the orientation of the ion and the dipole in the transition-state complex is $-(+\ -)$.

Specific Rate of Reaction of Free Ions. That k_i should be independent of the nature of the cation is a necessary consequence of the Acree hypothesis. Table I provides us with data to test if this is so.

To evaluate k_i, eq 1 was written in the form

$$\frac{k'}{\alpha} = k_i + k_m\frac{1-\alpha}{\alpha} \qquad (7)$$

where k' is the observed second-order specific rate, k, corrected for the kinetic salt effect to a common ionic strength of 2×10^{-4}, which corresponds to the lower limit of the concentration interval studied. Equations 5 and 6, giving minimum and maximum salt effect corrections, respectively, were used. Straight lines were fitted by the method of least squares to values of k'/α *vs.* $(1 - \alpha)/\alpha$. The results are given in Table III, in which errors quoted are standard deviations.

Inspection of this table reveals that the results differ insignificantly when eq 5 and 6, respectively, are used to correct for the kinetic salt effect.

The specific rate of reaction of unpaired iodide ions is independent of the alkali metal counterion. The values of k_i for NaI, KI, RbI, and CsI differ from the average by +0.1, +0.5, −0.2, and −0.5%, respectively. These deviations fall within the limits of experimental errors.

Values of k_m have also been quoted, though we cannot expect to obtain these constants with any degree of certainty because of the slight association of ions into pairs. For rubidium and cesium iodides the values of k_m are positive and larger than their standard deviations, and we cannot exclude a contribution from the ion pairs to the reaction rate.

Table III. Specific Rates, k_i and k_m, for the Exchange of Iodine between Methyl Iodide and Alkali Iodides in Methanol at 25°, Evaluated from k Values Corrected for Kinetic Salt Effect

Salt	$k_i \times 10^3$, M^{-1} sec^{-1}	k_i, rel units	$k_m \times 10^3$, M^{-1} sec^{-1}	Salt effect correction
NaI	3.335 ± 0.010	1.001 ± 0.003	Assumed = 0	Eq 5
KI	3.348 ± 0.023	1.005 ± 0.007	−4.5 ± 4.9	Eq 5
RbI	3.324 ± 0.013	0.998 ± 0.004	2.1 ± 1.1	Eq 5
CsI	3.316 ± 0.015	0.995 ± 0.005	2.4 ± 0.8	Eq 5
Av	3.331			
NaI	3.339 ± 0.009	1.001 ± 0.003	Assumed = k_i	Eq 6
KI	3.351 ± 0.021	1.005 ± 0.006	−1.8 ± 4.5	Eq 6
RbI	3.328 ± 0.013	0.998 ± 0.004	3.1 ± 1.1	Eq 6
CsI	3.319 ± 0.014	0.996 ± 0.004	3.1 ± 0.7	Eq 6
Av	3.334			

Consequence of Neglect of Kinetic Salt Effect. As mentioned above, the kinetic salt effect is generally neglected in evaluating the constants in the Acree equation. For those reactions in which the salt effect is negative, as in the present investigation, the increasing contribution of the ion pairs to the reaction rate with increasing concentration of the ionic reactant is counteracted by the salt effect. Neglect of the latter therefore results in an underestimate of the specific rate of reaction of the paired ions.

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Photolysis of Stannic Iodide in *n*-Heptane

T. N. Bell, M. Boonstra, and P. A. Dobud

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada. *Received October 1, 1969*

Abstract: Stannic iodide decomposes when irradiated in its first absorption band (λ_{max} 3550 Å). The decomposition is accounted for by a molecular split of iodine molecules, from an excited state of SnI_4 ($SnI_4 + h\nu \rightarrow Sn + 2I_2$). The quantum yield for this reaction is 0.19.

