

# Direct Measurements of the Isotope Exchange Reactions between $^{18}\text{OH}$ and $\text{NO}$ , $\text{NO}_2$ , $\text{N}_2\text{O}$ and $\text{O}_2$

P. Dransfeld, J. Lukacs-Paal\*, and H. Gg. Wagner

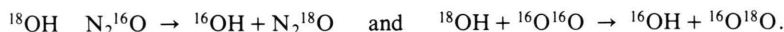
Max-Planck-Institut für Strömungsforschung, Göttingen, West Germany

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The isotope exchange reactions between  $^{18}\text{OH}$  and  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{O}_2$  were studied at room temperature in a discharge flow system with laser magnetic resonance detection of  $^{18}\text{OH}$  and  $^{16}\text{OH}$ . Exchange rate constants of



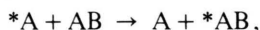
where obtained for  $\text{NO}$  and  $\text{NO}_2$ , respectively. Upper limits of  $k < 1 \cdot 10^8 \text{ cm}^3/\text{mol s}$  can be reported for the reactions



The results are compared with recombination rate data in the limit of high pressures and with vibrational deactivation measurements.

## Introduction

Isotopic labelling provides a useful tool for the investigation of the structure and the dynamics of collision complexes formed in the course of gas phase radical reactions. Apart from experiments concerned directly with the effect of isotopic substitution on the reaction rate, several papers have been published dealing with exchange reactions of the type



where  $^*A$  denotes an isotopically labelled single atom or reactive group A. In the case that  $^*A$  stands for a group the reaction scheme assumes that only a certain “central” bond is formed, respectively broken, during the exchange process. The individual bond relations within  $^*A$  or A remain practically unaffected.

Reactions in which this is no longer the case may be described by the more general scheme



The investigation of exchange reactions of this type may provide information about isomerisation within the collisional complex before redissociation.

As an example the exchange reaction



may be considered, which follows a simple version of the general scheme above omitting the Y of the XBY molecule.

This reaction should proceed through a complex similar to nitrous acid. Therefore the rate of this reaction could depend on the height of the potential barrier for the H atom to shift from being bonded to O to being bonded to N. One extreme may be a barrier which is too high allow any reaction at all. The other extreme is a potential barrier for the H atom shift which is sufficiently low so that the overall reaction rate is determined by the step of complex formation. In this case exchange rate measurements are useful for the determination of the high pressure recombination rate constant  $k_{\text{rec}}^\infty$  of the reaction mentioned. If the reaction proceeds somewhere inbetween these two limiting cases a quantitative interpretation of the isotope exchange results in terms of  $k_{\text{rec}}^\infty$  and the height of the potential barrier for the H atom shift is more complicated even if temperature dependent rate data are available. This may be a reason why isotope exchange investigations for the determination of  $k_{\text{rec}}^\infty$  have so far been mainly applied to

\* Permanent adress: Central Research Institute for Chemistry, Budapest, Hungary.

Reprint requests to Prof. Dr. H. Gg. Wagner, MPI für Strömungsforschung, Bunsenstraße 10, D-3400 Göttingen.



reactions between atoms and molecules. In this case the interpretation of the measurements is straightforward; for a more general case a lower limit for  $k_{\text{rec}}^\infty$  can be obtained immediately from exchange rate measurements.

Recent investigations of the vibrational relaxation of  $\text{OH}$  ( $v=1$ ) by  $\text{NO}$  and  $\text{NO}_2$  [1] suggest values for the recombination rate constants in the high pressure limit  $k_{\text{rec}}^\infty$  for the reactions of  $\text{OH}$  with  $\text{NO}$  and  $\text{NO}_2$ , which are definitely higher than those obtained by direct recombination studies [2–10]. Isotope exchange experiments should help to clarify this situation. We therefore investigated the exchange reactions between  $^{18}\text{OH}$  and  $\text{NO}$ ,  $\text{NO}_2$  and also  $\text{N}_2\text{O}$  and  $\text{O}_2$ .

## Experimental

The isotope exchange reactions have been studied in a conventional discharge flow system coupled to a far infrared Laser Magnetic Resonance (LMR) spectrometer combined with an EPR spectrometer described elsewhere [11].

