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TEMPERATURE DEPENDENCE OF THE TOTAL REACTION RATES FOR Cl + HI
and Cl + HBr

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Thermal reaction rate constants have been determined for the reactions $\text{Cl} + \text{HI}$ and $\text{Cl} + \text{HBr}$ in the temperature range 220 - 400°K. The rates vary slowly with temperature. For $\text{Cl} + \text{HI}$ the effective reaction cross section reaches a maximum of $31 \text{ \AA}^2$ near 300°K. A tentative reaction model is proposed in which the attacking halogen atom is attracted to the halogen end of the hydrogen halide and then rotation of the hydrogen, with little or no activation energy, completes the reaction.

I. INTRODUCTION

The exothermic reactions of halogen atoms with hydrogen halides have long been a favorite class of reactions for chemical kineticists.¹⁻³ Hydrogen atom transfer between two heavy atoms appears sufficiently simple to encourage attempts at a complete understanding of the dynamics of this class of reactions. Detailed studies of energy distributions among product molecules⁴⁻⁶ have been made and quantitatively interpreted in terms of dynamics on an LEPS potential surface.⁷ These distributions have been the subject of many surprisal analyses^{8, 9} and the substance of many excellent chemical lasers.¹⁰ Product angular distributions have been observed in molecular beams.^{11, 12} The reciprocity between product energy distributions for an exothermic reaction and reagent energy utilization in the reverse endothermic reaction has been demonstrated experimentally.^{13, 14} Laser-excited fluorescence measurements of reaction rates or cross sections¹⁵ have clouded this simple picture of the Cl + HI collision dynamics. The trajectories on the LEPS surface⁷ which so successfully explained the product energy distributions failed to predict the behavior of the reagents. For Cl + HI the magnitude of the rate constants, the deuterium isotope effect and the cross section change for hot atoms were altogether different from those predicted. The LEPS potential shape correctly describes the release of energy as the hydrogen atom moves toward its new partner but fails to describe the approach of the reactants. The shape of the potential in the entrance

valley and the dynamics of the reagents in this valley must be studied by measurements of reaction rates and cross sections as a function of reagent translational, rotational and vibrational energy.

Measurements of rate constants as a function of temperature are reported here for reactions (1) and (2).

A qualitative model based on these and earlier data is proposed for the dynamics of these reactions.

II. EXPERIMENTAL AND RESULTS

The laser-initiated chemical reaction method used to measure the total reaction rate for $\text{Cl} + \text{HX}$ ($\text{X} = \text{I}, \text{Br}$) at room temperature has been thoroughly described.¹⁵ A simple modification of the apparatus was required to extend these measurements to a broader temperature range. Figure 1 shows the fluorescence cell used in these experiments. The 3-chambered quartz cell was situated in a dewar which could be filled with coolant (e.g. a dry ice and acetone mixture) or heated oil to control the temperature. The two evacuated cylindrical outer chambers of the cell provided thermal isolation and optical access to the sample chamber. A calibrated thermistor was sealed into the gas flow through a pyrex sleeve. Cold bath temperatures were stable and uniform to better than $\pm 1^\circ\text{K}$ throughout the dewar. Dow Corning 550 silicone oil

was used as a heat transfer fluid above 300°K. An external, constant temperature circulator (Haake, model FT) was used to circulate the hot oil and keep the temperature stable to $\pm 2^\circ\text{K}$.

Gases were passed through coils immersed in the dewar. The HX was then injected through six holes (the first set of three is shown in Fig. 1) directed against the $\text{Ar} + \text{Cl}_2$ flow. This ensured good mixing. The Ar partial pressure was 30 - 100 times that of the reagents.

A Molelectron N_2 -laser (6 mJ/pulse, 25 pulses/sec, $\lambda = 337 \text{ nm}$) was used to dissociate Cl_2 into two ground state Cl atoms which were then rapidly thermalized by collisions with Ar. Fluorescence following the reaction $\text{Cl} + \text{HX} \rightarrow \text{HCl}^\dagger + \text{X}$ was collected with a 2" focal length CaF_2 lens and focused onto a liquid He cooled Ge:Hg detector. A liquid N_2 cooled, broadband filter with transmission range 3.2 - 4.2 μ was situated in front of the detector. This arrangement gave $\text{S/N} > 30$ for 1000 shot averages in experiments at temperatures above 220°K. Condensation of I_2 and Br_2 on the cell windows prevented work at lower temperatures.

