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DISCLAIMER

VIBRATIONAL RELAXATION OF DCl(v = 1) BY Cl AND Br ATOMS AND OF HBr(v = 1) BY Br ATOMS

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The rates of vibrational relaxation of DCl(v = 1) by Cl and Br are measured as $(5.5 \pm 1.6) \times 10^{-12}$ and $(2.3 \pm 0.7) \times 10^{-13}$ cm^3 $molec^{-1}$ sec^{-1} respectively. DCl is relaxed somewhat less rapidly than HCl in both cases. The rate for HBr(v = 1) relaxed by Br atoms is found to be $(2.6 \pm 1.0) \times 10^{-12}$ cm^3 $molec^{-1}$ sec^{-1}.

The extremely efficient removal of vibrationally excited molecules by potentially reactive or open shell collision partners provides the major vibrational relaxation path in many systems ranging from chemical lasers to the upper atmosphere. Determination of such vibrational relaxation rate constants is thus of considerable practical importance. A knowledge of the rate constants and mechanisms of energy transfer can give new information on the shapes of the potential energy surfaces involved. In the present work we report on the measurement of vibrational relaxation rate constants for the processes

$$Cl(^2P_{3/2}) + DCl(v = 1) \xrightarrow{k_1} DCl(v = 0) + Cl(^2P_{3/2}) + 2091\ cm^{-1} \quad (1)$$

$$Br(^2P_{3/2}) + DCl(v = 1) \xrightarrow{k_2} DCl(v = 0) + Br(^2P_{3/2}) + 2091\ cm^{-1} \quad (2)$$

$$Br(^2P_{3/2}) + HBr(v = 1) \xrightarrow{k_3} HBr(v = 0) + Br(^2P_{3/2}) + 2559\ cm^{-1} \quad (3)$$

at 294°K using a laser-induced fluorescence technique. These measurements will be compared with qualitative predictions based on proposed theories in a subsequent publication.[1]

EXPERIMENTAL

The experimental apparatus has been described in detail previously.[2] Either DCl or HBr was excited to v = 1 by a pulse of P-branch 1 → 0 laser radiation from the respective chemical laser. The R-branch of the 1 → 0 DCl or HBr infrared fluorescence was monitored as a function of time using a Hg:Ge detector cooled to 4.2°K. The output of the detector was amplified and displayed on an oscilloscope. The signal-to-noise of all fluorescence photographs was >10 for P_{DCl} > 0.020 torr and P_{HBr} > 0.010 torr.

The Br or Cl atoms were produced by dissociation of the parent halogen in a microwave discharge. As described previously,[2,3] the atom concentrations were determined by gas phase titration using NOCl.[4,5] The flow velocities were 9 - 10 m/sec.

The decay of atoms down the flow tube was monitored by observing the change in the atom afterglow intensity as a function of distance. The Cl atoms only decayed by ~ 10% from the titration position to the observation port, 25 cm. For Br atoms with or without DCl present this decay was less than ~ 20%. The addition of HBr to the Br flow reduced the Br atom afterglow intensity by 10% - 30% and significantly accelerated the decay of Br atoms along the flow tube. If this increased decay were due to gas-phase recombination of Br atoms, then HBr would be ~ 200 times more efficient than

Ar as a third body.[6] Recent measurements[7] have shown that HI is only 11 times more efficient than Ar for the recombination of I atoms at 300°K. Since the reported HBr_2 spectrum[8] has now been assigned[9] to HBr_2^-, there is no reason to expect an HBr_2 species with a lifetime longer than than for HI_2. Thus it is unlikely that the observed decay of Br atoms in the presence of HBr was due to gas-phase recombination. It is possible that recombination of Br atoms on the walls is catalyzed by HBr. It was estimated that with HBr present the wall recombination rate constant was ~ 50 times larger than without HBr. Any drift in the Br or Cl atom concentration during the course of an experiment was accounted for by continuously monitoring the atom afterglow intensity.

RESULTS

The experimental conditions and results for the determination of k_1 , k_2 and k_3 are summarized in Tables I - III, respectively. A summary of rate constants is given in Table IV. Semilogarithmic plots of the observed infrared fluorescence were linear over three or four lifetimes. The vibrational relaxation rate constants k_1 , k_2 and k_3 were determined in the usual manner. The results for k_3 were more scattered than for k_1 and k_2 because of the increased uncertainty in P_{Br} due to the HBr catalyzed removal of Br atoms.