There is a considerable literature on photochemical decompositions, and a number of reviews have recently appeared on the photochemistry of inorganic compounds, particularly on the coordination compounds of the transition elements.[1-4] The interpretation of the mechanism of the primary photochemical process is, in many cases, not clearly understood. The absorption spectra of inorganic compounds, particularly in the ultraviolet region, are often associated with charge-transfer transitions,[5] and any interpretation of photodecompositions resulting from such absorption is intimately bound to an understanding of the electronic transitions occurring. This work was undertaken to observe the photochemical behavior of some main-group element halides in the charge-transfer region. We suggest the photodecomposition proceeds through a molecular elimination mechanism, and have attempted to interpret the decomposition through molecular orbital considerations and also the characteristics of a particular vibrational mode.

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Experimental Section

Materials. *n*-Heptane (Fisher Spectra reagent) was dried over solidum and distilled. Stannic iodide (Alfa Inorganics) was sublimed under vacuum before use.

Apparatus and Procedure. Photolyses were carried out using a PEK 200-W medium-pressure mercury arc. The various spectral regions required were isolated as follows: (1) 3650 Å ($CuSO_4$ 5 cm, 10 g /100 ml; $CoSO_4$, 5 cm, 8.7 g /100 ml; Corning CS7-60 filter); (2) 2850 Å ($NiSO_4$, 5 cm, 27.5 g/100 ml; $CoSO_4$, 5 cm, 8.7 g/100 ml; KI, 1 cm, 0.17 g/100 ml; Cl_2, 1 cm at 1 atm); (3) >4700 Å, two Corning filters CS 3-71; (4) 2537 Å, a low-pressure mercury resonance lamp used.

The incident light intensity was varied using wire gauzes and neutral density filters of aluminum sputtered on thin Pyrex slides. A photocell was used to monitor the light intensity.

Photolyses were carried out in 1-cm silica cells having four clear sides, either in the cell compartment of a Shimadzu spectrophotometer, by focusing the radiation through a slit in the compartment wall, or in an arrangement external to the spectrophotometer. All experiments were carried out after the solutions had been purged with helium. Failure to observe this precaution led to irreproducible results; furthermore, the measured rates were in excess of those when air was absent. In concentrated solutions, a brown precipitate readily formed.

Thus the cell was fitted with a device to enable dry helium to be bubbled through the solution, and thus maintain an inert atmosphere over the solution in all experiments. All solutions were purged with helium for 10 min prior to photolysis.

Between runs, the cell was washed with concentrated hydrochloric acid followed by distilled water, then dried. The path length of the cells was determined by measuring the optical density of potassium chromate solutions.[6]

Initial rates of reaction were measured from the slopes of curves where the change in optical density was monitored as a function of time, at 3650 (SnI_4) and 5200 Å (I_2). Both compounds obeyed Beer's law over the range of concentrations used in this work, 3×10^{-5}–1.3×10^{-4} *M*. ϵ_{SnI_4} at 3650 Å = 6967, ϵ_{I_2} at 5200 Å = 847.

Results

Stannic iodide dissolves readily in *n*-heptane and shows three absorption regions, (1) at $\lambda < 2700$, (2) λ 2700–3100 (max 2800), and (3) λ 3100–4200 (max 3550) Å. Prolonged irradiation in bands 1 and 2, using the low-pressure mercury lamp or the PEK lamp with the corresponding filter combination, gave no measurable decomposition. Irradiation in the third region, mainly through the 3650-Å mercury line, resulted in rapid decomposition, the solutions becoming deeply colored through iodine formation. An absorption due to iodine at 5200 Å appeared, and the SnI_4 band measured at 3650 Å decreased.

From the absorption band intensities the initial rate of formation of iodine and loss of stannic iodide were measured. Thus a value for $-R_{SnI_4}/R_{I_2} = 0.55 \pm 0.3$ was obtained from a large number of experiments at 23°. This value was unchanged even for a threefold change in light intensity, and corresponds to a stoichiometry approximating to

$$SnI_4 \xrightarrow{h\nu} Sn + 2I_2 \tag{1}$$

Photolyses carried out to 80% decomposition still showed the same ratio, $-R_{SnI_4}/R_{I_2}$, as those determined from initial rate measurements. If the reaction mixture was allowed to stand in the dark after photolysis, for long periods, some consumption of iodine occurred.