Prereaction¹⁵ between Cl_2 and HX molecules was minimized by maintaining the reagent partial pressures below 0.15 torr for Cl_2 and HI and below 0.46 torr for Cl_2 and HBr. A relatively high pumping speed of 185 cm/sec was used. The relative flows $[\text{Ar}]:[\text{Cl}_2]:[\text{HX}]$ were varied in the range of 100:0.3:1 to 100:3:1. Hastings-Raydist electronic flowmeters were used for measuring individual flows and were calibrated each time for each gas before an experiment. The gases and their

purities were described previously.¹⁵

The experimental conditions and measured rates as a function of temperature are summarized in Tables I and II. In general, at least 2 independent sets of experiments were carried out for each temperature. Each set contained 5 - 10 runs corresponding to different combinations of $[Cl_2]$ and $[HX]$ pressures. The measured rates were independent of the $[Cl_2]/[HX]$ ratios. Hence, the influence of the prereaction was suppressed to a negligible level. The uncertainties in the table are the standard deviation of a single value from the mean of the complete sets of data. Since there are more than 12 values in each set, these cover random and systematic errors. Systematic errors due to the calibration of the flow meter and capacitance manometer should be less than 5%. The room temperature results agree well with the previously reported values¹⁵ of k_1 (295°K) = $(1.64 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and k_2 (295°K) = $(7.4 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ within the error limits. Graphs of $\log k$ and $\log \sigma$ vs T^{-1} are shown in Figs. 2 and 3. Since the systematic errors are nearly independent of temperature, the error bars show only the random errors.

III. DISCUSSION

The observed temperature dependence of the reaction rates is very different from the usual Arrhenius form. For reaction (1) the effective cross section increases with temperature,

passes through a maximum between 295 and 345°K and then decreases as the temperature is increased further, Fig. 2. For reaction (2), although no maximum is observed within the limited temperature range the rate is increasing much less rapidly at high temperature than at low temperature, Fig. 3. Approximate activation energies may be derived from the slope of $\log \sigma$ vs $1/T$; they are 0.5 kcal/mole for $\text{Cl} + \text{HI}$ and 0.8 kcal/mole for $\text{Cl} + \text{HBr}$. Thus any barriers along the reaction path must be less than a kilocalorie or so. Of course no quantitative barrier heights may easily be deduced from these data. In work with hot Cl atoms it was shown that a factor of 4 increase in translational velocity over room temperature actually decreased the cross section for $\text{Cl} + \text{HI}$ by a factor of 6.¹⁵ The simultaneous excitation of translation and rotation in the thermal rate constant experiments contrasts sharply with the excitation of translation alone in the hot atom case. Since the hot atom velocity is much larger than the 400°K velocity, conclusions must be cautiously considered.

From the available data it is now possible to draw some conclusions about the shape of the ClHI potential surface and to propose a qualitative model for some features of the surface and the associated reaction dynamics. Since the spin-orbit splittings of Cl and I are large, 881 and 7600 cm^{-1} respectively, only one potential surface is relevant here. At the highest temperature of this study the population of the excited $\text{Cl}(^2\text{P}_{1/2})$ is 2%. Searches for the production of $\text{I}(^2\text{P}_{1/2})$ have produced negative results.⁶

Parr et al.⁷ have performed three-dimensional classical trajectory calculations for $\text{Cl} + \text{HI}$ using an LEPS surface. They were able to match the observed product energy state distribution. However, the calculated cross section, $7 \text{ \AA}^2$, at 300°K is a factor of five less than the experimental cross section which was later measured. In fact, it was necessary to use an HCl stretching force constant for the LEPS surface less than that for the diatomic in order to avoid even smaller cross sections. The LEPS surface restricts reaction by Cl to a narrow cone of approach toward the H atom about the HI bond axis. Since the experimental reaction rate is about half the gas kinetic rate,¹⁶ it is clear that no serious geometric limitation is possible, and thus the LEPS shape is inadequate as a description of the entrance channel for this reaction at thermal energies.

Recently, Bass et al.¹⁷ have carried out quasiclassical trajectory calculations for reaction (1) on a semi-empirical potential energy surface with shallow wells for collinear ClHI . However, the surface is still largely restricted in direction for reactive collisions and neither of these shallow wells has any discernable effect on the dynamics.¹⁷ Kafri¹⁸ et al. used the Born approximation for an oversimplified potential surface which neglects the repulsion between the non-bonded Cl and I atoms and thus eliminates constraints on the direction of approach for reactive collisions. Since these calculations also fail to reproduce

the experimental rate constants, a significantly different potential surface is indicated.

