Title
A FOUR-CENTER, CONCERTED, BIMOLECULAR REACTION: ICl*(A3n) + H2 HC1 + HI

Author
Harris, Stephen J.

Publication Date
1977-04-01

Submitted to Journal of the American Chemical Society

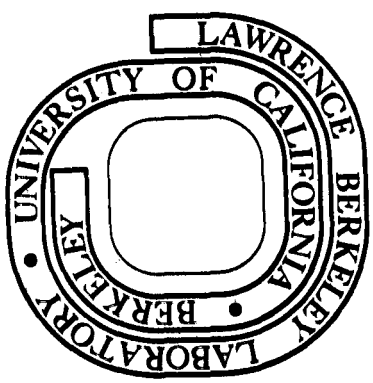
LBL-6223
Preprint

A FOUR-CENTER, CONCERTED, BIMOLECULAR REACTION: $IC1^*(A^3\Pi_1) + H_2 \rightarrow HC1 + HI$

Stephen J. Harris

April 15, 1977

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48



DISCLAIMER

A Four-Center, Concerted, Bimolecular Reaction: LBL #6223

$ICl^*(A^3\Pi_1) + H_2 \rightarrow HCl + HI$

ABSTRACT

The rate of the laser-induced reaction $ICl^*(A^3\Pi_1) + H_2 \rightarrow HI + HCl$ has been measured as a function of ICl^* vibrational energy. The rate constant for $ICl^*(v' = 15)$, 1200 cm^{-1} or 6 kT below the dissociation limit, is $k_1 = (9.0 \pm .8) \times 10^{-14}$ cm^3 $molecule^{-1}$ sec^{-1}, corresponding to an activation energy of less than 5.5 kcal/mole. It is demonstrated conclusively that radicals (e.g. Cl atoms) are not important in these reactions. It is suggested that the reactivity of ICl^* is due to the change in sign of the dipole moment in the A state, to I^-Cl^+.

Communication submitted to the Journal of the American Chemical Society by Stephen J. Harris

A Four-Center, Concerted, Bimolecular Reaction:
$ICl^*(A^3\Pi_1) + H_2 \rightarrow HCl + HI$

Sir:

The rate of the laser-induced chemical reaction

$$ICl^*(A^3\Pi_1) + H_2 \rightarrow HI + HCl \qquad (1)$$

has been measured as a function of ICl^* vibrational energy. Like the $I_2 + H_2$ and $Cl_2 + H_2$ systems, there is no dark reaction. The reaction appears similar to $I_2^*(I^1\Sigma_u^+) + H_2$.[1-3] Other examples are reported which involve electronic excitation of I_2.[4]

ICl (~ 5 or 9 torr), prepared from I_2 and Cl_2,[5, 6] and H_2 (10 - 600 torr) are photolyzed for about 90 minutes in a 1 m quartz reaction cell by a Chromatix CMX-4 flashlamp-pumped dye laser ($\Delta\nu \approx 0.3$ cm^{-1}). A calibrated thermopile monitors the laser power. Approximately 60% absorption of the laser light is measured at $I^{35}Cl$ A-X bandheads. (Excitation of bandheads avoids hot bands.)

After photolysis, HCl is distilled from the reactants. Care is taken to eliminate the Cl_2 which is necessarily present.[5] HCl pressure is measured with a Validyne capacitance manometer. Mass spectra confirm that the product is HCl. HI and ICl react to form HCl and I_2; thus, two molecules of HCl are formed in each reaction.

ICl^* is removed by reaction (1) and by quenching:

$$ICl^* + ICl \rightarrow ICl + ICl \qquad (2)$$

$$ICl^* + H_2 \rightarrow ICl + H_2 \qquad (3)$$

The quantum yield for reaction is

$$\Phi = \frac{(HCl \text{ produced})/2}{\text{photons absorbed}} = \frac{k_1 [H_2]}{k_2[ICl]+(k_1+k_3)[H_2]}. \quad (4)$$

A Stern-Volmer plot of ICl^* fluorescence lifetime vs H_2 pressure gives $(k_1 + k_3) = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}; similarly, Steinfeld[7] has measured $k_2 = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}; both are nearly independent of wavelength. k_1 is determined from the quantum yield, Fig. 1. The solid curve is a least-square fit to the data using Eq. (4). Note that a two-parameter curve is fit with a single free parameter. The result, $k_1 = (9.0 \pm .8) \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1} (90% confidence limits), corresponds to 9000 gas kinetic collisions. Assuming that the pre-exponential factor does not exceed the gas kinetic collision frequency, the activation energy is less than 5.5 kcal/mole. The reaction rate is quite large; the quantum yield is low because the quenching rate is even larger.

