Halogen Atom Complexes. Thermodynamic and Kinetic Properties of the Iodine Atom–*o*-Xylene Charge-Transfer Complex

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Abstract: Thermodynamic and kinetic properties of the transient complex between iodine atoms and *o*-xylene in the liquid phase have been determined by flash spectrophotometry. The formation constant and enthalpy of formation at 25° are reasonably consistent with those inferred from kinetic recombination studies for the gas-phase complex when solvation effects are considered, and show that charge-transfer interactions can lead to both the specificities and observed negative temperature coefficients for relatively efficient third-body species.

The homogeneous gas-phase recombination of halogen atoms (X) in the presence of a third body (M) is now generally considered[1] to occur either by the energy-transfer mechanism

$$X + X \rightleftarrows XX^* \qquad (1)$$

$$XX^* + M \longrightarrow X_2 + M \qquad (2)$$

or the radical–molecule complex mechanism

$$X + M \rightleftarrows XM \qquad (3)$$

$$XM + X \longrightarrow X_2 + M \qquad (4)$$

In these mechanisms, XX* represents a short-lived diatom with more than sufficient energy to dissociate, and XM is a complex of sufficiently long life to be collisionally deactivated and to participate in step 4, leading to recombination

$$X + M \rightleftarrows XM^* \qquad (3a)$$

$$XM^* + M \rightleftarrows XM + M \qquad (3b)$$

the over-all rate of recombination in either case being

$$\frac{d[X_2]}{dt} = k_{\text{app}}[X]^2[M] \qquad (5)$$

The first mechanism satisfactorily describes the recombination of iodine atoms in the presence of atomic or relatively simple molecular third bodies.[2] In more complex systems, however, the large rate constants cannot adequately be explained by energy transfer alone, and the second mechanism accounts for recombination where the binding energy of XM is greater than *kT*. Dispersion forces alone, although leading to reasonable binding energies,[2,3] do not result in the large variations actually observed in third-body efficiencies,[4-6] whereas charge-transfer interactions lead to quite large binding energies but reasonable specificities among the donor third bodies.

Following the flash photolysis of molecular iodine, a transient absorption attributed to a strong intermediate complex between a nitric oxide molecule and an iodine atom has been detected in the gas phase.[7] Similarly, charge-transfer complexes between iodine atoms and aromatic donors have been observed spectrophotometrically in the liquid phase;[7-9] the absorption spectra of these relatively weak complexes have not been observed in the gas phase, but formation constants deduced from the gas-phase atom recombination studies are at least an order of magnitude greater than the comparable molecular iodine–aromatic complexes in the liquid phase.[10] A stronger atom complex is, in fact, to be expected, as the electron affinity of the iodine atom is greater than that of the iodine molecule. Although the formation constant for the iodine atom–hexamethylbenzene complex has been shown[11] to be somewhat larger than that for the molecular iodine–hexamethylbenzene complex (2.7 and 1.5 l. mole^{-1}, respectively, both at 25°, CCl_4 solvent), this difference is not large enough to account for the at least tenfold difference cited above and may indicate a compensating effect between the standard enthalpies and entropies of formation not present in the gas phase. In addition, however, it has recently been shown[12] that gas-phase molecular iodine complexes are appreciably stronger than comparable liquid-phase complexes (although the enthalpies of formation are approximately the same), the effect diminishing with increasing strength of the complex.[13]

Determination of the thermodynamic properties of the liquid-phase iodine atom–aromatic complexes requires the precise measurement of absorbance changes as a function of temperature and donor concentration at two wavelengths, one of which corresponds to change in molecular iodine concentration only. Accordingly, the flash spectrophotometric apparatus of this laboratory has been modified to permit the simultaneous recording of two absorbance changes as a function of

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(13) J. M. Goodenow and M. Tamres, *J. Chem. Phys.*, **43**, 3393 (1965).

time following flash photolysis, one in the ultraviolet region (due to dissociation of iodine in the molecular iodine–aromatic complex) and the other in the visible region (resulting from the simultaneous dissociation of iodine and formation of the atom complex).