Thus, for example, a solution of SnI_4 (1.21×10^{-4} *M*), photolyzed to 90% decomposition (15 min), yielded during photolysis $-R_{SnI_4}/R_{I_2} = 0.55 \pm 0.02$ (average of nine readings). After the solution was allowed to stand 19 hr in the dark, this ratio rose to 0.61.

Deviation from the stoichiometric ratio of 0.5 suggested by reaction 1, and the slow loss of iodine on standing, could be due to reaction 2 or an adsorption

$$Sn + I_2 \longrightarrow SnI_2 \tag{2}$$

process (reaction 3).

$$Sn + I_2 \longrightarrow Sn(I_2)_{adsorbed} \tag{3}$$

In an attempt to show the presence of SnI_2, which should be insoluble in *n*-heptane, a photolysis of SnI_4 was carried out, after which the heptane solution was removed. The reaction vessel was then washed with heptane to remove any residual SnI_4 and I_2, then dried. The dried vessel was then washed with water, and the resultant aqueous extract was analyzed for tin by titration with iodate, and for iodide by precipitation with silver. Following this procedure we obtained from the decomposition of 3×10^{-3} mol of SnI_4 an analysis of the aqueous extract corresponding to 7×10^{-6} g-atom of Sn and 2×10^{-5} g-atom of I. These small quantities correspond to the formation of trace amounts of SnI_2.

Similar experiments, wherein the dried reaction vessel was extracted with HCl instead of water, gave a much greater yield of Sn. On no occasion, however, was the amount of tin determined equal to the amount expected from the quantity of SnI_4 decomposed, and we are unable to account for this discrepancy. Thus, for example, decomposition of 6×10^{-4} mol of SnI_4 yielded 1.4×10^{-4} g-atom of Sn, a tin recovery of 25%.

The photolyses discussed above were all carried out at 23°; accordingly, the rate of decomposition and the stoichiometry were checked at 44, 55, and 68°. No measurable difference was observed, and the photolysis was considered independent of temperature over this range.

Of consequence to the determination of the mechanism of photolysis is the effect on the reaction rate of the light intensity and of the light absorbed.

In a series of experiments at various fixed concentrations of stannic iodide, the rate of formation of iodine and rate of loss of stannic iodide were measured over a range of incident light intensity. The results are shown in Figure 1 and conform to a linear dependence of rate on the light intensity.

In a separate series of experiments, the amount of light absorbed was varied by adjusting the concentration of stannic iodide, at various fixed light intensities. The results are plotted in Figure 2 and show a linear relationship between the rate of photolysis and the amount of radiation absorbed. Thus, rate of photolysis $\propto I_{abs} = I_{incident}(1 - e^{-\epsilon cl})$. This simple relationship is in accord with the mechanism proposed below.

The photochemical quantum yield is of importance in any mechanistic considerations, and was estimated for the SnI_4 decomposed and the iodine formed by comparing the extent of the photolysis with corresponding changes in the ferrioxalate actinometer. In order to compensate for the change in solvent from one system to the other, conditions were so adjusted as to make the light absorbed in both systems as close as possible.

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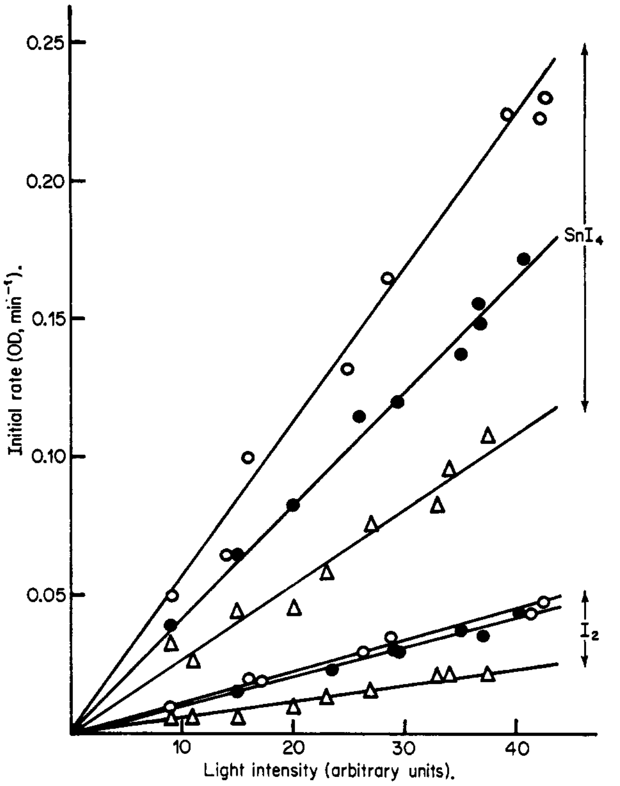