The large thermal reaction rate, the decrease in rate with increasing temperature and the hot atom effect can be understood in terms of an attractive force between Cl atoms and HI. A substantial attraction would pull slow Cl atoms at moderately large impact parameters into reactive distances while fast Cl atoms would speed by. Both Van der Waals attraction and the chemical bonding characteristic of linear trihalogen and bihalide complexes^{19, 20} should produce a significant potential basin with the Cl atom near the I rather than the H of HI. Both types of attraction will be weaker for Cl + HBr. There should be no barrier in the translational approach coordinate to the configuration ClIH.

To complete the reaction the H atom must then rotate around to the Cl atom and react. The rotation must be fast compared to translational separation of the reagents and must have sufficient energy to overcome any barrier in that coordinate. Thus for hot Cl atoms the cross section is small on two counts: the attractive potential has much less effect on the trajectory and the translational velocity is much larger and does not allow time for the H atoms to rotate before the Cl departs. The reaction of hot atoms may in fact result from nearly head-on collinear encounters of Cl with the H of HI. For the thermal reaction, the ratio of the rotational velocity of the H in HI and the Cl-HI relative

velocity is independent of temperature. Because of the light mass of the rotating H atom compared to the reduced mass for translational motion the H moves about five times faster than the Cl relative to the HI. It is tempting to speculate that the increase in reaction rate at lower temperatures is the result of a barrier to reaction in the rotational coordinate. At room temperature the reaction $\text{Cl} + \text{HI}$ is 1.8 times faster than $\text{Cl} + \text{DI}$. Classical trajectory calculations show no isotope effect for a LEPS surface. The decrease in rotational velocity by $\sqrt{2}$ between HI and DI may account for the isotope effect. It is also possible that some tunneling through a barrier in the rotational coordinate is involved. Collinear tunneling of the H in ClHI for a surface with an early barrier cannot occur.

Thus a model for the $\text{Cl} + \text{HI}$ reaction in which the Cl atom is attracted to I and the H atom then rotates to react with Cl before it departs, provides a qualitative understanding of the thermal reaction rate data. A similar mechanism has been proposed as the main route for the formation of the same product from a different starting point, $\text{H} + \text{ICl} \rightarrow \text{HICl} \rightarrow \text{I} + \text{HCl}$, on the basis of a bimodal product energy distribution and trajectory studies.²¹ Several qualitative features of the entry valley for the $\text{Cl} + \text{HI}$ surface remain to be established. There is no quantitative information on either the shape of the potential surface or the collision dynamics for this reaction. Thus the model proposed is plausible but

by no means fully proven. More detailed experimental information on reaction cross section as a function of reagent translational and rotational energy in addition to both elastic and inelastic scattering cross sections from molecular beams will be very useful. Extensive theoretical work will be required to derive quantitative information about the shape of the potential surface.

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REFERENCES

1. R.D. Levine and R.B. Bernstein, Molecular Collision Dynamics (Oxford U.P., New York, 1974).
2. R.B. Bernstein and R.D. Levine, J. Chem. Phys. 57, 434 (1972).
3. R.D. Levine and R.B. Bernstein, Acc. Chem. Res. 7, 393 (1974).
4. K.G. Anlauf, J.C. Polanyi, W.H. Wong, and K.B. Woodall, J. Chem. Phys. 49, 5189 (1968).
5. L.T. Cowley, D.S. Horne, and J.C. Polanyi, Chem. Phys. Lett. 12, 144 (1971).
6. D.H. Maylotte, J.C. Polanyi, and K.B. Woodall, J. Chem. Phys. 57, 1547 (1972).
7. C.A. Parr, J.C. Polanyi, and W.H. Wong, J. Chem. Phys. 58, 5 (1973).
8. A. Ben-Shaul, R.D. Levine, and R.B. Bernstein, J. Chem. Phys. 57, 5427 (1972).
9. R.B. Bernstein and R.D. Levine, Adv. Atomic and Molecular Phys. 11, 215 (1975).
10. J.R. Airey, J. Chem. Phys. 52, 156 (1970).
11. J.D. McDonald and D.R. Herschbach (unpublished results quoted in Ref. 7).
12. J.R. Grover, C.R. Iden, and H.V. Lilienfeld, J. Chem. Phys. 64, 4657 (1976).
13. D.S. Perry, J.C. Polanyi, and C.W. Wilson, Jr., Chem. Phys. Lett. 24, 484 (1974).