Experimental Section

Flash Apparatus. The flash spectrophotometric apparatus used in this work was a modification of the unit used in previously reported experiments in this laboratory on transient charge-transfer species.[8] The flash lamp consisted of two parallel quartz tubes (15-mm i.d., 1.5-mm wall thickness), each approximately 15 cm long with either cup stainless steel or 5-mm tungsten rod electrodes 12 cm apart. Semicircular Pyrex manifolds at each end positioned the tubes at a distance of 8 cm from each other and provided for common gas filling of both tubes (Xe, 60–120 mm). The lamp was mounted horizontally on the optical bench in a polished cylindrical reflector, and the reaction cell was positioned midway between the two tubes.

The discharge tubes were connected in series electrically. Two ASEA Type CTUA capacitors (625 joules each) charged in parallel were discharged across the lamp, triggering being effected by a 20–35-kv pulse applied at the midpoint connection between the two tubes. The maximum capacitance voltage possible was 10 kv. However, as with flash units elsewhere,[14] a "saturation effect" was also encountered here; *i.e.*, at low energies the peak light intensity is directly proportional to the electrical energy, but at higher discharge energies the peak intensity becomes roughly constant and the flash duration time (or "tailing") increases. The voltage at which this effect becomes significant apparently is a function of the design of the apparatus and was encountered here at a much lower voltage (*ca.* 8 kv) than on the unit described previously[14] (23 kv), although the energies dissipated per unit length of discharge path (33 and 42 joules/cm, respectively) are more comparable. For the relatively fast recombination reactions reported here, it was desirable to minimize flash tailing as much as possible consistent with a high peak light intensity, and therefore all measurements were made at not more than 8 kv (800 joules).

Analyzing light from the continuous light source (Osram Type XBO 450W/P xenon lamp, powered by a Sola dc constant wattage supply further stabilized by two parallel 18-v storage battery units) was partially collimated so that it passed through the reaction cell without hitting the sides and was split past the cell with a partially silvered mirror. The transmitted portion (70%) was focused on the entrance slit of a Zeiss MM12 double monochromator and detected by an EMI 9558Q photomultiplier tube; this unit involving the larger fraction of the analyzing beam was used for lower wavelength (ultraviolet) measurements. The reflected light, for measurements in the visible spectral region, was focused on the entrance slit of a Beckman DU monochromator and detected by an EMI 9558B photomultiplier. Voltage outputs developed across load resistors (variable in steps from 10 kilohms to 1 megohm) and shunting capacitors (from 0 to 600 pf) were dc-coupled through 12AU7 cathode followers to the upper and lower 2A63 amplifier plug-in units of a Tektronix Type 565 dual-beam oscilloscope. The two traces were maintained on the cathode ray screen by opposing the dc voltages from the continuous analyzing light with variable dc voltage applied at the negative inputs of the two amplifier sections. The two sweeps were simultaneously initiated by a manual trigger switch, and the gate-out signal from the oscilloscope was used to initiate the high-voltage flash trigger pulse. The rise time of the 2A63 amplifier is 1 μsec, and this was the limiting factor for fast time resolution. However, the time constant of each detecting assembly could be stepwise increased to a maximum of 600 μsec by the appropriate combination of load resistor and shunting capacitor in order to give the optimum signal-to-noise ratio consistent with negligible signal distortion.

Reaction Cell. The Pyrex reaction cell was cylindrical (10 cm light path, 2.5 cm i.d.) with evacuated 2-cm cylindrical chambers at each end. Surrounding the cell compartment and approximately three-fourths of each end section was an annular jacket (*ca.* 1-cm inside thickness) through which was circulated the thermostated aqueous filter solution (1 *M* $CuCl_2 \cdot 2H_2O$ + 0.5 *M* $CaCl_2 \cdot 2H_2O$). With this arrangement, temperature control and uniformity over the entire cell was sufficiently precise to prevent any distortion of the analyzing light beam by density gradients at the highest temperature used.

