# The Relative Importance of Charge-Transfer Interactions in Gas-Phase Halogen Atom Recombination

James R. Basila and Robert L. Strong*

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. Received April 16, 1973

Abstract: The gas-phase rates of recombination are compared for bromine and iodine in benzene and in the alkyl halides ethyl bromide, methyl bromide, ethyl chloride, and methyl chloride. Both halogens exhibit an inverse relationship between the recombination rate constant and third-body ionization potential, consistent with either specific charge-transfer (CT) interactions or generally accepted trends in van der Waals forces involving the intermediate species of the complex recombination mechanism. At low ionization potentials, the bromine recombination is greater than that for iodine, consistent with the greater bromine atom electron affinity for predominant CT interaction in the complexation. At higher third-body ionization potentials, however, iodine recombination becomes somewhat more efficient (although relatively insensitive to the ionization potential of the third body), reflecting the greater polarizability and quadrupole moment of atomic iodine and increasing dominance of classical electrostatic binding interactions. The formation constants of the gas-phase bromine atom–alkyl halide complexes are estimated from the recombination rate data.

The study of halogen molecule photodissociation and atom recombination processes has been one of the most fruitful areas of research resulting from development of the flash photolysis technique.[1] There is a marked dependency on the nature of the third body M used in the "termolecular" recombination, and (with the exception of the very light third bodies) halogen atom recombination is generally accepted to occur *via* a mechanism involving an M–X complex intermediate.[2]

$$X + M \rightleftarrows (M-X)^* \tag{1}$$

$$(M-X)^* + M \rightleftarrows M-X + M \tag{2}$$

$$M-X + X \longrightarrow X_2 + M \tag{3}$$
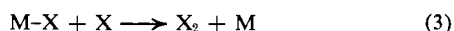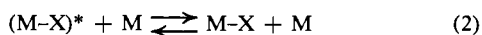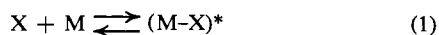
The efficiency of the recombination is thus determined in most cases by the stability of M–X.

The nature of M–X is uncertain, however. Russell and Simons[3] showed a rough correlation between the logarithm of the recombination rate constants and the boiling points (and hence intermolecular force fields) of M; a regular variation of the rate constant with ionization potential of M was also stated.[3] Although the results may be adequately described in some cases in terms of van der Waals type forces,[4] in general the energetics are such that more specific types of bonding have been considered to be necessary, and the stronger charge-transfer (CT) type of interactions have been proposed.[5,6] Indeed, CT complexes between halogen atoms and various solvents acting as donor species have been directly observed spectrally in the liquid phase;[7] Porter observed the unstable NOI molecule[8] and a weak visible-region absorbance in methyl iodide[9] following the gas-phase

flash photolysis of molecular iodine, and gas-phase CT spectra have recently been detected also by flash photolysis for iodine in benzene or cyclohexane, iodine or bromine in alkyl halides, and bromine in xenon.[10] Since charge-transfer complex strength increases with decreasing donor ionization potential,[11] the recombination rate constant (which according to the above mechanism increases with increasing M–X stability) should show an inverse dependence on the ionization potential of the donor molecule (M), and this behavior is generally followed.[3,12,13]

Unfortunately, this same general dependence on the ionization potential of M for a given acceptor X might also be expected to follow for normal van der Waals forces[3,14] so that the correlation between ionization potential and recombination rate constant does not confirm the charge-transfer nature of the specific complex binding even with the presence of a strong CT absorption spectrum. (In the same sense, the major contribution of CT forces to the ground-state binding energy of weak $\pi-\pi$ and π–halogen molecular complexes has been recently questioned,[15–17] although it has been shown from enhancements of dipole moments and infrared intensities[18] that these forces are important in ground-state bonding for n–σ complexes.) For different halogen atom acceptors (*i.e.*, iodine and bromine) with a given third body, however, opposite effects should be observed depending on the dominant nature of the intermolecular forces. The electron affinity of the io-

(1) R. G. W. Norrish and G. Porter, *Nature (London)*, **164**, 658 (1949); G. Porter, *Proc. Roy. Soc., Ser. A*, **200**, 284 (1950).

(2) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 283 (1937).

(3) K. E. Russell and J. Simons, *Proc. Roy. Soc., Ser. A*, **217**, 271 (1953).

(4) D. L. Bunker and N. Davidson, *J. Amer. Chem. Soc.*, **80**, 5090 (1958).

(5) D. E. Hoare and A. D. Walsh, *Chem. Soc., Spec. Publ., No. 9*, 17 (1957).