$^{18}\text{OH}$  has been observed here, to our knowledge for the first time, by LMR. The assignment of the spectrum ( $79.2\ \mu\text{m}$   $\text{H}_2\text{O}$ -laser,  $\pi$ -pol., 0.36 Tesla) to  $^{18}\text{OH}$  results simply from its chemical origin.  $^{18}\text{OH}$  has been obtained by the reaction of F-atoms with  $\text{H}_2^{18}\text{O}$  of 98% isotopic purity, and entered the teflon coated reactor of 70 cm effective length through a moveable inlet.

The F atoms were produced by microwave dissociation of highly diluted  $\text{F}_2$  in helium. All gases used were of maximum commercially available purity. Helium as the main carrier gas was purified by passing it through liquid nitrogen cooled traps. Known mixtures of He with (ca. 1%)  $\text{F}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$  were used without further purification.

The flow rates were controlled either by calibrated flow controllers (TYL AN) or determined by the pressure rise in a known volume.

## Calibrations

Absolute concentrations of  $^{18}\text{OH}$  and  $^{16}\text{OH}$  were determined by the titration of F atoms with water. At high microwave power levels and insufficient cooling of the discharge tube (alumina) appreciable amounts of F atoms are lost at the hot walls and the

occurrence of oxygen atoms can be observed, whereas at moderate power levels and good cooling the dissociation of  $\text{F}_2$  is better than 98% as has been checked by EPR measurement of the absolute F atom concentration. These [F] measurements fail at the low concentrations needed for the  $\text{OH}$ -calibrations. There the F atom concentration can be obtained from the  $\text{F}_2$  flow rate. The sensitivities established in such a way were checked by converting  $^{18}\text{OH}$  and  $^{16}\text{OH}$  with an excess of oxygen atoms into H atoms, monitored by EPR. The reaction is  $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ . This titration yields, irrespective of the knowledge of the H atom sensitivity, the important relative sensitivities of the instrument for  $^{18}\text{OH}$  to  $^{16}\text{OH}$  with high accuracy. In conjunction with the absolute H-atom concentrations, calibrated by the reaction  $\text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH}$ , a second independent determination of the LMR sensitivity for  $\text{OH}$  has been made.

## Results

### Reaction of $^{18}\text{OH}$ with $\text{NO}$

The decay of  $^{18}\text{OH}$  and the formation of  $^{16}\text{OH}$  in the exchange reaction



has been studied in a large excess of  $\text{N}^{16}\text{O}$  at room temperature and pressure around 3 mbar.

The experimental data and the results obtained are given in Table 1. Column 3 of the table lists the pressure drop along the flow tube. As this drop is not too pronounced, an average pressure  $\langle p \rangle$  was used in the evaluations.

Figure 1 shows the measured pseudo first order rate vs. the  $\text{NO}$  concentration. Since the rates have

Table 1. Experimental conditions and results for the reaction  $^{18}\text{OH} + \text{NO} \rightarrow ^{16}\text{OH} + \text{N}^{18}\text{O}$ .

$\langle p \rangle$ mbar	$\varnothing$ $\text{cm}^3/\text{s}$	$\Delta p$ mbar	$v$ m/s	$[\text{NO}] \cdot 10^{12}$ $\text{mol}/\text{cm}^3$	$[^{18}\text{OH}]_0 \cdot 10^{13}$ $\text{mol}/\text{cm}^3$	$k_1(\text{exp})$ 1/s
3.06	119.4	0.56	87.8	3.6	2.6	81
2.49	46.8	0.29	40.1	4.3	5.0	79
3.06	112.7	0.59	83.1	22.7	1.0	293
2.90	83.1	0.45	86.2	8.2	1.7	121
2.93	86.2	0.43	64.9	46.2	2.5	493
2.61	28.5	0.19	24.6	30.2	1.6	46
2.61	28.5	0.19	24.6	15.3	2.3	36

not been corrected for the heterogeneous reaction, the plot exhibits an intercept corresponding to a wall rate of 15/s, whereas the direct determination of the wall losses in the absence of  $\text{NO}$  yielded a somewhat lower value. The difference is insignificant for the determination of the reaction rate constant. The line in Fig. 1 represents the best fit to the data when minimising the relative errors. The slope of the line leads to the exchange rate constant