Purification of Materials. To Eastman *o*-xylene was added a small amount of iodine and the solution illuminated for 36 hr. Excess iodine was removed with sodium sulfite solution; the wet *o*-xylene was shaken with portions of concentrated sulfuric acid until no discoloration of the acid occurred, washed, shaken with a 10% sodium hydroxide solution, washed, and distilled twice over sodium through a 48-cm Vigreux column, the second distillation being at a high reflux ratio. A similar procedure was used for carbon tetrachloride (Fisher reagent grade), except that chlorine was added instead of iodine before illumination, and distillation was performed over phosphorus pentoxide instead of sodium. Iodine (Fisher) was freshly resublimed and used without further purification.

Calculations. At λ_1, where it is assumed that the changes in absorbance (optical path length *d*) are due only to changes in total molecular iodine concentration, $\Delta[I_2]$ (either free or complexed)

$$\Delta A_{\lambda_1} = \epsilon_{I_2,\lambda_1} d\Delta[I_2] \tag{6}$$

(Values for the apparent molar extinction coefficient of iodine, ϵ_{I_2,λ_1}, were determined at the temperatures and donor molecule concentrations used in this work in independent measurements with a thermostated Beckman DU spectrophotometer using 1-cm quartz absorption cells.) At λ_2, the other wavelength at which absorbance changes as a function of time are simultaneously measured

$$\Delta A_{\lambda_2} = \epsilon_{C,\lambda_2} d[C] + \epsilon_{I_2,\lambda_2} d\Delta[I_2] \tag{7}$$

where [C] is the concentration of the iodine atom–aromatic complex, and ϵ_{C,λ_2} and ϵ_{I_2,λ_2} are the molar extinction coefficients at λ_2 of the complex and molecular iodine, respectively. The formation constant K_x of the 1:1 complex between an iodine atom and the donor aromatic molecule (mole fraction X_D) is

$$K_x = \frac{[C]}{X_D[I]} = \frac{[C]}{X_D(-2\Delta[I_2] - [C])} \tag{8}$$

Rearrangement of eq 6, 7, and 8 leads to an equation similar to the well-known Benesi-Hildebrand equation[15] in the form suitable in particular to relatively weak complexes[16]

$$-\frac{2R_A}{(1 - R_A R_\epsilon)\epsilon_{I_2,\lambda_1}} = \frac{1}{\epsilon_{C,\lambda_2} K_x}\frac{1}{X_D} + \frac{1}{\epsilon_{C,\lambda_2}} \tag{9}$$

where $R_A = \Delta A_{\lambda_1}/\Delta A_{\lambda_2}$ and $R_\epsilon = \epsilon_{I_2,\lambda_2}/\epsilon_{I_2,\lambda_1}$.

Trotter and Hanna have recently pointed out[17] that solution nonideality will lead to different values for ϵ_C depending on the concentration units of the donor, D, although linear plots of the Benesi-Hildebrand equation still result. This will affect also the values for *K* determined from these plots in addition to the conversion unit factors. In this work, however, within the rather wide experimental errors, no differences were found in ϵ_C for the different concentration scales; mole fraction units have therefore been used throughout for comparison purposes.