(6) G. Porter and J. A. Smith, *Nature (London)*, **184**, 446 (1959); *Proc. Roy. Soc., Ser. A*, **261**, 28 (1961).

(7) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, p 280.

(8) G. Porter, Z. G. Szabó, and M. G. Townsend, *Proc. Roy. Soc., Ser. A*, **270**, 493 (1962).

(9) T. A. Gover and G. Porter, *Proc. Roy. Soc., Ser. A*, **262**, 476 (1961).

(10) V. A. Brosseau, J. R. Basila, J. F. Smalley, and R. L. Strong, *J. Amer. Chem. Soc.*, **94**, 716 (1972).

(11) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

(12) M. Eusuf and K. J. Laidler, *Trans. Faraday Soc.*, **59**, 2750 (1963).

(13) N. Harada, Y. Mori, and I. Tanaka, *Bull. Chem. Soc. Jap.*, **44**, 375 (1971).

(14) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

(15) J. L. Lippert, M. W. Hanna, and J. P. Trotter, *J. Amer. Chem. Soc.*, **91**, 4035 (1969).

(16) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron, Suppl.*, **7**, 97 (1966).

(17) R. J. W. LeFevre, D. V. Radford, and P. J. Stiles, *J. Chem. Soc. B*, 1297 (1968).

(18) H. Ratajczak and W. J. Orville-Thomas, *J. Mol. Struct.*, **14**, 149, 155 (1972).

dine atom is less than that of bromine, so that if CT interactions dominate the recombination rate constant for iodine atoms should be less than that of bromine atoms;[11] however, the greater polarizability of the iodine atom would tend to make the recombination rate constant for iodine atoms greater than that for bromine if the interactions are predominantly van der Waals forces.[14]

DeGraff and Lang[19] studied the gas-phase recombination of bromine atoms with various third bodies and compared the results with those available in the literature for iodine; in each case the iodine value was greater. In a recent paper, Widman and DeGraff[20] report similar measurements on the recombination of chlorine atoms, showing the recombination rate constant for chlorine atoms to be somewhat greater than that for iodine atoms and approximately twice that for bromine atoms with corresponding third bodies. In this paper we present results for the recombination of iodine atoms and bromine atoms in a variety of third bodies, for which a direct comparison between the two halogens is possible, over a sufficiently wide range of donor ionization potentials, to show a transition from predominantly charge transfer to major van der Waals contribution to the total binding energy of M–X.
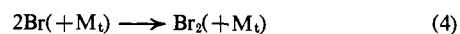
Experimental Section

The characteristics of the flash spectrophotometer, flash optical filters for the iodine and bromine systems, preparation of reaction cells, and method of transient spectrophotometric analysis have been described.[10] The use of Pyrex rectangular cells (10-mm optical path length) containing saturated uranyl nitrate solution (lower wavelength cut off at 490 nm) for cells containing iodine, or a solution consisting of 64 g of uranyl nitrate per 200 ml water (lower wavelength cut off at 450 nm) for the bromine cells, as the flash optical filters prevented any flash light absorption by benzene or the alkyl halide third bodies. For the iodine systems, the continuous xenon analyzing light was filtered with a 3-mm plate glass before passage through the reaction cell, and the atom recombination was followed in the molecular iodine continuum at 480 nm; under these conditions no irreversible reactions occurred by analyzing light illumination alone. With bromine, however, where recombination analysis was at 420 nm, photochemical side reactions did occur with all third bodies, the extent of reaction being minimized by filtering the analyzing light with plate glass, a 420-nm interference filter, and 10 mm of an I_2 ($>10^{-3}$ M)–CCl_4 solution. Irreversible photobromination from the flash itself was assumed to occur totally during the lifetime of the flash (see discussion below on the irreversible photobromination of benzene) prior to the start of kinetic measurements (75 μsec after flash initiation) and was corrected for by subtracting off the absorbance change remaining after atom recombination was complete. (Since roughly the same amount of photobromination occurred with each alkyl halide (ca. 7% of the bromine dissociated per flash), the recombination rate constants should be comparable using this method of correction.) Argon was added to the bromine-benzene to increase the third-body pressure and thereby to minimize the transient gas-phase temperature rise; the vapor pressures of the other donor species (the alkyl halides) were sufficiently high at room temperature to preclude the need for the addition of another third body. Under the conditions used in this work (maximum illumination of the cell by the analyzing beam and flash, kinetic analysis between 75 and 300 μsec after flash initiation, and third-body pressures at least 200 torr), no measurable thermal concentration effect resulting from a thermal gradient within the cell[21,22] was observed. Although the oscilloscope trace did not return at long times to the original base line in the bromine systems (indicative of a possible thermal effect), the difference in each case could be accounted for

entirely by irreversible photobromination as confirmed by conventional spectrophotometric determination of the total change in bromine concentration after a series of flashes was completed.