The observed decay rates contain only small contributions from other relaxation processes. For DCl, deactivation rates by DCl,[10] HCl,[11] and Ar[12] have been measured as 220, 575 and 0.06 sec^{-1} $torr^{-1}$ respectively. The DCl-DCl rate contributes less than 0.2% in the DCl-Cl experiments and less than 1.5% in the DCl-Br experiments. The HCl impurity is less than 10% and does not affect the DCl-Cl or DCl-Br data. Argon is completely negligible. For HBr-Br the effect of the HBr-HBr rate was 2% or less and Ar negligible.[13] The deactivation of DCl(v = 1) by Br_2 was barely observable in these experiments and a rate constant was estimated to be $(4 \pm 4) \times 10^2$ $torr^{-1}$ sec^{-1}. The deactivation of DCl(v = 1) by Cl_2 and HBr(v = 1) by Br_2 could not be determined. This fits well with expectations based on the deactivation of HCl by Cl_2 at a rate of 180 sec^{-1} $torr^{-1}$.[14] The E $\leftrightarrow$ V transfer

$$AB(v = 1) + Br(^2P_{3/2}) \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} AB(v = 0) + Br(^2P_{1/2}) \qquad (4)$$

has been considered in detail for the relaxation of HCl(v = 1) by Br atoms.[3] The V $\rightarrow$ E rate constant, k_5, for HBr is 30 times less than for HCl[15] and for DCl, it is at least 500 times less than for HCl.[16] Thus V $\leftrightarrow$ E transfer may be completely neglected here.

The rate constant k_1 has been measured by Brown et al.[17] to be 7.6×10^{-12} cm^3 $molec^{-1}$ sec^{-1} at 297°K in good agreement with our measurement. Rates for the relaxation of HCl and DCl by Br atoms have just been reported by Brown et al.[18] Their rate constants $k_2^H = 5.6 \times 10^{-13}$ and $k_2^D = 9.4 \times 10^{-13}$ cm^3 $molec^{-1}$ sec^{-1} are much larger than the $k_2^H = 2.8 \times 10^{-13}$

(Ref. 3) and $k_2^{D'} = 2.3 \times 10^{-13}$ cm^3 molec^{-1} sec^{-1} which we find in our laboratory. Karny and Katz[19] have reproduced both the results of Ref. 3 and 18; it is clear that the systematic difference is due to the different chemistry of the two methods of producing and measuring the concentration of Br atoms. Brown et al.[18] produced their Br atoms by reaction of Br_2 with a measured flow of O atoms. It is possible that the OBr present in the O + Br_2 titration is responsible for the increased relaxation rate. Residual O atoms could be partially responsible. Systematic errors in titration procedure must also be considered. The much simpler, direct dissociation of Br_2 and titration by NOCl should give the most reliable determination. Donovan et al.[20] give a value for k_3 of $(1.6 \pm 0.7) \times 10^{-12}$ cm^3 molec^{-1} sec^{-1} at 300°K in agreement with the value found in the present work. There had been some question since many of their results on HBr(v = 1) have proven to be incorrect.[13,21]

DISCUSSION

The ratios k^D/k^H in Table IV show that the deuteride is relaxed less rapidly or at about the same rate as the hydride. If the non-adiabatic electronic curve crossing mechanism proposed by Nikitin and Umanski[22] were largely responsible for the relaxation, then it would be expected that DCl(v = 1) should be relaxed more rapidly than HCl(v = 1). Such behavior has been observed in the vibrational relaxation of HF(v = 1) and DF(v = 1) by Cl, F and O atoms and taken to be evidence for the applicability of the non-adiabatic mechanism to these systems.[23] This argues against the importance of the non-adiabatic mechanism for HCl(v = 1) deactivated by Br and Cl. The results of adiabatic classical dynamical calculations by Smith[24] on LEPS surfaces are in accord with experimental results on Cl + HCl(v = 1) and Cl + DCl(v = 1) for some ClHCl surface parameters. Since the transfer is largely V → R,[24] the results will depend sensitively on the angular dependence of the potential. The ClHCl LEPS surface is probably far too repulsive for configurations, Cl-Cl-H, with a central halogen atom.[25] Proper treatment of these configurations could have a substantial effect on the energy transfer calculations.

REFERENCES

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1. R.G. Macdonald and C.B. Moore, in preparation.
2. R.G. Macdonald, C.B. Moore, I.W.M. Smith and F.J. Wodarczyk, J. Chem. Phys. **62**, 2934 (1975).
3. S.R. Leone, R.G. Macdonald and C.B. Moore, J. Chem. Phys. **63**, 4735 (1975).
4. M.A.A. Clyne and D.H. Stedman, Trans. Faraday Soc. **64**, 1816 (1968).
5. M.A.A. Clyne, J.A. Coxon and A.R. Woon Fat, Discuss. Faraday Div. **53**, 82 (1972).
6. J.K.K.Ip and G. Burns, J. Chem. Phys. **51**, 3414 (1969).
7. H.W. Chang and G. Burns, J. Chem. Phys. **64**, 349 (1976).
8. V. Bondybey, G.C. Pimentel and P.N. Noble, J. Chem. Phys. **55**, 540 (1971).
9. B.S. Ault and L. Andrews, J. Chem. Phys. **64**, 1986 (1976).
10. P.F. Zittel and C.B. Moore, J. Chem. Phys. **58**, 2922 (1973).
11. H.L. Chen and C.B. Moore, J. Chem. Phys. **54**, 4072 (1971).
12. R.V. Steele, Jr. and C.B. Moore, J. Chem. Phys. **60**, 2794 (1974).
13. H.L. Chen, J. Chem. Phys. **55**, 5551 (1971).
14. N.C. Craig and C.B. Moore, J. Phys. Chem. **75**, 1622 (1971).