$$k^{298}(\text{I}) = (1.25 \pm 0.3) \cdot 10^{13} \text{ cm}^3/\text{mol s}.$$

If the amount of  $^{18}\text{OH}$  consumed during the course of the reaction is correlated with the  $^{16}\text{OH}$  produced, corrections have to be made at longer reaction times accounting for increasing wall losses. Within the uncertainties of the wall rate described above, a 1:1 stoichiometry has been obtained for all runs. These results would become more reliable if wall effects could be neglected at all. Therefore, in additional experiments  $^{18}\text{OH}$  has been converted with different amounts of  $\text{NO}$  very close to the absorption volume, thus avoiding any appreciable wall influence. In Fig. 2 the consumption of  $^{18}\text{OH}$  observed is plotted against the concentration of  $^{16}\text{OH}$  produced. The good linearity of this correlation makes sure that processes other than the exchange reaction, in particular wall effects, should not be important within the limits of experimental error.

#### Reaction of $^{18}\text{OH}$ with $\text{NO}_2$

The exchange reaction



has been studied in the same way as the one with  $\text{NO}$ . The experimental data and the results are collected in Table 2. In Fig. 3 the measured first order decay rate including wall losses is plotted against the  $\text{NO}_2$  concentration.

As indicated by the intercept, the wall activity has increased to 20/s, and again the direct measurement of the wall rate without  $\text{NO}_2$  led to slightly lower values. The line in Fig. 3 is a least squares fit<sup>1</sup> to the data points. From the slope of the line one obtains the reaction rate constant

$$k^{298}(\text{II}) = (6.9 \pm 1.4) \cdot 10^{12} \text{ cm}^3/\text{mol s}.$$

In analogy to the experiments described for the exchange reaction with  $\text{NO}$ , additional experiments

<sup>1</sup> As before, the *relative* errors have been minimised.

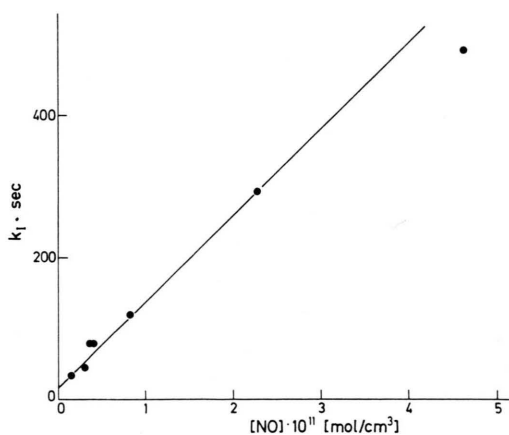


Fig. 1. First order rate of the reaction  $^{18}\text{OH} + \text{NO} \rightarrow \text{OH} + \text{N}^{18}\text{O}$  as a function of  $\text{NO}$  concentration.

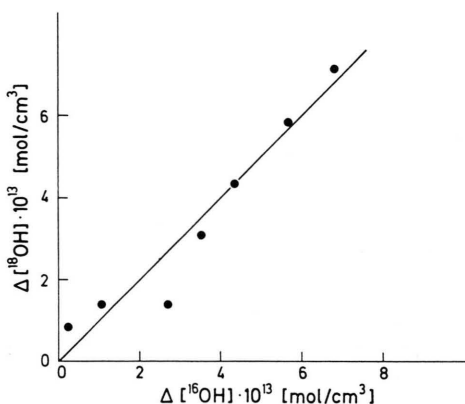


Fig. 2. Turnover of  $^{18}\text{OH}$  vs.  $^{16}\text{OH}$  for the reaction  $^{18}\text{OH} + \text{NO} \rightarrow \text{OH} + \text{N}^{18}\text{O}$ .

Table 2. Experimental conditions and results for the reaction  $^{18}\text{OH} + \text{NO}_2 \rightarrow ^{16}\text{OH} + \text{N}^{16}\text{O}^{18}\text{O}$ .

$\langle p \rangle$ mbar	$\emptyset$ $\text{cm}^3/\text{s}$	$\Delta p$ mbar	$v$ m/s	$[\text{NO}_2] \cdot 10^{12}$ $\text{mol}/\text{cm}^3$	$[^{18}\text{OH}]_0 \cdot 10^{13}$ $\text{mol}/\text{cm}^3$	$k_1(\text{exp})$ 1/s
2.18	37.0	0.27	38.1	21.2	18	165
2.22	37.0	0.27	37.5	5.2	2.7	55
2.22	37.0	0.27	37.5	30.0	2.7	236
2.22	37.0	0.27	37.5	9.4	2.7	83
2.22	37.0	0.27	37.5	42.8	2.7	302

were carried out in order to exclude any interference of wall effects. At a fixed short reaction time the conversion of  $^{18}\text{OH}$  with different amounts of  $\text{NO}_2$  has been monitored together with the corresponding increase in  $^{16}\text{OH}$ . Figure 4 shows the conversion of the two isotopes. A 1:1 stoichiometry

is observed, thus reducing any influence of wall effects on the measurements below the stated limits of error.

