Title

REACTIVE SCATTERING IN MOLECULAR BEAMS: EVIDENCE FOR A STRIPPING MECHANISM IN REACTIONS OF ALKALI ATOMS WITH HALOGENS

Authors

Wilson, K.R.
Kwei, G.H.
Norris, J.A.
et al.

Publication Date

1964-06-01

UCRL-11791

University of California

Ernest O. Lawrence Radiation Laboratory

REACTIVE SCATTERING IN MOLECULAR BEAMS: EVIDENCE FOR A STRIPPING MECHANISM IN REACTIONS OF ALKALI ATOMS WITH HALOGENS

Berkeley, California

DISCLAIMER

1964-440

UCRL-11791

Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 41, No. 4, 1154–1156, 15 August 1964
Printed in U. S. A.

Reactive Scattering in Molecular Beams: Evidence for a Stripping Mechanism in Reactions of Alkali Atoms with Halogens*

K. R. WILSON,† G. H. KWEI,† AND J. A. NORRIS‡

Department of Chemistry and Lawrence Radiation Laboratory
University of California, Berkeley, California

AND

R. R. HERM, J. H. BIRELY, AND D. R. HERSCHBACH

Department of Chemistry, Harvard University
Cambridge, Massachusetts

(Received 11 June 1964)

CROSSED-beam studies have been made of the reactions of K, Rb, and Cs atoms with Br_2, I_2, ICl, and IBr. It is found that, for all these systems: (1) the reaction cross sections are remarkably large, $\gtrsim 100$ Å^2; (2) much of the alkali halide product recoils forward with respect to the incident alkali-atom beam; and (3) most of the chemical energy released appears as vibrational excitation of the alkali halide. Properties (1) and, especially, (2) suggest a "stripping mechanism" of the type familiar in nuclear physics,[1] in contrast to the "rebound mechanism" which was found in a previous study of the reactions of alkali atoms with alkyl iodides.[2,3]

The apparatus is essentially the same as before,[3] including the two-filament surface-ionization detector[4] (a Pt–8% W alloy wire to measure the M-atom background, a W or Re[5] wire to measure the sum of M and MX product). In initial studies of the halogen reactions, the Pt–W filament often showed anomalous behavior indicative of "poisoning," and filament conditions apparently identical to those used in previous calibrations[4,5] gave erratic results. This difficulty was eliminated by means of a procedure due to Touw and Trischka.[6] They demonstrated that two distinct surface conditions of the Pt–W wire could be produced: Mode D, obtained by heating the wire in oxygen, detects both M and MX with high efficiency; Mode N, obtained by heating the wire in methane, is essentially nondetecting for MX. These two modes were found to remain immune to halogens for long periods of time.

For all the halogen systems, the angular distributions measured on W, Re, or Pt–W in Mode D are practically identical, and display a relatively gradual falloff at wide angles, whereas the distribution measured on Pt–W in Mode N falls very rapidly, as illustrated in Fig. 1(a). Examples of MX distributions derived by subtracting the relative intensity read on Mode N Pt–W from that read on W are shown in Fig. 1(b). Outside the region $\theta \lesssim \pm 20°$ the subtraction is a small correction, but it introduces considerable uncertainty at small angles (points within $\theta \lesssim \pm 5°$ had to be discarded). The precise location of the MX peaks thus remains uncertain by $\sim 10°$, but their general form is well determined and is verified by a magnetic deflection experiment.[7]

The nominal reaction yield (integrated intensity of MX divided by total M scattered from parent beam) is $\sim 10\%$ for all the halogen systems; in addition, there is a contribution from out-of-plane scattering which misses the detector. The reaction cross sections are thus $\gtrsim 10\%$ of the total beam scattering cross section (compared with only 0.5% for the $K+CH_3I$ case[2]), or roughly $\gtrsim 100$ Å^2. A kinematic analysis[3] of the MX distributions, illustrated by the vector diagrams in