A single vibrational level if ICl^* is excited initially, but vibrationally inelastic collisions spread the population distribution so that reaction may occur from other levels. The extent of this spread, which is limited by quenching, can be estimated by comparison with the analogous H_2-$I_2^*(B^3\Pi_0, v'=15)$ system.[8] Here, V-T events occur with a cross section of about 1/6 gas kinetic. This is expected to be an upper limit to the V-T rate in ICl^*-H_2, since the energy level spacing in ICl^* is greater than that in I_2^*. The result is that about 75% of the ICl^* which reacts does so from within 3 vibrational levels of

the originally excited level. Figure 2 shows the quantum yield (proportional to k_1) as a function of the excitation energy. About 600 cm^{-1}(3 kT) of vibrational energy increases the rate constant by a factor of e.[9]

Halogen atoms, formed from sufficiently energetic collisions of ICl^*, could conceivably be contributing to the measured quantum yields. The dissociation probability, however, should decrease by about 1/e for each 200 cm^{-1} (kT) of vibrational energy,[10] dashed line in Fig. 2. I atoms formed simply recombine, and Cl atoms are mostly scavenged by the fast reaction $Cl + ICl \rightarrow Cl_2 + I$:[11] when ICl is excited 1400 cm^{-1} above dissociation there is a low quantum yield of HCl (Fig. 2), implying that for excitation well below dissociation, radical reactions are not important. Finally, a quenching gas may be added to the system. Experiments with $ICl:H_2:Ar$ of 1:25:110, 1:19:95, 1:14:69, and 1:9:41 at λ = 616.8 nm (v' = 15) give quantum yields in very good agreement with those predicted from the measured quenching rate constant for ICl^* by Ar, $(4.9 \pm .5) \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1} (dashed line in Fig. 1). These results prove conclusively that radicals are not important, since Ar should not inhibit their reactions, and that $ICl^*(A^3\Pi_1)$ is the reactive species.

The reactivity of ICl^* may be due to the fact that the dipole moment changes sign upon excitation[12] to I^-Cl^+. The positive Cl atom, with its partially filled valence shell, might be expected to be very reactive. Experiments are in progress to learn more about the reactivity of this molecule.

The success of these experiments is due in large part to the help and suggestions given by Professor C.B. Moore. Discussions with Dr. N.S. Nogar are gratefully acknowledged. This work was supported by the U.S. Energy Research and Development Administration.

Stephen J. Harris*
Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, and
Department of Chemistry
University of California
Berkeley, CA 94720

(Received)

REFERENCES

*Fellow of the Miller Institute for Basic Research in Science

1. G.M. Harris, J.E. Willard, J. Am. Chem. Soc. 76, 4678 (1954).
2. T.A. Grover, J.E. Willard, J. Am. Chem. Soc. 82, 3816 (1960).
3. L.C. Glasgow, J.E. Willard, J. Phys. Chem. 77, 1585 (1973).
4. a) V.I. Balykin, V.S. Letokhov, V.I. Mishin, V.A. Semchishen, Chém. Phys. 17, 111 (1976).
   b) F. Engelke, J.C. Whitehead, R.N. Zare, Faraday Discussions on Potential Energy Surfaces, Vol. 62, (1976). (in press)
5. G.V. Calder, W.F. Giauque, J. Phys. Chem. 69, 2443 (1965).
6. R.E. Buckles, J.M. Bader, Inorganic Synthesis 9, 130 (1967) and references therein.
7. G.W. Holleman, J.I. Steinfeld, Chem. Phys. Letters 12, 431 (1971).
8. R. Brown, W. Klemperer, J. Chem. Phys. 41, 3072 (1964).
9. M.H. Mok, J.C. Polanyi, J. Chem. Phys. 53, 4588 (1970).
10. A. Gelb, R. Kapral, G. Burns, J. Chem. Phys. 59, 2980 (1973).
11. M.A.A. Clyne, H.W. Cruse, J. Chem. Soc. Far. Trans. 2, 68, 1377 (1972).
12. F.E. Cummings, W. Klemperer, J. Chem. Phys. 60, 2035 (1974).

