm{H}^{18}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{OH}] \xrightarrow{b} {}^{16}\mathrm{OH} + \mathrm{H}^{18}\mathrm{O}^{16}\mathrm{O} \qquad (1\,\mathrm{b})$$
$$\xrightarrow[+\mathrm{M}]{c} \mathrm{H}_2{}^{18}\mathrm{O}^{16}\mathrm{O}_2$$

A mechanism of this kind has already been suggested [4]. The requirements of both, theory and experiment, may be met assuming reaction (1 a) to proceed by direct H atom transfer or passing through a short lived H bonded collision complex, whereas reaction (1 b) leads to an O bonded intermediate whose lifetime possibly may be long enough to account for the observed pressure dependent part of the reaction.

This mechanism may also explain the apparent disagreement of the present results with those of Kurylo et al. [7]. In that study, mixtures of about 10 torr $H_2{}^{18}O$, 1 torr $^{16}O_2$ and 750 torr SF_6 were irradiated with a low pressure mercury lamp for several minutes. The production of $^{16}O^{18}O$ was determined mass spectrometrically after removal of the condensable products (SF_6, $H_2{}^{18}O$) by liquid N_2 trapping. Since only minor amounts of $^{16}O^{18}O$ (ca. 10%) were found compared with those predicted by model calculations the authors concluded that the existence of a linear adduct as intermediate in reaction (1) was not supported. The two studies can be adjusted, assuming that within the reaction channel (1 b) route c dominates for the conditions applied in [7]. As SF_6 is generally assumed to be a very efficient collisional quencher it is not unlikely that reaction (1 b) comes close to the high pressure regime at one atmosphere of SF_6. Clearly this explanation will hold only if the H_2O_3, once formed this way, remains subsequently inert. Assuming an absorption coefficient for H_2O_3 similar to that of H_2O_2, only about 10% of the H_2O_3 produced will be photolyzed. Problems may arise when the stability of H_2O_3 with respect to HO_2 or OH radical attack is considered, if these reactions would cause isotopic scrambling. In order to keep the depletion of H_2O_3 by these reactions below 10% of the total amount of H_2O_3 formed, the corresponding rate constants should be $< 10^9\ \mathrm{cm^3/mol\cdot s}$. Alternatively one may think of a heterogeneous sink for H_2O_3 in analogy to the wall removal already assumed [7] for H_2O_2 that is present as a side-product in the experiments described in [7].

From the gas phase self disproportionation reaction of HO_2 accelerated by the presence of polar gases it is well known that this molecule exhibits some special features. Thus, complex structures like [HOO ... H_2O] or [HOO ... SF_6] may occur that still react with OH by H atom abstraction but prevent at the same time the formation of an H_2O_3 intermediate.

High Pressure Limit of the Reaction (1 b)

From the observed difference between the rates of the reactions $^{16}OH + H^{16}O_2$ and $^{18}OH + H^{16}O_2$ the high pressure limit of reaction (1 b) can be obtained. This determination does not require the pressure dependence of $k(1)$ observed as input data but is based merely on the assumption that a HO_3H complex will be formed during the course of the reaction.

With the usual steady state approximation for the HO_3H intermediate the temporal decay of $[^{18}OH]$ may be expressed as

$$\frac{d[^{18}OH]}{dt} = -\left[\frac{(k_b + k_c[M])\,k_a}{k'_b + k_b + k_c[M]} + k_{1a}\right][^{18}OH][H^{16}O_2]$$
$$= -k^{18}_{\mathrm{exp}}[^{18}OH]\cdot[H^{16}O_2].$$

The temporal decay of $[^{16}OH]$ in the control experiment is

$$\frac{d[^{16}OH]}{dt} = -\left[\frac{k_c[M]\,k_a}{2k_b + k_c[M]} + k_{1a}\right][^{16}OH]\cdot[H^{16}O_2]$$
$$= -k^{16}_{\mathrm{exp}}[^{16}OH]\cdot[H^{16}O_2]$$

k_{1a} is the rate constant of the – pressure independent – reaction (1 a) and k_a, k_b, k'_b, k_c denote the rate constants of the corresponding processes within reaction (1 b). At pressures of a few mbar the term $k_c[M]$ can be dropped. Neglecting isotope effects sets k_b equal to k'_b, and thus the difference of the experimental rate constants obtained in this study leads to a high pressure limit $k_\infty(1\,b)$ (identical with k_a) of $k_\infty(1\,b) = 2(k^{18}_{\mathrm{exp}} - k^{16}_{\mathrm{exp}}) = (6 \pm 5)\cdot 10^{13}$ cm^3/mol · s.

These large errors bars can be reduced by replacing the difference of the rate constants by the probably more accurate relative ratio $k^{18}_{\mathrm{exp}}/k^{16}_{\mathrm{exp}}$ and the average $\langle k(1)\rangle$ of the three low pressure studies cited above. Then a value of

$$k_\infty(1\,b) = 2\langle k(1)\rangle\left(\frac{k^{18}_{\mathrm{eff}}}{k^{16}_{\mathrm{eff}}} - 1\right)$$
$$= (7.4 \pm 2.3)\cdot 10^{13}\,[\mathrm{cm^3/mol\cdot s}]$$

is obtained. The stated error represents the statistical scattering of the experimental data only within one standard deviation. Systematic errors caused, e. g., by impurities are not accounted for.

These results agree with just published RRKM calculations [12] which predict $k_\infty(1\,\mathrm{b}) = 7.2 \cdot 10^{13}$ cm^3/mol · s, also on the basis of two independent reaction channels. However, RRKM calculations assuming a hydrogen bonded intermediate give results which agree with the magnitude and temperature dependence of $k(1)$ as well.

Conclusions

The results of the present study seem to indicate that the pressure effect of the rate of the reaction OH + HO$_2$ is real.

As already discussed, impurities present at the reaction system may cause a misleading interpretation of the experimental findings. We estimated this effect to be of minor importance for the experimental conditions of this study. The present results need additional verification by proving the formation of $H^{18}O^{16}O$ during the course of the reaction. A search for the LMR spectra of this radical employing the independent source $^{18}OH + {}^{16}O_3 \rightarrow H^{18}O^{16}O + {}^{16}O_2$ is in progress.

By comparison of the sum $k(1\,\mathrm{a}) + k_\infty(1\,\mathrm{b})$ with the experimental rate data obtained at atmospheric pressures it may be concluded that reaction (1 b) is still in the fall-off region at these pressures with He and Ar as collision partners but not with SF$_6$. Nevertheless, substantial amounts of H_2O_3 may be present in the atmosphere, when the lifetime of H_2O_3 is estimated with respect to thermal decomposition by the equilibrium constant of the process (1 b) and by the reaction rate $k(1\,\mathrm{b})$ at atmospheric pressures [12].

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