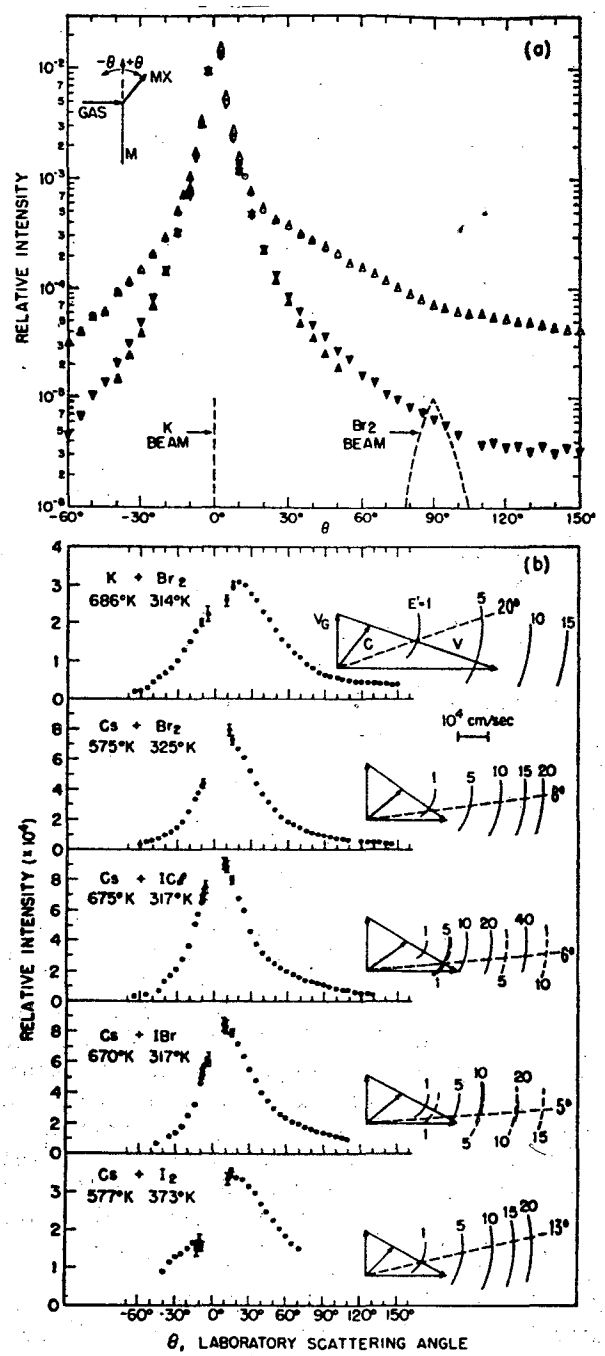

FIG. 1. Sample data and analysis: (a) Scattering of K+Br_2 measured on various filaments (all 0.076 min diameter). The parent K beam (2×10^{-8} A, 0.5° wide at half intensity) is attenuated about 12% by the crossed Br_2 beam (about 12° wide, as measured by electron bombardment ionization). The ordinate scale gives the ratio of the actual signal to the attenuation of the parent K beam measured on the same filament. ⊙, W (0.60 A); △ Pt–W (0.30 A, Mode D); ▲, Pt–W (0.30 A, Mode N); ▼, Pt–W (0.20 A, Mode N). (b) Angular distributions of alkali halide products and kinematic diagrams showing most probably velocities of reactants, center of mass vector **c**, and relative velocity vector **v**; circles indicate the length of recoil velocity vectors for MX produced with various amounts of final relative translational kinetic energy E′ (kcal/mole); for the IX reactions, dashed circles refer to MX, solid circles to MI.

Fig. 1(b), shows that for the X_2 reactions (which are 40–50 kcal/mole exothermic), most of the MX+X is produced with relative translational energy $E' \lesssim 5$ kcal/mole; at the peak of the MX distribution, the nominal $E' \approx 1$ kcal/mole. For the IX reactions, again the nominal $E' \approx 1$ kcal/mole if MX+I are the principal products (exothermic by ~50 kcal/mole), whereas the nominal $E' \approx 5$ kcal/mole if MI+X are the products (exothermic by 26–40 kcal/mole).[8] Since only a few kcal/mole can appear in rotation,[3] most of the exothermicity in all of these reactions must appear as vibrational excitation.

The large rates of sodium-atom–halogen reactions have been attributed to a nonadiabatic "electron-jump" model.[9] This is effect makes these ionic reactions, $M^+ + X^- - X$, and would provide the strong attractive forces required to give the forward peaking of MX characteristic of a "stripping" mechanism. However, since nonadiabatic contributions are expected to vary considerably for the various reactions, especially M+IX, the present results suggest that the stripping behavior is a more general, adiabatic mechanism. Although the available computer studies[10,11] of reaction dynamics apply to the "rebound" mechanism, it appears that stripping could predominate if attractive forces are strong and orientational effects favor reaction in collisions with large impact parameters. Other reactions in which stripping appears likely, including M with CCl_4 and CH_2I_2, are under study.[12]

* This work was supported at Berkeley by the U. S. Atomic Energy Commission and the Alfred P. Sloan Foundation and at Harvard by the National Science Foundation.

† Present address: Department of Chemistry, Harvard University.

‡ Present address: Massachusetts Institute of Technology, Cambridge, Massachusetts.

[1] S. T. Butler, *Nuclear Stripping Reactions* (John Wiley & Sons, Inc., New York, 1957); N. K. Glendenning, Ann. Rev. Nucl. Sci. **13**, 191 (1963).

[2] D. R. Herschbach, G. H. Kwei, and J. A. Norris, J. Chem. Phys. **34**, 1842 (1961).

[3] D. R. Herschbach, Discussions Faraday Soc. **33**, 149, 281 (1962).

[4] E. H. Taylor and S. Datz, J. Chem. Phys. **23**, 1711 (1955); **25**, 389, 395 (1956).

[5] R. J. Ivanetich and K. R. Wilson, UCRL Rept. 10706 (University of California Radiation Laboratory, Berkeley, February 1962).

[6] T. R. Touw and J. W. Trischka, J. Appl. Phys. **34**, 3635 (1963).

[7] R. R. Herm, R. Gordon, and D. R. Herschbach, J. Chem. Phys. (to be published).

[8] MI+X appears more likely, since the scattering kinematics suggests that for MX+I the angular distribution would be considerably broader than observed.

[9] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 301–310.

[10] N. C. Blais and D. L. Bunker, J. Chem. Phys. **37**, 2713 (1962); **39**, 315 (1963).

[11] M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. **40**, 2033 (1964); M. Karplus and L. M. Raff, *ibid.* **41**, (to be published).

[12] S. Datz and R. E. Minturn (private communication, Oak Ridge National Laboratory) have recently obtained similar results for K and Cs+Br_2.