Results

The gas-phase room-temperature recombination of bromine atoms has been measured in benzene and in the alkyl halides methyl chloride, ethyl chloride, methyl bromide, and ethyl bromide. At least ten oscillograms, corrected for permanent photoreaction, were averaged for each experimental condition; in all cases kinetic data second order with respect to the transient change in molecular bromine concentration were obtained, consistent with the recombination reaction

$$2Br(+M_t) \longrightarrow Br_2(+M_t) \tag{4}$$

$$d[Br_2]/dt = k_2[Br]^2 \tag{5}$$

where [Br] is the total (complexed and free) bromine atom concentration and M_t is the total third body. The experimental second-order rate constant k_2 (obtained from the appropriate plot of the integrated form of (5)) for the bromine–benzene–argon system is

$$k_2 = k_{Ar}[Ar] + k_M[C_6H_6] + k_{Br_2}[Br_2] \tag{6}$$

and for the alkyl halide (RX) third bodies it is

$$k_2 = k_M[RX] + k_{Br_2}[Br_2] \tag{7}$$

Under the conditions of third-body and molecular bromine pressures used, it follows that the $k_{Br_2}[Br_2]$ term is negligible in the work reported here.[23] Hence

$$\frac{k_2}{[M_t]} = k_{Ar} + (k_M - k_{Ar})\frac{[C_6H_6]}{[M_t]} \tag{8}$$

Values for k_M were obtained from plots of $k_2/[M_t]$ vs. $[C_6H_6]/[M_t]$ for benzene, using the value[23] $k_{Ar} = 2.7 \times 10^9$ $l.^2/(mol^2 sec)$, and from plots of k_2 vs. [RX] for the alkyl halides.

Similarly, the recombination of iodine in methyl bromide, methyl chloride, and ethyl chloride has been determined. No irreversible photoiodination occurred in any case, but the very high third-body efficiency of molecular iodine[21] necessitated inclusion of the term $k_{I_2}[I_2]$ in the determination of k_M.

$$k_2 = k_M[RX] + k_{I_2}[I_2] \tag{9}$$

Values for k_M were obtained from plots of k_2 vs. [RX], with $k_{I_2} = 1.4 \times 10^{12}$ $l.^2/(mol^2 sec)$.[24]

Results of this work are summarized in Table I and

Table I. Gas-Phase Recombination Rate Constants for Iodine and Bromine at Room Temperature

M	I_p, eV	$k_M \times 10^{-9}$, $l.^2/(mol^2 sec)$ Bromine	Iodine
Benzene	9.24	525 ± 25%	85[a]
Ethyl bromide	10.29	251 ± 11%	80[a]
Methyl bromide	10.53	120 ± 9%	54
Ethyl chloride	10.97	54 ± 3%	57
Methyl chloride	11.33	35 ± 7%	40

[a] Reference 3.

compared with other work on the recombination of iodine in benzene and in ethyl bromide.

(19) B. A. DeGraff and K. J. Lang, *J. Phys. Chem.*, **74**, 4181 (1970).
(20) R. P. Widman and B. A. DeGraff, *J. Phys. Chem.*, **77**, 1325 (1973).
(21) M. I. Christie, A. J. Harrison, R. G. W. Norrish, and G. Porter, *Proc. Roy. Soc., Ser. A*, **231**, 446 (1955).
(22) G. Burns, *Can. J. Chem.*, **46**, 3229 (1968).

(23) M. R. Basila and R. L. Strong, *J. Phys. Chem.*, **67**, 521 (1963).
(24) J. A. Blake and G. Burns, *J. Chem. Phys.*, **54**, 1480 (1971).

Discussion

Estimate of the Non-Charge-Transfer Contributions to the Stability of the M–X Intermediate.

Calculated estimates were made of the non-charge-transfer interactions between the atomic iodine or bromine (X) and the methyl halide (M) for the axially symmetric methyl bromide and methyl chloride systems. Interactions considered are the polarizability (M)–polarizability (X), dipole (M)–polarizability (X), dipole (M)–quadrupole (X), and quadrupole (M)–quadrupole (X).

The geometry of the intermediate was chosen so as to allow maximum charge-transfer interaction between the methyl halide donor and the halogen atom acceptor. The donation orbital in the third-body M was assumed to be a nonbonding p orbital on the halogen atom (X') in the methyl halide, while the accepting orbital in the halogen atom X is the singly occupied p orbital. These assumptions lead to the geometry shown in Figure 1.