Results and Discussion

Iodine–*o*-Xylene System. The transient absorbance changes, present 100 μsec following initiation of the flash discharge, were measured simultaneously at 350 and 570 mμ as functions of temperature (25, 45, and 65°) and *o*-xylene mole fraction (0.082:1, CCl_4 solvent), but constant (3.9×10^{-5} *M*) initial molecular iodine concentration. The choice of the former wavelength represents a compromise between maximum ultraviolet absorption by iodine in *o*-xylene (316 mμ[18]) and the increasing noise-to-signal ratio at lower wavelengths; the latter wavelength is the maximum of the *o*-xylene–iodine atom complex.[9]

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[18] L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

The ratios of these absorbance changes are shown in Figure 1 as a function of the reciprocal of the *o*-xylene mole fraction according to eq 9, each point representing the average of at least ten oscillograms. From these plots ϵ_{C,λ_2} and K_x were calculated from the intercepts and slopes of the best straight lines using the method of least squares. The results are given in Table I and are compared at 25° with those of the molecular iodine–*o*-xylene complex. (In practice, the data were also plotted using the technique of Rose and Drago[19] in order to determine experimental scattering and to verify the validity of the thermodynamic data resulting from the specific range of conditions used; no significant differences resulted using this latter technique.)

Table I. Comparison of Thermodynamic Constants for the Iodine Atom– and Molecular Iodine-*o*-Xylene Complexes in the Liquid Phase

	I complex (λ_{max} 590 mμ)	I_2 complex[a] (λ_{max} 316 mμ)
K_x, mole fraction units		
25°	7.4	2.96
45°	3.5	
65°	2.9	
$\Delta H°_x$, kcal mole^{-1}	−4.4	−2.0
$\Delta S°_x$, eu	−10.9	−4.9
ϵ_{max}, l. mole^{-1} cm^{-1}	3400	12,500

[a] J. A. A. Ketelaar, *J. Phys. Radium*, **15**, 197 (1954).

Since the slopes of the lines in Figure 1 can be determined more accurately than K_x, which depends on both the slope and the intercept (*i.e.*, the extinction coefficient), the enthalpy and entropy of formation at 25° were calculated according to the integrated form of the van't Hoff equation from the reciprocals of the slopes, thereby assuming ϵ_{C,λ_2} and $\Delta H°_x$ are independent of temperature. These thermodynamic properties are also given in Table I.

That the equilibrium constant at 25° for the atom complex is greater than that for the molecular complex is to be expected from Mulliken's treatment of charge transfer[20] because of the greater electron affinity of the iodine atom, leading also to the visible shift of the charge-transfer band. The correspondence between enthalpy and entropy is also quite general, the relative values for the iodine atom complex agreeing well with those for a large number of donor species with molecular iodine.[21] The energy of formation of the complex, *ca.* −4.1 kcal/mole, is essentially the same as the calculated binding energy for a gas-phase, charge-transfer complex according to Mulliken following the method of Eusuf and Laidler.[2] There is little question, therefore, of the charge-transfer nature of this intermediate.

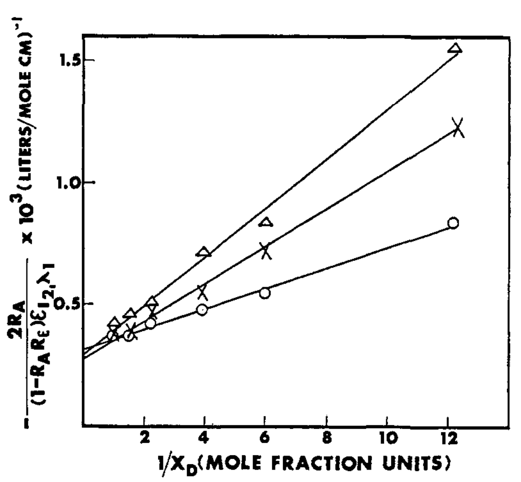

Figure 1. Absorbance changes at 100 μsec as a function of *o*-xylene mole fraction, plotted according to eq 9: ○, 25°; ×, 45°; △, 65°.

