Heteronuclear Recombination of Chlorine and Iodine Atoms

Publication costs assisted by the U.S. Department of Energy

Sir: Although review articles have been written[1] summarizing work over a period of 40 years on three-body atomic recombinations which result in the formation of homopolar halogen molecules, only one study of such reactions yielding an interhalogen diatomic (ICl) has appeared[2] in press. A very surprising result of this work,[2] which is based on an experimental study of the flash photolysis of ICl, is that relatively inert third bodies, such as N_2 and CO_2, are reported to catalyze ICl formation much faster than the homonuclear recombination that produces I_2 or Cl_2. The result was rationalized[2] in terms of the radical–molecule complex (RMC) mechanism[3] which predicts[2] a bond energy of 3.85 kcal/mol for Cl–CO_2 and a similarly strong interaction in I–N_2 radical molecules.

On the other hand, a recent study of the N_2-catalyzed recombination of I atoms over a wide temperature range[4] yields slow recombination rates and a weak temperature dependence, facts which are consistent with an RMC mechanism involving a very weak van der Waals type bond (i.e., <1.0 kcal/mol) in the I–N_2 radical–molecule complex. Similarly, a study[5] of the recombination of Cl atoms can be rationalized only by assuming the existence of a very weak van der Waals interaction in the Cl–CO_2 radical–molecule complex.

It does not seem possible to resolve these inconsistencies by applying trajectory studies[6] to the I + Cl, I + I, and Cl + Cl reactions as long as the RMC mechanism is thought to be dominant. Therefore, it seems reasonable to reexamine the results reported in the experimental study[2] of the heteronuclear recombination of I and Cl atoms.

The experimental observations in the flash photolysis of ICl were explained[2] on the basis of reactions 1–5.[7]

$$\mathrm{ICl} + h\nu \rightarrow \mathrm{I} + \mathrm{Cl} \quad (1)$$

$$\mathrm{Cl} + \mathrm{ICl} \rightarrow \mathrm{I} + \mathrm{Cl_2} \quad (2)$$

$$2\mathrm{I} + \mathrm{M} \rightarrow \mathrm{I_2} + \mathrm{M} \quad (3)$$

$$\mathrm{I} + \mathrm{Cl} + \mathrm{M} \rightarrow \mathrm{ICl} + \mathrm{M} \quad (4)$$

$$2\mathrm{Cl} + \mathrm{M} \rightarrow \mathrm{Cl_2} + \mathrm{M} \quad (5)$$

Furthermore, the determination of the rate constant for heteronuclear recombination, k_4, was based on the report[7] that k_2 had the rather low value of 1.7×10^{-16} cm^3/molecule s. With such a low value for k_2, reaction 2 could be playing only a very minor and insignificant role in the depletion of the Cl-atom concentration subsequent to the photodissociation (i.e., only about 1% of the Cl atoms formed could react by (2) over the entire course of an experiment, namely 500 μs). It was, therefore, concluded[2] that the depletion of the Cl and I atoms must occur by (3), (4), and (5) and the application of this conclusion to the experimental data led to the surprisingly large values of k_4[2].

However, a subsequent study[8] of (2) reports a direct measurement of the rate constant of $k_2(298\ \mathrm{K}) = (8 \pm 1) \times 10^{-12}$ cm^3/molecule s, a value some 48 000 times larger than the value of k_2[7] upon which the determination of k_4 was based.[2] This more recent, and apparently more reliable, value of k_2 means that 99% of the Cl atoms will have reacted by (2) within 4 μs. Since all reaction times reported in the flash photolysis of ICl were measured[2] from 50 μs after the onset of the flash (50-μs duration), essentially all the Cl atoms had disappeared via (2) before any measurements were made. Therefore, the only atomic recombination reaction that could have been measured in the flash photolysis[2] was that of I atoms, namely (3). We must conclude that the values of k_4 reported by Maier and Lampe[2] actually have no basis in fact. In support of this conclusion we note that the time-dependent growth of the light absorption at 470 nm (used by Maier and Lampe to monitor ICl concentration) yields a value of $k_3(298\ \mathrm{K})$ within 14% of that obtained at 520 nm. There is thus no reason to doubt that the time-dependent changes in light absorption observed by Maier and Lampe subsequent to the photodissociation flash were due solely to (3). Therefore, (4) and (5) do not play significant roles in the flash photolysis of ICl. On the other hand, the value of the ICl catalyzed recombination of I atoms determined by Maier and Lampe,[2] namely, k_3^{ICl}, is valid and is quite consistent with the data of other investigators on similar reactions.

With this reinterpretation of the results of Maier and Lampe[2] on the flash photolysis of ICl, it appears that there is no known example of a three-body heteronuclear atomic halogen recombination reaction. There is a need for such studies and data on the formation of other heteronuclear diatoms via recombination are now beginning to appear in press.[9-11]

Acknowledgment. One of the authors (G.B.) acknowledges the support of the Air Force Office of Scientific Research, AFSC, USAF, under Grant No. AFOSR-74-2620, as well as the National Research Council of Canada. The other author (F.W.L.) acknowledges the support of the U.S. Department of Energy under Contract No. EY-76-S-02-3416.

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Received September 27, 1979