15. S.R. Leone and F.J. Wodarczyk, J. Chem. Phys. 60, 314 (1974).

16. S.R. Leone, Ph.D. thesis, University of California, Berkeley, Ca [1974].

17. R.D.H. Brown, G.P. Glass and I.W.M. Smith, J. Chem. Soc. Faraday Trans. II, 71, 1963 (1975).

18. R.D.H. Brown, I.W.M. Smith and W.J. van der Merwe, Chemical Physics 15, 143 (1976).

19. Z. Karny and B. Katz, Chem. Phys. Lett. 38, 382 (1976).

20. R.J. Donovan, D. Husain and C.D. Stevenson, Trans. Faraday Soc. 66, 2148 (1970).

21. B.M. Hopkins and H.L. Chen, J. Chem. Phys. 59, 1495 (1973).

22. E.E. Nikitin and S.Ya. Umanski, Discuss. Faraday Soc. 53, 7 (1972).

23. G.P. Quigley and G.J. Wolga, J. Chem. Phys. 63, 5263 (1975).

24. I.W.M. Smith, J. Chem. Soc. Faraday Trans. II, 71, 1970 (1975).

25. J.D. McDonald, P.R. LeBreton, Y.T. Lee, and D.R. Herschbach, J. Chem. Phys. 56, 769 (1972).

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TABLE I: Summary of average pressures and rate constants for sets of experiments at 294°K on the deactivation of DCl(v = 1) by Cl atoms.

P_{Ar}	P_{Cl_2}	P_{DCl}	P_{Cl}	$k_1 \times 10^{-5}$
pressures (torr)				($torr^{-1}\ sec^{-1}$)
3.70	0.068	0.025	0.024	1.69 ± .04
2.76	0.057	0.022	0.039	1.57 ± .10
1.83	0.089	0.031	0.017	2.01 ± .14

TABLE II: Summary of average pressures and rate constants for sets of experiments at 294°K on the deactivation of DCl(v = 1) by Br atoms.

P_{Ar}	P_{Br_2}	P_{DCl}	P_{Br}	$k_2 \times 10^{-3}$
pressures (torr)				($torr^{-1}$ sec^{-1})
3.27	0.13	0.021	0.043	9.0 ± 1.0
2.82	0.12	0.023	0.052	7.1 ± .05
2.16	0.088	0.023	0.042	7.0 ± .5

TABLE III: Summary of average pressures, HBr pressure range and rate constants for sets of experiments at 294°K on deactivation rate constant for HBr(v = 1) by Br atoms.

P_{Ar}	P_{Br_2}	P_{HBr}	P_{Br}	$k_3 \times 10^{-4}$
pressures (torr)				($torr^{-1}$ sec^{-1})
3.32	0.060	0.040 - 0.097	0.023	8.1 ± 1.0
3.32	0.15	0.010 - 0.038	0.072	8.0 ± 0.8
2.84	0.16	0.012 - 0.038	0.046	11. ± 1.0
2.61	0.10	0.024 - 0.094	0.038	7.6 ± 0.1
2.47	0.17	0.012 - 0.12	0.061	7.8 ± 0.9

TABLE IV: Deactivation rates for $v = 1 \rightarrow 0$ at 294°K.

	k^a		$\frac{k^D}{k^H}$ [b]
	$(sec^{-1}\ torr^{-1})$	$(cm^3\ molec^{-1}\ sec^{-1})$	
DCl+Cl	$(18\pm2.3)x10^4$	$(5.5\pm0.7)x10^{-12}$	0.62±0.13
DCl+Br	$(7.7\pm1.1)x10^3$	$(2.3\pm0.3)x10^{-13}$	0.86±0.31
HBr+Br	$(8.4\pm1.6)x10^4$	$(2.6\pm0.5)x10^{-12}$	----

a. Uncertainties are upper limits on random errors judged from total spread of data in Tables I - III. Possible systematic errors are limited to 10% in absolute concentration of the atoms and 10% in other calibrations. Total error margins are ± 30% for DCl and ± 40% for HBr.

b. k^H values from this lab, Refs. 2 and 3, are used since systematic errors between HCl and DCl are thus eliminated.

Printer: Please set Table IV so that it may be seen while reading the Discussion.

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