The third-order, gas-phase recombination rate constant, k_{app} (defined by eq 5), for iodine atoms with *p*-xylene as the third body is approximately 3.3 × 10^{11} l.^{2} mole^{-2} sec^{-1} at room temperature.[4] For the recombination mechanism given by eq 3 and 4, $k_{app} = k_2(K_c)_{gas}$, where $(K_c)_{gas} = k_3/k_{-3}$ is the formation constant (in concentration units) for the assumed equilibrium between I atoms, xylene, and the charge-transfer complex. The bimolecular rate constant k_4 is easily estimated since this metathetical reaction would be expected to have essentially zero activation energy and therefore should proceed at a rate proportional to collisional frequency, the specific collision number between unlike molecules being given by

$$Z_{12}' = \sigma^2\left(\frac{8\pi kT}{\mu}\right)^{1/2} \qquad (10)$$

where σ is the collision diameter of the I–I pair[6] (4.3 × 10^{-8} cm) and μ is the reduced mass of the I–IM pair. The major uncertainty in this calculation is the statistical factor giving the fraction of iodine atom pairs, each atom being in its ground ($^2P_{3/2}$) state, that lead to a stable configuration. Porter and Smith[6] have used $^1/_{16}$ since the total degeneracy of the ground-state iodine atom is 16, whereas the degeneracy of the stable singlet molecular ground state is unity. However, Eusuf and Laidler[2] point out that 8 of the 16 possible states from combination of two iodine atoms are attractive and can lead to combination if stabilized by collisional deactivation; the appropriate statistical factor is therefore $^1/_2$. On this basis, $(k_4)_{calcd}$ = 4.8 × 10^{10} l. mole^{-1} sec^{-1} at 25° and $(K_c)_{gas}$ = 6.9 l. mole^{-1}. The formation constant in solution for this same intermediate species IM at 25° (Table I) is 7.4 in mole fraction units; in concentration units, $(K_c)_{liquid}$ = 0.9 l. mole^{-1}. Agreement between the formation constants in the two phases is considered to be reasonably close in view of the experimental errors associated with the transient absorbance measurements in solution and the uncertainties in the calculation of k_4. The results do, however, indicate a smaller formation constant in the liquid phase than in the gas phase, in agreement with results for weaker complexes between atomic iodine and ethyl iodide or bromide[10] and between molecular iodine and benzene or diethyl ether.[12] This behavior is presumably due to competition between complexing and solvation of the donor molecule in the liquid phase,[22] the disagreement between the formation constants in the two phases decreasing with increasing strength of the complex.[12] (For the stronger complex between molec-

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(19) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).
(20) R. S. Mulliken, *ibid.*, **74**, 811 (1952).
(21) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p 141.
(22) S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 2048 (1965).

ular iodine and diethyl sulfide, the agreement between the two phases is much closer.[13])

The negative temperature dependence of the gas-phase recombination of iodine atoms with xylene as a third body has not been determined, but certainly is less than that for toluene (−3.4 kcal/mole) and is probably close to the −4.1-kcal/mole complex formation energy obtained in this liquid-phase work. It is thus quite clear that charge-transfer interactions can account for both the third-body specificities and observed negative recombination temperature coefficients for relatively efficient third-body species.

The formation of molecular iodine in the liquid phase after the dissociation flash intensity has decayed to a negligible value is second order (as shown by linear time plots of $1/\Delta A_{350}$) and is consistent with a bimolecular recombination mechanism involving free or complexed iodine atoms where a third body is essentially in contact in every bimolecular encounter. The second-order rate constant, k, defined by

$$\frac{d[I_2]}{dt} = -\frac{1}{2}\frac{d[I]_{total}}{dt} = k[I]_{total}{}^2 \qquad (11)$$

where $(I)_{total}$ is the total iodine atom concentration (free or complexed) was calculated from the slope of this second-order plot and eq 6 ($[I]_{total} = -2\Delta[I_2]$) for each oscillogram, and the average values are summarized in Table II for each concentration at 25, 45, and 65°. At 25°, the rate of recombination is in good agreement with the rate of recombination in pure carbon tetrachloride.[23]

Table II. Rate of Recombination of Iodine in *o*-Xylene–Carbon Tetrachloride Solutions