Figure 1. Variation of rate with light intensity. Initial concentration SnI_4 (M): ○, 1.21×10^{-4}; ●, 0.61×10^{-4}; △, 0.35×10^{-4}.

Concentrations of stannic iodide were varied between 1.2×10^{-4} and 3×10^{-5} M, and the light intensity was varied over a twofold range. The results yielded $\Phi_{SnI_4} = 0.19 \pm 0.02$, $\Phi_{I_2} = 0.34 \pm 0.04$.

Iodine is formed in the reaction, and the possibility that this iodine could affect the photolysis must be considered. This possibility was investigated by adding iodine to the stannic iodide solutions. Irradiation of the $I_2 + SnI_4$ solutions at 3650 Å yielded rates indistinguishable from those for the photolysis of corresponding solutions of SnI_4 without added iodine. Irradiation of $SnI_4 + I_2$ mixtures with the filter combination designed to pass light at wavelengths >4700 Å, where only iodine absorbs, gave a very slow rate of decomposition. However, in the absence of iodine, the result was reproducible. We presume this is due to the tail of the SnI_4 band extending into this region, or to a trace of the highly intense 3650-Å mercury line being transmitted through the cutoff filters.

Discussion

The possibility that the photolysis of stannic iodide proceeds through a radical reaction must be considered. The quantum yield is certainly not indicative of a chain process. Experimentally we have shown that iodine atoms from the photolysis of iodine molecules do not promote the decomposition of stannic iodide. Further, if the decomposition proceeded through a radical process, it might be expected that molecular iodine would inhibit the decomposition through such reactions as

$$R + I_2 \longrightarrow RI + I$$

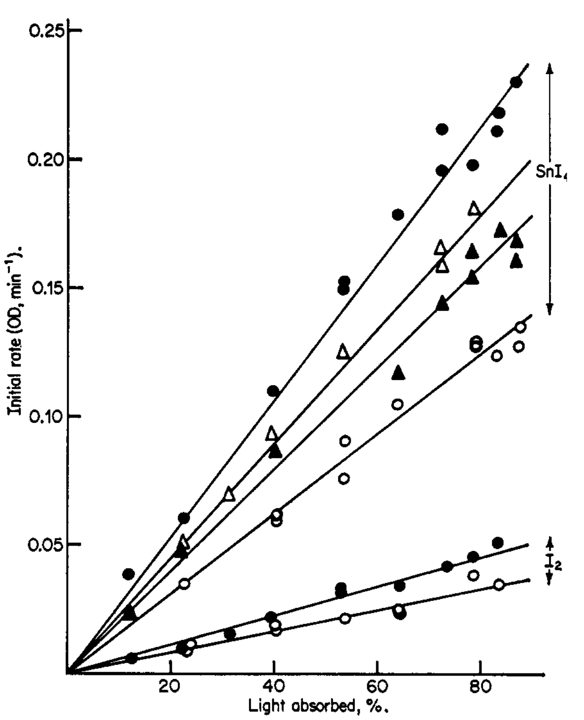

Figure 2. Variation of rate with light absorbed. Light intensities (arbitrary units): ○, 24; ▲, 31; △, 34; ●, 41.

Molecular iodine has been shown not to affect the rate of reaction. Steps in a radical mechanism would be expected to have temperature-dependent rates; on increasing the temperature by 50° no effect on the rate of reaction was observed.