#### Reaction of $^{18}\text{OH}$ with $\text{N}_2\text{O}$

No  $^{18}\text{OH}$  losses in addition to the decay on the wall could be observed for the reaction

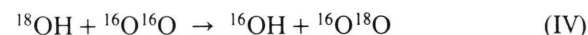


even when helium as the carrier gas was replaced mainly by  $\text{N}_2\text{O}$  ( $[\text{N}_2\text{O}] \cong 4 \cdot 10^{-8} \text{ mol/cm}^3$ ). Attributing the observed wall losses of  $^{18}\text{OH}$  to reaction (III) (though no formation of  $^{16}\text{OH}$  could be monitored!), one obtains

$$k^{298}(\text{III}) < 1 \cdot 10^8 \text{ cm}^3/\text{mol s}.$$

#### Reaction of $^{18}\text{OH}$ with $^{16}\text{O}_2$

Some experiments have been performed with  $\text{O}_2$  as reactant. For the reaction



no  $^{18}\text{OH}$  losses besides the wall losses could be observed at  $\text{O}_2$  concentrations up to 1 mbar partial pressure.

Thus an upper limit of

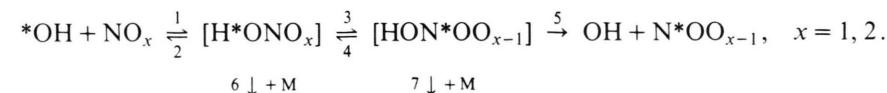
$$k^{298}(\text{IV}) \leq 1 \cdot 10^8 \text{ cm}^3/\text{mol s}$$

at room temperature can be stated for this reaction constant.

### Discussion

No other experimental data are available on the isotope exchange reactions presented here.

The data obtained here will be discussed in comparison with recombination rate data in the limit of high pressures and with rate constants obtained for the vibrational deactivation of  $\text{OH}$  ( $v=1$ ) in the presence of  $\text{NO}_x$ . The different steps can be presented by the reaction scheme (the asterisk denotes the  $^{18}\text{O}$  atom)



where  $\text{M} = \text{He}$ .

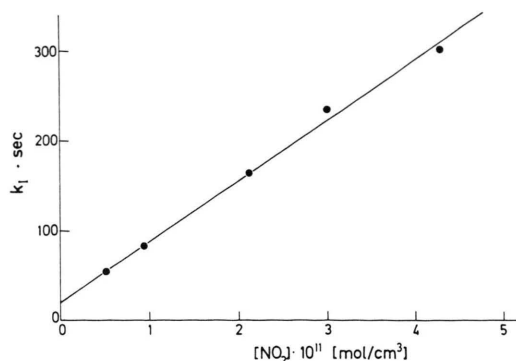


Fig. 3. First order rate of the reaction  $^{18}\text{OH} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}^{18}\text{O}$  as a function of  $\text{NO}_2$  concentration.

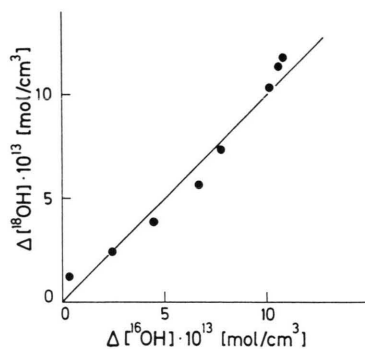


Fig. 4. Turnover of  $^{18}\text{OH}$  vs.  $^{16}\text{OH}$  for the reaction  $^{18}\text{OH} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}^{18}\text{O}$ .

Reaction step (1) may be identified with the high-pressure limit recombination (rate constant  $k_{\text{rec}}^\infty$ ). Oxygen isotope effects are small and can be neglected here. Therefore the rate constants  $k_5$  and  $k_2$  as well as  $k_3$  and  $k_7$  can be assumed to be equal.