The quadrupole moments of bromine and iodine atoms are not known. However, since the bromine and iodine atoms are both axially symmetric charge distributions with their symmetry axes passing through a singly occupied p_z orbital, it was assumed that the z component of the quadrupole moment is principally determined by the charge distribution in this singly occupied orbital with the filled inner orbitals presenting a spherical charge. The quadrupole moment of the resulting cylindrically symmetric charge distribution is equivalent to the z component, Q_z, and the following expression can be used to calculate the quadrupole moment of p_z states[25]

$$Q_z = [-N^2(N^2 - 1)er^2]/Z^2 \qquad (10)$$

where r is the van der Waals radius of the halogen atom, e is the electronic charge, N is the effective quantum number, and Z is the nuclear charge corrected for screening by the other electrons in the atom. The values for N and Z were calculated from the rules developed by Slater.[26,27] The resulting halogen atom electronic quadrupole moments are

$$Q_{Br} = -5.5 \times 10^{-26} \text{ esu cm}^2$$

$$Q_I = -9.2 \times 10^{-26} \text{ esu cm}^2$$

The polarizability–polarizability interaction was calculated from the expression derived by London[28] for the case of interaction between unlike point atoms or molecules.

$$E_{\alpha-\alpha} = \frac{-3I_M I_X \alpha_M \alpha_X}{2(I_M + I_X)r_{MX}^6} \qquad (11)$$

In this expression I is the ionization potential, α the polarizability, and r_{MX} the sum of the van der Waals radii of X' and X.

The permanent dipole of the methyl halide molecule results in an electric field in a direction perpendicular to the dipole, which is in the direction of the X atom (Figure 1). The dipole (M)–polarizability (X) inter-
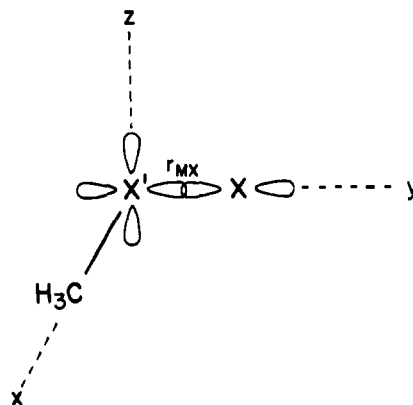
(25) A. D. Buckingham, Quart. Rev., Chem. Soc., 13, 183 (1959).
(26) J. C. Slater, Phys. Rev., 36, 57 (1930).
(27) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," Wiley, New York, N. Y., 1967, p 163.
(28) L. A. Carreira and W. B. Person, J. Amer. Chem. Soc., 94, 1485 (1972).

Figure 1. Assumed M–X geometry for calculation of non-charge-transfer interactions.

action energy between M and X is thus given by[29]

$$E_{D-X} = \alpha_X D_M^2/2r_{MX}^6 \qquad (12)$$

The dipole–quadrupole interaction was obtained by dividing the dipole moment of the alkyl halide into point charges located at the atomic centers A (C and X' in CH_3X') and calculating the interaction between these point charges, q_A, and the halogen atom quadrupole moment, Q_X. The energy of this interaction is then given by[15]

$$E_{D-Q} = \sum_A \frac{q_A Q_X}{2r_{AX}^3}(3\cos^2\theta_X - 1) \qquad (13)$$

where θ_X is the angle formed by the z component of the quadrupole moment of X, which is along the line of centers of X and X', and the line between X and the atomic center A.

The quadrupole–quadrupole interaction was calculated similarly by dividing the experimental quadrupole moment into point quadrupoles located at the atomic centers in the methyl halides; the point quadrupole located at atomic center A possessing charge q_A is

$$Q_A = q_A r_A^2 \qquad (14)$$

and r_A is the distance between atomic center A and the center of mass. The Q–Q interaction can then be expressed as[15]

$$E_{Q-Q} = \sum_A \frac{3Q_A Q_X N}{4r_{AX}^5} \qquad (15)$$

where, for the configuration chosen above for the M–X species

$$N = (1 - 5\cos^2\theta_A - 5\cos^2\theta_X +$$
$$17\cos^2\theta_A\cos^2\theta_X + 2\sin^2\theta_A\sin^2\theta_X +$$
$$16\sin\theta_A\sin\theta_X\cos\theta_A\cos\theta_X)$$

and θ_A is defined in a similar manner to θ_X for the quadrupole moment on A.