Figure 1. Solid points are data without Ar, P_{ICl} = 8.9 torr; the solid line is a fit to these points. The dashed line is the predicted yield with P_{Ar}/P_{H_2} = 4.75; open circles are corresponding data. Here, P_{ICl} = 4.9 torr except for lowest pressure point, where P_{ICl} = 8.9 torr. λ = 616.8 nm, exciting 1200 cm^{-1} below dissociation.

Figure 2. Quantum yield vs excitation energy. P_{ICl} = 8.9 torr.

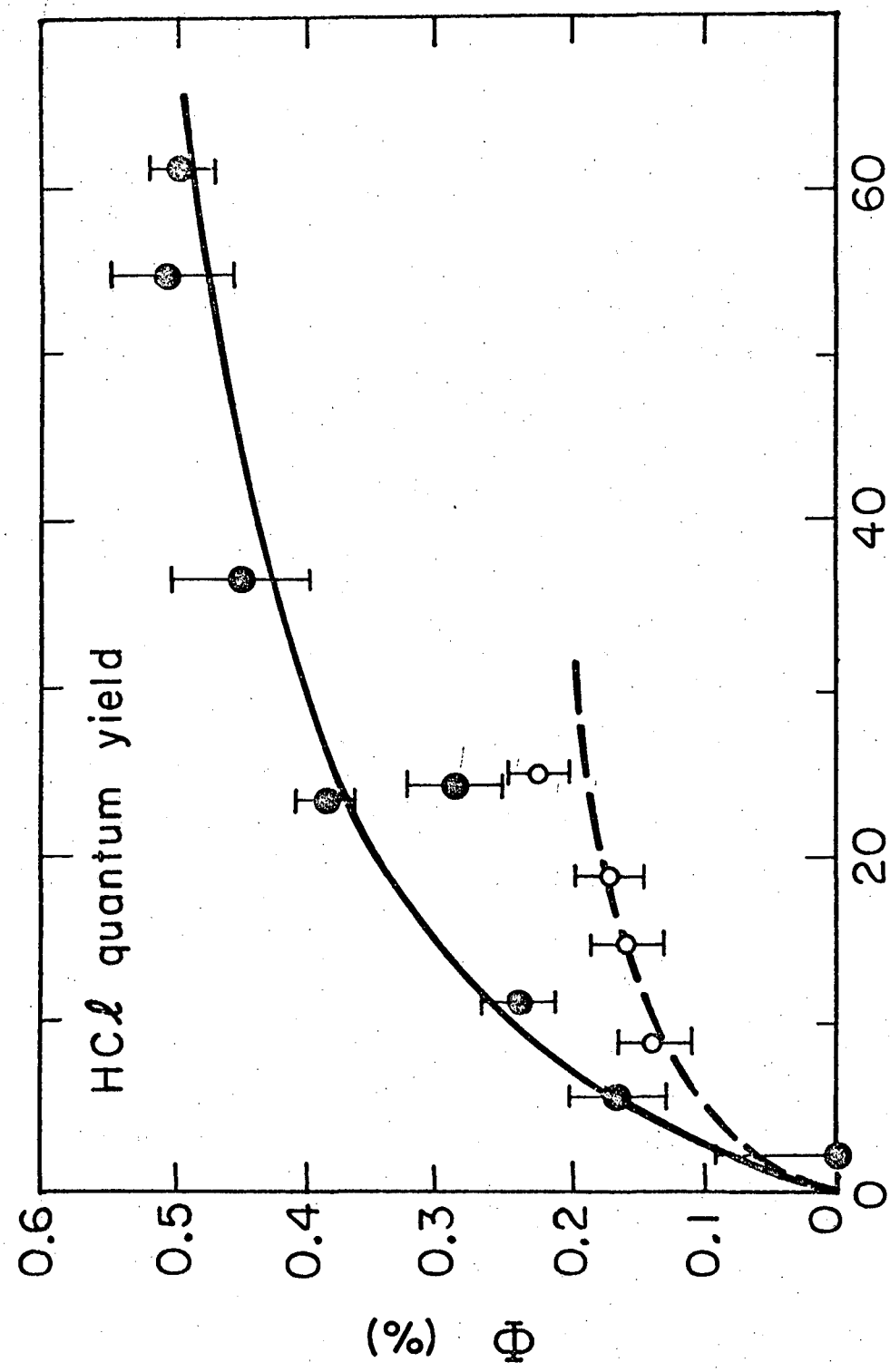

HCl quantum yield
Φ (%)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
P_{H_2}/P_{ICl}
XBL774-723