With the usual steady state approximation for the transient species the decay of  $^{18}\text{OH}$  (sufficiently far away from equilibrium) may be expressed as

$$\frac{d[^{18}\text{OH}]}{dt} = -k_1 \left[ \frac{k_6[\text{M}]}{k_2 + k_6[\text{M}]} + \frac{k_2}{k_2 + k_6[\text{M}]} \cdot \frac{k_3}{k_2 + k_3 + k_4 + k_6[\text{M}]} \right] [^{18}\text{OH}][\text{NO}_x].$$

As  $k_1$  equals  $k_{\text{rec}}^\infty$  the term in brackets may be regarded as a correction factor that correlates  $k_{\text{rec}}^\infty$  with the measured isotope exchange reaction rate constant  $k_{\text{ex}}$ .

The pressure dependence of the correction factor itself may be employed to establish  $k_{\text{rec}}^\infty$  by isotope exchange measurements.

At the low pressures of about 3 mbar used throughout the present study,  $k_6[\text{M}]$  is negligible compared to the remaining rate constants. Thus, the correction factor reduces to  $k_3/(k_2 + k_3 + k_4)$ .

If the lifetime of the collision complex is sufficiently long to allow complete randomisation of the H atom in the complex  $k_2 \ll (k_3 + k_4)$  simple expressions result. For  $^{18}\text{OH} + \text{N}^{16}\text{O}$  the rate constants  $k_3$  and  $k_4$  would be equal, whereas for  $^{18}\text{OH} + \text{N}^{16}\text{O}_2$  the relation  $k_3 = 2k_4$  would hold because of the two identical forms of  $\text{H}^{16}\text{ON}^{16}\text{O}^{18}\text{O}$ .

On the basis of that approximation correction factors of 1/2 and 2/3 are obtained for the reactions of  $^{18}\text{OH}$  with  $\text{NO}$  and  $\text{NO}_2$  respectively. Thus arriving at values for  $k_{\text{rec}}^\infty$  of

$$k_{\text{rec}}^\infty(1) = 2 \cdot k(\text{I}) = (2.5 \pm 0.6) \cdot 10^{13} \text{ cm}^3/\text{mol s},$$

$$k_{\text{rec}}^\infty(2) = 1.5 \cdot k(\text{II}) = (1.04 \pm 0.2) \cdot 10^{13} \text{ cm}^3/\text{mol s}.$$

It cannot be excluded, that the condition  $k_2 \ll (k_3 + k_4)$  leading to the approximation used represents an inappropriate simplification. In this case, however, the true value of  $k_{\text{rec}}^\infty$  could only be larger than that calculated from the isotope exchange rate data, which represents a lower limit for  $k_{\text{rec}}^\infty$ .

The interpretation of vibrational relaxation rate data in the limit of strong collisions is in complete analogy to the interpretation of the isotope exchange reactions, as can be visualised by identifying the isotopomers  $^{18}\text{OH}$  and  $^{16}\text{OH}$  in the above reaction scheme with  $\text{OH}(v=1)$  and  $\text{OH}(v=0)$ , respectively. The two different intermediates in this scheme may than be reinterpreted as the collisional complex before and after redistribution of the energy initially stored in the vibrating mode of the excited reactant. In case this energy is well above the thermal average and as long as other effective routes for vibrational deactivation (e.g. transitions between the different potential surfaces prior to the reactants entering the strong coupling complex region) are not present, the vibrational relaxation rate constant  $k_{\text{vib}}$  will be very similar to the step of complex formation  $k_{\text{rec}}^\infty$ . If in the more general case

the redistribution of the energy within the collisional complex is not fast compared to the redissociation,  $k_{\text{vib}}$  may serve as a lower limit for  $k_{\text{rec}}^\infty$  [12].

Table 3 compares our results for  $k_{\text{rec}}^\infty$  with direct measurements and vibrational relaxation rate data. Theoretical predictions have been added too. For the sake of compatibility, values predicted by the same statistical adiabatic channel model [13] have been included.

In contradiction to the direct measurements, the vibrational relaxation rate data form a set of distinctly higher values. The present isotope exchange experiments do not favour results from one of these methods. They support on the one hand the relaxation rate data in the case of  $\text{OH}(v=1) + \text{NO}$ . For the system  $\text{OH} + \text{NO}_2$  they agree quite well with the direct measurements of the recombination reaction  $\text{OH} + \text{NO}_2$ .