The parameters used in these calculation are given in Table II, and the resulting interaction energies are summarized in Table III.

As pointed out by Hanna,[15] and further demonstrated here, the quadrupole contributions are significant in the electrostatic interactions involving polar third

(29) F. O. Rice and E. Teller, "The Structure of Matter," Wiley, New York, N. Y., 1949, p 66.

Table II. Parameters Used in Calculating M–X Interactions

	I_D,[a] eV	E_A,[b] eV	$\alpha \times 10^{25}$, cm^3	$Q^e \times 10^{26}$, esu cm^2	$D^f \times 10^{18}$, esu cm
CH$_3$Br	10.53		55.5[c]	3.55	1.81
CH$_3$Cl	11.33		45.6[c]	1.23	1.87
Br		3.65	33.4[d]	−55	
I		3.24	51.1[d]	−92	

[a] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1959). [b] S. P. Tandon, M. P. Bhutra, and K. Tandon, *Indian J. Phys.*, **41**, 70 (1967). [c] H. H. Landolt and Börnstein, "Zahlenwerte und Functionen," Vol. I, Part 3, Springer-Verlag, Berlin, 1951, p 511. [d] J. Ketelaar, "Chemical Constitution," Elvesier, Amsterdam, 1958, p 201. [e] D. Vanderhart and W. Flygare, *Mol. Phys.*, **18**, 77 (1970). [f] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1964–1965, p E-28.

Table III. Non-Charge-Transfer Interaction Energies Contributing to M–X Stability (eV)

M–X	$D \leftrightarrow Q$	$Q \leftrightarrow Q$	$\alpha \leftrightarrow \alpha$	$D \leftrightarrow \alpha$	Total non-CT
CH$_3$Br–Br	−0.26	−0.11	−0.04	−0.0005	−0.41
CH$_3$Cl–Br	−0.31	−0.05	−0.05	−0.001	−0.41
CH$_3$Br–I	−0.28	−0.14	−0.05	−0.001	−0.47
CH$_3$Cl–I	−0.41	−0.06	−0.05	−0.0015	−0.52

bodies and cannot be neglected in the evaluation of the total stabilization of the intermediate species. On the other hand, recent calculations[30] indicate that the halogen atom electric quadrupole has negligible effect on the potential between a halogen atom and an inert gas atom.

For both the methyl chloride and methyl bromide systems, these calculations indicate that (a) for a given methyl halide M the total non-CT electrostatic interaction is greater for iodine atoms than for bromine atoms, and (b) for a given halogen atom X the interaction is independent of or increased in only a minor way with increasing ionization potential. The first conclusion was assumed qualitatively in the introductory section based solely on the relative halogen atom polarizabilities. The relative insensitivity of the interaction to the ionization potential of M, in contrast to earlier predictions,[3,14] further shows the need to include multipoles of higher order than 2.

Estimation of Charge-Transfer Contributions to M–X Stability. The absolute evaluation of charge-transfer energies is very difficult and subject to large uncertainties as a result of errors in experimental determinations of complex dipole moments and extinction coefficients of the CT electronic transition.[15] Carreira and Person have recently carried out INDO and CNDO/2 molecular orbital calculations on several complexes[28] but were limited to atoms in the first and second rows of the periodic table.

In the work reported here we are primarily interested in the trends to be expected in the M–X charge-transfer binding energies (and hence in the recombination rate constant) by varying M or X. For relatively strong interactions, it has been shown that the variation method leads to the following expression for the energy of the spectral absorption band.[31]

$$h\nu_{CT} = [(W_1 - W_0)/(1 - S_{01})^2][1 + 4\beta_0\beta_1/(W_1 - W_0)^2]^{1/2} \quad (16)$$

where S_{01} is the overlap integral, β_0 and β_1 are the resonance integrals $(H_{01} - S_{01}W_0)$ and $(H_{01} - S_{01}W_1)$, respectively, and W_0 and W_1 are the respective energies of the nonbond and dative structures. Thus, $W_1 - W_0 = I_D - E_A + G_1 - G_0$, where G_0 and G_1 are the interactive energies between donor and acceptor species in the ground and excited state, respectively. The

resonance integral β_0 is difficult to evaluate but may be determined from the appropriate plot of eq 16; it is closely related to the separation of the donor and acceptor species in the complex and to the energy of formation of the complex and thus is indicative of the strength of the complex. The best fit of the spectral data reported previously from this laboratory for the alkyl halide donors,[10] using the method and graph of Mulliken and Person,[32] gives $\beta_0 = -1.0$ eV for iodine atoms and -1.6 eV for bromine atoms. These results are thus in qualitative agreement with the generalization that the strength of an acceptor (and hence the CT interaction energy for a given donor, assuming identical geometry and interatomic distance in the complex) increases with its electron affinity.[11] Similarly, the donor strength of a molecule increases with decreasing ionization potential, resulting also in increasing CT interaction with decreasing ionization potential for a series of comparable donors with a given acceptor.[11]