14. A.M.G. Ding, L.J. Kirsch, D.S. Perry, J.C. Polanyi, and J.L. Schreiber, Faraday Disc. Chem. Soc. 55, 252 (1973).
15. K. Bergmann and C.B. Moore, J. Chem. Phys. 63, 643 (1975).
16. J.O. Hirshfelder, C.F. Curtiss, and R.B. Bird, Molecular Theory of Gases and Liquids, (Wiley, New York, 1954, p. 1111).
17. H.E. Bass, L.S. Kenton, and D.L. Thompson, Chem. Phys. Lett. 44, 452 (1976).
18. A. Kafri, Y. Shimoni, R.D. Levine, and S. Alexander, Chem. Phys. 13, 323 (1976).
19. Y.T. Lee, J.D. McDonald, P.R. LeBreton, and D.R. Herschbach, J. Chem. Phys. 49, 2447 (1968).
20. J.M. Farrar and Y.T. Lee, J. Am. Chem. Soc. 96, 7570 (1974).
21. M.A. Nazar, J.C. Polanyi and W.J. Skrlac, Chem. Phys. Lett. 29, 473 (1974) and J.C. Polanyi and W.J. Skrlac, Chem. Phys. (to be published).

Table I. Summary of the experimental conditions and results for Cl + HI from 221°K to 400°K.

T (°K)	P _{Ar}	P _{Cl₂} (torr)	P _{HI}	k ₁ x 10 ¹⁰ (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ₁ ^a (Å ²)
400	12.2 - 13.4	0.06 - 0.09	0.03 - 0.08	1.46 ± 0.08	25.2 ± 1.4
345	12.2 - 13.4	0.05 - 0.09	0.04 - 0.07	1.56 ± 0.08	29.0 ± 1.5
294.5	10.4 - 13.4	0.03 - 0.15	0.06 - 0.14	1.55 ± 0.08	31.2 ± 1.6
274.5	10.5 - 10.9	0.04 - 0.10	0.06 - 0.11	1.41 ± 0.06	29.5 ± 1.3
253	10.5 - 10.9	0.04 - 0.09	0.06 - 0.08	1.24 ± 0.05	27.0 ± 1.1
233	10.3 - 11.0	0.03 - 0.12	0.05 - 0.07	1.08 ± 0.05	24.5 ± 1.1
221	10.4 - 11.0	0.04 - 0.11	0.06 - 0.08	1.02 ± 0.04	23.4 ± 1.0

a) σ₁ ≡ k₁/v̄.

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Table II. Summary of the experimental conditions and results for Cl + HBr from
218°K to 402°K

T (°K)	P _{Ar}	P _{Cl₂} (torr)	P _{HBr}	k ₂ x 10 ¹² (cm ³ mole- cule ⁻¹ sec ⁻¹)	σ ^a (Å ²)
402	11.7 - 12.2	0.11 - 0.24	0.06 - 0.19	10.10 ± 0.77	1.68 ± 0.13
349	11.7 - 12.2	0.17 - 0.24	0.04 - 0.12	9.42 ± 0.58	1.66 ± 0.10
294.5	10.1 - 15.0	0.07 - 0.37	0.09 - 0.41	8.40 ± 0.50	1.63 ± 0.10
274.5	10.0 - 15.1	0.09 - 0.38	0.10 - 0.45	7.65 ± 0.52	1.54 ± 0.10
243	9.9 - 15.2	0.10 - 0.35	0.10 - 0.46	6.20 ± 0.43	1.31 ± 0.09
230	9.8 - 15.2	0.25 - 0.35	0.28 - 0.36	5.24 ± 0.35	1.15 ± 0.08
218	15.4 - 15.5	0.18 - 0.25	0.20 - 0.41	4.99 ± 0.40	1.12 ± 0.09

a) $\sigma_2 \equiv k_2/\bar{v}$.

Figure 1. Fluorescence cell for temperature dependence measurements.

Figure 2. Semi-log plot of rate constant k_1 and effective cross section σ_1 , for the reaction $\text{Cl} + \text{HI}$ vs $10^3/T$. -O-, experimental rate constant. -Δ-, cross section. The error bars show standard deviations.

Figure 3. Semi-log plot of rate constant k_2 and effective cross section σ_2 , for the reaction $\text{Cl} + \text{HBr}$ vs $10^3/T$. -O-, experimental rate constant. -Δ-, cross section. The error bars show standard deviations.

Fig. 1

Fig. 2

Fig. 3

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