For the reaction  $\text{OH} + \text{NO}$  the direct measurements lead to markedly lower values for  $k_{\text{rec}}^\infty$  than the limit given by the present results and by relaxation data. The experimental recombination measurements never came very close to the high pressure "plateau". Therefore, they had to be extrapolated to  $k_{\text{rec}}^\infty$  using suitable theoretical models describing the fall-off region. The theoretical predictions also yielded lower values, they are however compatible within their limits of error with the present results.

The vibrational relaxation rate constant reported for the reaction  $\text{OH}(v=1) + \text{NO}_2$  is nearly four

Table 3. Comparison of high pressure limit recombination rate data obtained by different methods.

Reaction	$k_{\text{rec}}^\infty(\text{dir})$ $\cdot 10^{13}$ $\text{cm}^3/\text{mol s}$	$k_{\text{rec}}^\infty(\text{rel})$ $\cdot 10^{13}$ $\text{cm}^3/\text{mol s}$	$k_{\text{rec}}^\infty(\text{th})$ $\cdot 10^{13}$ $\text{cm}^3/\text{mol s}$	$k_{\text{rec}}^\infty(\text{ex})$ $\cdot 10^{13}$ $\text{cm}^3/\text{mol s}$
$\text{OH} + \text{NO}$	0.51 [2] 0.48 [3] 1.1 [4] 0.72 [5] 0.72 [6] 0.6 <sup>a</sup> [7]	2.3 [1]	0.87 [2]	2.5 (this work)
$\text{OH} + \text{NO}_2$	0.96 [8] 0.96 [9] 1.8 [10]	3.8 [1]	1.3 [14]	1.04 (this work)

<sup>a</sup> Evaluation. —  $k_{\text{rec}}^\infty(\text{dir})$ : direct studies,  $k_{\text{rec}}^\infty(\text{rel})$ : vibrational relaxation studies,  $k_{\text{rec}}^\infty(\text{ex})$ : isotope exchange studies,  $k_{\text{rec}}^\infty(\text{th})$ : theoretical predictions (statistical model, maximum free energy concept).



times larger than the corresponding high pressure rate constant obtained by direct measurements and by the isotope exchange experiments. If the route via the strong collision complex  $[\text{HONO}_2]$  solely is able to describe the vibrational deactivation process sufficiently (the requirements that have to be met are mentioned above), the difference between the vibrational relaxation measurements and the isotope exchange results might be taken as a hint that the H atom exchange is not faster than the complex dissociation. In this case additional measurements using deuterated reactants should be instructive.

Conversely, assuming the rate data of the direct measurements and of the isotope exchange experiments to represent the true value of  $k_{\text{rec}}^\infty$ , the vibrational relaxation process must be enhanced by other very effective routes.

A potential pathway increasing the vibrational deactivation rate might be the often proposed formation of a peroxonitrous acid  $\text{H}-\text{O}-\text{O}-\text{N}=\text{O}$  intermediate. Although this substance is still unknown in the gas phase, it is easily prepared in solution by acidification of a nitrite solution treated with  $\text{H}_2\text{O}_2$ .

Clearly, this interpretation of the different results between the isotope exchange experiments and the vibrational relaxation measurements implies that no

hydrogen shift will occur within the pernitrous acid intermediate. Otherwise both methods should yield similar results. The mobility of the H atom in the  $\text{HOONO}$  complex can be checked by repeating the exchange experiment with reversed initial isotopic labelling. If the reaction channel through an  $\text{HOONO}$  intermediate participates to an appreciable amount in the total exchange rate, the ratio of the exchange rate constants with the two different labellings should deviate from the statistical factor  $1/3:2/3$ , because the O atoms are no longer chemically equivalent in the  $\text{HOONO}$  complex.

The present investigation of isotope exchange reactions involving larger radicals has proven to be a good alternative route to the high pressure regime of gas phase recombination reactions. As the results for the exchange reactions of  $^{18}\text{OH}$  with  $\text{N}_2^{16}\text{O}$  and  $^{16}\text{O}_2$  exemplify, the method is restricted to reactions passing through a strong collision complex. This restriction has not necessarily to be regarded as a disadvantage, as in comparison to the vibrational relaxation rate measurements the observation of an isotope exchange makes sure that the same reactants will recombine if the pressure is chosen sufficiently high.

J. L. P. thanks the MPG for a stipend in 1984.

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