Comparison of Bromine and Iodine Atom Recombination. The gas-phase third-order rate constants, k_M, for bromine and iodine recombination are given in Table I. For both halogens the rate constant decreases rather consistently with increasing ionization potential of M. However, the effect is much more pronounced for the recombination of bromine atoms, so much so that while the rate of recombination of bromine atoms is approximately six times faster than that of iodine with benzene ($I_D = 9.24$ eV) as a third body, iodine atom recombination is slightly greater than bromine recombination with methyl chloride ($I_D = 11.33$ eV).

Based on the "complex mechanism" (eq 1, 2, and 3), the stability of the intermediate (M–X) essentially determines the efficiency of the recombination. These results thus suggest that both charge-transfer and classical electrostatic forces must be considered in the stability interactions. For low-ionization potential third bodies, charge-transfer interactions are predominant ($k_{Br} > k_I$), whereas at high-ionization potentials the non-charge-transfer forces become relatively more important ($k_I > k_{Br}$).

In the recent work of DeGraff and Lang,[19] as well as for other inert gas third bodies, it was found that k_I is either equal to or only slightly greater than k_{Br} for all of the third bodies except for the molecular halogens themselves, and it was concluded that charge-transfer interactions are still important but that factors other than the electron affinity of the halogen atom must be the dominant influence. It is clear, however, that the range of ionization potentials used by DeGraff and Lang (except for C$_6$F$_6$) puts the recombination in the region of predominant electrostatic interactions.

(30) T. Kihara and K. Yamazaki, *Chem. Phys. Lett.*, **16**, 32 (1972).
(31) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969, p 12.

(32) Reference 31, pp 148 and 149.

This is further shown by the relative insensitivity of k_M to large variations in I_p at the higher ionization potentials as predicted from the results given in Table III.

Halogen atoms have very large electron affinities in comparison to most acceptors involved in charge-transfer studies and therefore should most favorably exhibit CT binding in the ground state. The results of this work showing predominant CT interactions only at the lower ionization potentials even for these favorable acceptors suggest that classical electrostatic forces may be predominant for most systems even when strong CT spectra are present.

Formation Constants of M–X. In principle, the formation constants K_c of the intermediate M–X can be obtained from spectral measurements as a function of donor pressure, in the same manner as for transient halogen atom complexes in the liquid phase.[33] In practice, pressure limitations and the resulting small percentage complexation and small absorbances make spectral determinations of K_c and extinction coefficients very difficult in the gas phase even for stable molecular complexes,[34] and the experimental errors in absorbance changes for the transient gas-phase complexes involved in the recombinations reported here preclude formation constant determinations for these systems by this technique.

It is possible, however, to make a rough estimation of K_c from the rates of recombination. On the basis of the mechanism represented by eq 1–3 (which neglects the reaction $2M-X \rightarrow X_2 + 2M$ because of the low degree of complexation), the reciprocal of the experimental second-order rate constant k_2 (eq 5) is given by

$$\frac{1}{k_2} = \frac{1}{k_3 K_c[M]} + \frac{2 + K_c[M]}{k_3} \cong \frac{1}{k_3 K_c[M]} + \frac{2}{k_3} \quad (17)$$

if $K_c[M] \ll 2$. Step 3 should occur with collisional frequency (with the appropriate steric factor) so that k_3 would be expected to be approximately the same for all of the alkyl halide third bodies. The data for bromine atom recombination were plotted for the four alkyl halide systems according to eq 17, an average value for k_3 was obtained $(4.5 \times 10^{10}\ 1./(\text{mol sec}))$ from the intercepts, and the formation constants for the four systems were determined from the least-squares plots according to eq 17 using the average k_3 value to determine the intercept. These values for K_c are summarized in Table IV. As expected, these formation constants

Table IV. Estimated Formation Constants at $25°$ for Bromine Atom–Alkyl Halide Complexes

M	K_c, l./mol
Ethyl bromide	6.5 ± 4
Methyl bromide	2.9 ± 2.9
Ethyl chloride	1.2 ± 0.5
Methyl chloride	0.8 ± 0.8

are larger than that for the I–Ar complex (0.3 l./mol), as determined from high-pressure I-atom recombination measurements.[35]

The collisional rate constant k_3 can be estimated from collision theory, assuming hard sphere (van der Waals radii) interactions and reaction occurring at every collision. On this basis, $(k_3)_{calcd} \cong 1.3 \times 10^{11}\ 1./(\text{mol sec})$, thus leading to an experimental total (geometric plus electronic) steric factor of ca. 0.35 when compared to the average value for k_3 cited above.