[*o*-Xylene], mole fraction	25°	45°	65°
	$k \times 10^{-9}$, l.^{2} mole^{-2} sec^{-1}		
0.082	5.3	7.1	7.7
0.167	5.4	6.7	7.1
0.255	5.3	6.2	6.4
0.446	5.2	5.6	6.8
0.651	5.4	6.1	6.5
1.00	4.5	5.0	4.7

Combination of the Smoluchowski relation

$$k = \frac{8\pi aDN}{1000} \quad (\text{l. mole}^{-1}\ \text{sec}^{-1}) \qquad (12)$$

which gives the diffusion-controlled recombination rate constant assuming that even on a molecular scale the solvent can be treated as a continuous medium of viscosity η and the Stokes–Einstein equation for the diffusion coefficient

$$D = \frac{kT}{6\pi\eta a_s} \quad (\text{cm}^2\ \text{sec}^{-1}) \qquad (13)$$

shows that the product $k\eta$ should be a function only of temperature

$$k\eta = \frac{4RTa}{3000a_s} \qquad (14)$$

if the encounter diameter in solution ($2a$) pertinent to the recombination process is taken to be the same as the diffusion diameter ($2a_s$). The viscosities for all the *o*-xylene–carbon tetrachloride solutions used in this work were determined at 25, 45, and 65° with an Ostwald viscometer (modified at the top to prevent evaporation of the solution at the higher temperatures) which was calibrated with the two pure liquids *o*-xylene and carbon tetrachloride at 25°; these are tabulated in Table III with the densities (measured at room temperature with a Westphal balance and assumed to be independent of temperature) and values for $k\eta$.

Table III. Values of $k\eta$ for Iodine Atom Recombination in *o*-Xylene–Carbon Tetrachloride Solutions

[*o*-Xylene], mole fraction	ρ_{25}, g cc^{-1}	η_{25}, cp	25°	45°	65°
			$k\eta \times 10^{-7}$ poise l.^{2} mole^{-2} sec^{-1}		
0.00	1.590	0.901			
0.082	1.508	0.886	4.7	5.0	4.4
0.167	1.430	0.875	4.7	5.1	4.1
0.255	1.360	0.860	4.6	4.2	3.6
0.446	1.216	0.831	4.3	3.7	3.7
0.651	1.080	0.803	4.4	3.9	3.4
1.00	0.880	0.753	3.4	3.0	2.3

It is seen that $k\eta$ is, in fact, roughly constant at room temperature but decreases with increasing *o*-xylene concentration at the higher temperatures. Since two iodine atoms must come into close proximity for recombination to occur, the apparent encounter diameter ($2a$) should be approximately constant (or decrease by a steric effect), whereas the average diffusion diameter ($2a_s$) must surely increase with increased extent of complexing, both factors leading to the observed behavior. The net effect, however, is to give an inverse temperature relationship in $k\eta$ at the higher *o*-xylene concentrations, approximately 90% of the iodine atoms being complexed in pure *o*-xylene. A similar effect (or constancy of k, as shown in Table II) in a pure donor has also been observed by Gover and Porter for iodine in benzene[10] and has been interpreted in part as a possible compensation by a temperature dependence of the extinction coefficient, since in the benzene–iodine system only the ratio k/ϵ can be determined. The fact that there is appreciable overlapping of the molecular iodine–iodine atom–benzene complex spectra in the visible region would be expected to lead to just such an effect, but should not be a major factor in measurements made at 350 mμ on the atomic iodine–*o*-xylene complex since presumably there is negligible contribution to the absorbance at 350 mμ of the atomic complex absorption curve. At the lowest concentration, the expected constancy of $k\eta$ is roughly followed and is consistent with the temperature coefficient for the recombination of iodine atoms in carbon tetrachloride.[24]

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[24] S. Aditya and J. E. Willard, *ibid.*, **79**, 2680 (1957).