We suggest, therefore, that stannic iodide photolyzes through a molecular elimination process. In gas-phase studies[7] on this molecule, it has been suggested that iodine eliminates molecularly in the photodecomposition. Studies of the vapor-phase flash photolysis of some group IV halides[8] have shown the formation of several species such as MI, and atomic germanium has been observed[9] in corresponding experiments with germanium halides. This indicates that extensive breakdown of the molecules occurs under these photolyzing conditions.

The evidence that molecular elimination processes occur in the gas phase from thermally activated molecules is extensive. These processes have been extensively reviewed by Maccoll and Thomas,[10] and many examples are known of molecular elimination reactions from vibrationally hot molecules; for example, the haloethanes.[11]

In the interpretation of the mechanism of gas-phase photolyses there is an increasing awareness of the importance of molecular elimination processes. Thus, for example, the photolysis of methylamine occurs[12] through a molecular hydrogen elimination reaction path by 17%; and of particular relevance to the present

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work, some molecular production of ethane has been observed in the photolysis[13] of $SnMe_4$.

In solution, the concerted elimination of carbon monoxide from carbonyl compounds, for example, 3,5-cycloheptadienone, has been observed. This molecule undergoes[14] concerted CO elimination under photochemical excitation.

The symmetry requirements for such elimination processes are clearly important and are discussed by Woodward and Hoffmann.[15]

We propose the mechanism below for the photodecomposition of stannic iodide, which leads to the observed stoichiometry

$$SnI_4 \xrightarrow{h\nu} SnI_4^*$$

$$SnI_4^* \xrightarrow{M} SnI_4$$

$$SnI_4^* \longrightarrow Sn + 2I_2$$

together with a small extent of the back reaction

$$Sn + I_2 \longrightarrow SnI_2$$

Experimentally we have shown that the rate of photolysis is linearly dependent on the amount of light absorbed and also on the light intensity: $R \propto I_{abs} = I_{incident}(1 - e^{-\epsilon cl})$. These simple relationships are expected from such a mechanism.

The molecular elimination of iodine requires a molecular model which would allow the iodine atoms to come close enough to interact. This consideration leads us to suggest that the ν_2 vibrational mode is important in the excited state, possibly being reached by a Franck–Condon vibronic transition from the ground state, Figure 3.

From the qualitative molecular orbital description of Liehr[16] for a tetrahedral system, we suggest that the electronic transition involves promotion of a nonbonding ligand π electron (t_1) into an empty antibonding e* orbital. This would represent the lowest energy $\pi^* \leftarrow \pi$ transition, and corresponds to a charge-transfer process from ligand to metal. This is compatible with the extinction coefficient of ~7000.

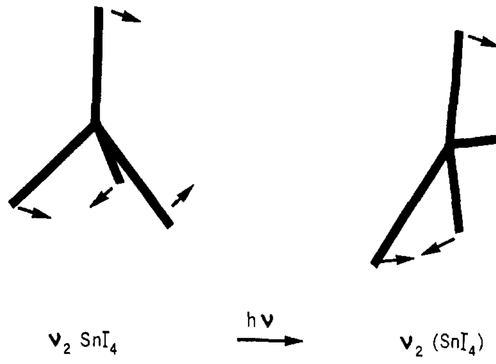

Figure 3. Vibrational model.

The transition suggested would weaken the Sn–I bond and reduce the electrostatic repulsion between the iodine atoms. The amount of electrostatic repulsion is difficult to estimate; for example, the extent of ionic character in stannic iodide has been variously estimated between 15 and 37%, from Mössbauer[17] and nuclear quadrupole coupling[18] measurements. However, it should be pointed out that an interpretation of 0% ionic bonding has been given for the Mössbauer studies.[19]

The charge-transfer transition suggested could lead to an increase in the amplitude of vibration in the ν_2 mode, and also give rise to a Jahn–Teller distortion of the tetrahedral molecule. Both these effects would contribute in bringing the iodine atoms into close enough proximity to interact and yield molecular iodine (Figure 3).

The observed quantum yield of 0.19 is in keeping with the ideas proposed above.

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