Much has been published concerning the appropriate electronic statistical factor to use in the recombination of halogen atoms. Even assuming recombination occurs only with ground-state $(^2P_{3/2})$ atoms, there are 16 possible combinations, of which only half (eight) lead to attractive forces and hence stable states. If, however, only combination to the ground molecular state leads to effective recombination, then the appropriate factor is 1/16, and this has been assumed by Porter and Smith.[6] On the other hand, Eusuf and Laidler[12] suggest that any of the eight attractive states can lead to recombination with appropriate energy transfer, so that the correct statistical factor is 1/2. Mulliken[36] has pointed out, however, that intraatomic spin–orbit coupling prevents most of the attractive states from having pronounced minima. Recent emission studies have shown that recombination of ground-state bromine atoms does lead to appreciable population of electronically excited molecular bromine[37,38] in support of the conclusion to be drawn from this work that the appropriate statistical factor is greater than 1/16 and possibly close to 1/2.

Irreversible Photobromination. As pointed out above, side photobromination reactions did occur with all third bodies used in this work, leading in each case to a net decrease in molecular bromine absorbance. The very small amounts of reactants present in these gas-phase systems and the minor extent of reaction per flash, however, precluded any detailed or quantitative determination of the overall mechanism.

Product analysis was attempted only on the most reactive system, bromine and benzene. Mass spectrometric, infrared, and gas chromatographic analyses gave no evidence of substitution products. Two major products were separable on a silicone gum rubber–Diatoport S chromatograph column at 170°: one was definitely identified as hexabromocyclohexane; the other probably tetrabromocyclohexene (the major product in low-bromine concentration liquid-phase photolyses[39]).

The addition reaction

$$Br \cdot + C_6H_6 \longrightarrow C_6H_6Br \cdot \quad (18)$$

involving a ground-state $(^2P_{3/2})$ bromine atom and resonance-stabilized radical is estimated thermochemically to be endothermic by approximately 40 kJ/mol and therefore highly unlikely as an initiating step unless a very efficient chain reaction results. The excitation energy of $^2P_{1/2}$ bromine atoms is 44 kJ/mol,[40] so that a more probable first addition reaction would involve only excited atoms. To check this, the overall quantum yield of photobromination was determined following

(33) R. L. Strong and J. Perano, *J. Amer. Chem. Soc.*, **83**, 2843 (1961); *ibid.*, **89**, 2535 (1967).
(34) J. Grundnes, M. Tamres, and S. N. Bhat, *J. Phys. Chem.*, **75**, 3682 (1971).
(35) H. Hippler, K. Luther, and J. Troe, *Chem. Phys. Lett.*, **16**, 174 (1972).
(36) R. S. Mulliken, *J. Chem. Phys.*, **55**, 288 (1971).
(37) R. J. Browne and E. A. Ogryzlo, *J. Chem. Phys.*, **52**, 5774 (1970).
(38) M. A. A. Clyne, J. A. Coxon, and A. R. Woon-Fat, *Trans. Faraday Soc.*, **67**, 3155 (1971).
(39) G. D. Howard, Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1966.
(40) R. J. Donovan and D. Husain, *Chem. Rev.*, **70**, 489 (1970).

photoexcitation with a uranyl nitrate flash filter solution[10] (which transmitted throughout the bromine absorption band and thus led to both $^2P_{3/2}$ and $^2P_{1/2}$ atoms) and with a potassium chromate–dichromate flash filter solution which transmitted only above the 511-nm convergence limit for bromine[41] (1% at 516 nm, 4% at 520 nm, 55% at 540 nm), so that only ground-state bromine atoms were produced. Within the rather large experimental errors, the two quantum yields were identical (0.31 vs. 0.38). Although some reactions involving only $^2P_{1/2}$ halogen atoms have been observed with photolysis above the convergence limit,[42] the effect

is strongly wavelength dependent and extends only a few kilojoules into the banded region. It is thus concluded that photobromination of benzene resulting in this work is not initiated solely by excited bromine atoms.