Fig. 1

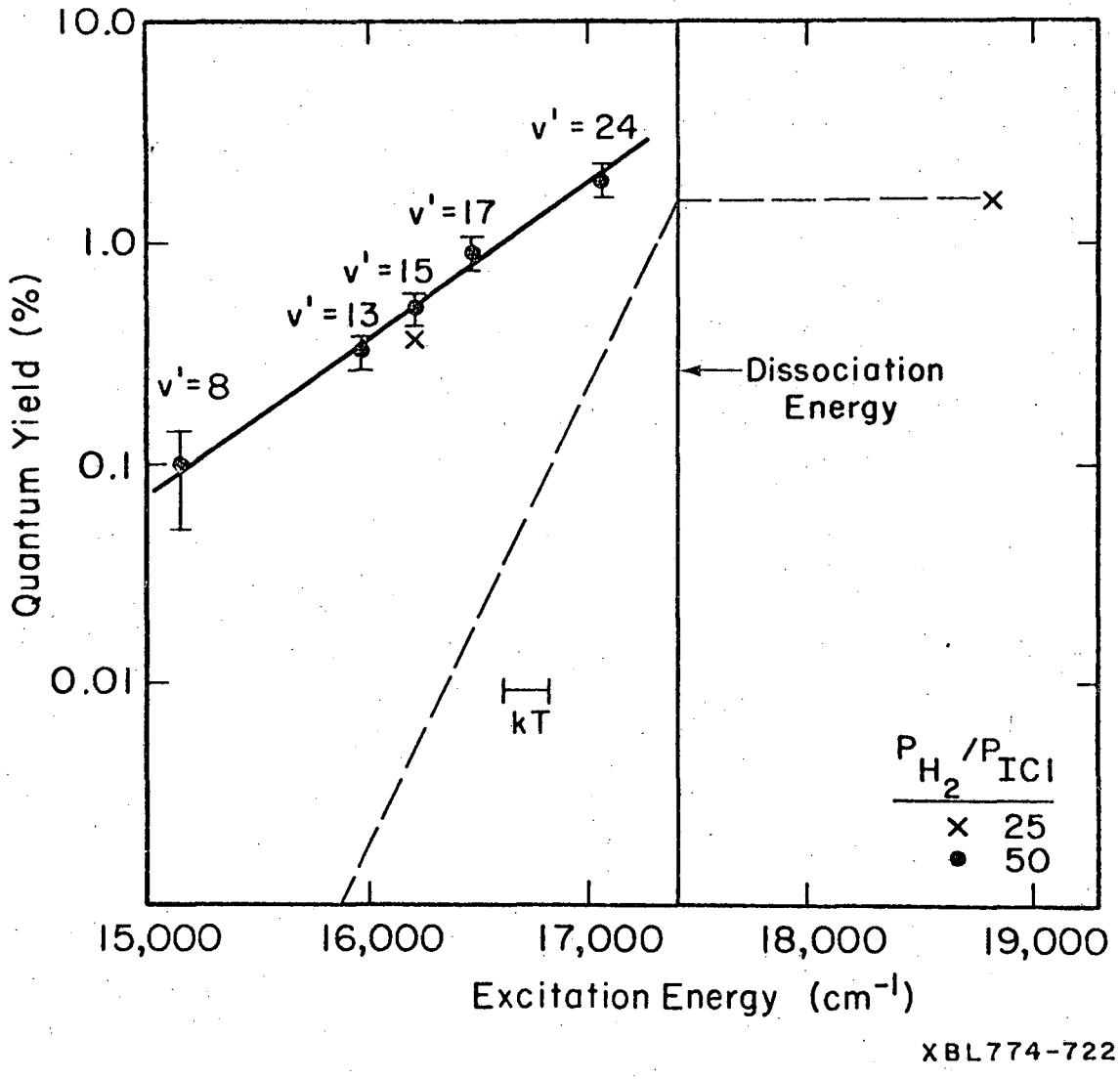

10.0
1.0
0.1
0.01
Quantum Yield (%)
v' = 24
v' = 17
v' = 15
v' = 13
v' = 8
Dissociation Energy
kT
P_{H_2}/P_{ICl}
× 25
● 50
15,000
16,000
17,000
18,000
19,000
Excitation Energy (cm^{-1})
XBL774-722

Fig. 2

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720