Although the gas-phase formation constant is not known for either the molecular or atomic bromine complex with benzene, it is highly unlikely that either complex could be present in sufficiently high concentration to participate in the bromination reactions to the extent observed, again unless a very efficient chain process results. The fact that good second-order kinetic plots result from assuming that all of the bromine loss occurs during the flash (<75 μsec), with all third bodies used and under all flash conditions, suggests, however, that some species other than $^2P_{3/2}$ bromine atoms initiate the irreversible photobromination.

(41) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 184.
(42) A. B. Callear and J. F. Wilson, *Trans. Faraday Soc.*, **63**, 1358 (1967).

Fluorescence Studies of Europium(III) and o-Benzoylbenzoate in Ethanol–Water Solution

Stephen P. Tanner* and Donna L. Thomas

Contribution from the Department of Chemistry, The University of West Florida, Pensacola, Florida 32504. Received July 21, 1973

Abstract: Fluorescence measurements on ethanol–water solutions of europium(III) and o-benzoylbenzoate (o-BB) have shown that energy transfer takes place from the organic ligand to the europium ion followed by narrow line emission characteristic of the lanthanide ion. From the intensities of the emission line at 590 nm, stability constants for the Eu(o-BB) complex have been calculated, and these constants are in agreement with those determined by potentiometry. The results are interpreted to indicate that energy transfer takes place only when a complex is formed between the ligand and lanthanide ion. No energy transfer is observed in strongly acid solution, conditions in which complex formation is negligible.

Since the first observance of energy transfer from an organic absorber to a rare-earth ion with subsequent narrow line emission,[1] extensive investigation has been carried out on such systems, stimulated by the interest in liquid laser devises. Evidence for both intermolecular and intramolecular energy transfer has been obtained. The investigation of energy transfer within rare-earth chelates has established that intramolecular energy transfer takes place between the excited triplet state of the ligand and a resonance level of the metal ion.[2-4] Actinide chelates show a similar behavior.[5] Several groups have observed transfer of energy between aromatic ketones and lanthanide ions in organic liquid solutions.[6-8] Heller and Wasserman[6] suggested that in these cases the energy transfer takes place *via* a second-order diffusion-controlled mechanism, i.e., an intermolecular transfer process. Energy transfer from

benzophenone to tris(hexafluoroacetylacetonato)europium(III) was shown to take place through an intermolecular mechanism from ketone to ligand followed by an intramolecular energy transfer from ligand to metal ion.[9] Both intermolecular energy transfer[10] and intramolecular energy[11,12] transfer have been utilized in the analysis of low concentrations of luminescent rare-earth ions.

Relatively few investigations have been carried out on aqueous systems. A study of the fluorescence of europium(III) in aqueous solution in the presence of potential ligands such as NO_3^-, Cl^-, ethylenediaminetetraacetate (EDTA), and diethylenetriaminepentaacetate (DTPA) showed that complexation caused a general intensification of the spectra, a shift to longer wavelengths, and increased crystal field splitting.[13] This effect was particularly marked for strongly chelating ligands such as EDTA and DTPA. In these cases, however, no energy transfer from ligand to the europium ion was observed. In aqueous solutions containing

(1) S. I. Weissman, *J. Chem. Phys.*, **10**, 214 (1942).
(2) R. E. Whan and G. A. Crosby, *J. Mol. Spectrosc.*, **8**, 315 (1962).
(3) G. A. Crosby, R. E. Whan, and J. J. Freeman, *J. Phys. Chem.*, **66**, 2493 (1962).
(4) A. N. Sevchenko and A. G. Morachevskii, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **15**, 628 (1951).
(5) L. J. Nugent, J. L. Burnett, R. D. Baybarz, G. K. Werner, S. P. Tanner, J. R. Tarrant, and O. L. Keller, Jr., *J. Phys. Chem.*, **73**, 1540 (1969).
(6) A. Heller and E. Wasserman, *J. Chem. Phys.*, **42**, 949 (1965).
(7) E. Matovich and C. K. Suzuki, *J. Chem. Phys.*, **39**, 1442 (1963).
(8) M. L. Bhaumik and M. A. El-Sayed, *J. Phys. Chem.*, **69**, 275 (1965).
(9) M. A. El-Sayed and M. L. Bhaumik, *J. Chem. Phys.*, **39**, 2391 (1963).
(10) W. J. McCarthy and J. D. Winefordner, *Anal. Chem.*, **38**, 848 (1966).
(11) G. Alberti, R. Bruno, M. A. Massucci, and A. Saini, *Gazz. Chim. Ital.*, **95**, 1021 (1965).
(12) G. Alberti and M. A. Massucci, *Anal. Chem.*, **38**, 214 (1966).
(13) P. K. Gallagher, *J. Chem. Phys.*, **41**, 3061 (1964).