Charge Transfer Spectra of Halogen Atoms in Water. Correlation of the Electronic Transition Energies of Iodine, Bromine, Chlorine, Hydroxyl, and Hydrogen Radicals with Their Electron Affinities

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Abstract: Bromine and chlorine atoms were produced in water from the photolysis of acid solutions of Br_2 and Cl_2 and from C_6H_5Br, $ClCH_2COCH_3$, and other halogenated compounds. Using the laser photolysis technique (optical excitation at 265 nm, single pulses ~15 nsec duration), the observed transient absorption spectra with maxima at 275 and ~315 nm have been assigned to charge transfer complexes of Br· and Cl· atoms, respectively, with water molecules. A simple theory is presented, using a model of point charges at the centers of solvent cavities in a continuous dielectric, to calculate the electronic transition energies of these complexes in solution. The theory is shown to apply to the absorption bands of Br, Cl, I, OH, and H radicals in water. A correlation between the $h\nu_{max}$ and the electron affinities of these radicals is presented. Direct evidence is also presented for the reaction $Br_3^- + h\nu \rightarrow Br + Br_2^-$. The kinetics of the reaction $Br + Br^- \rightleftharpoons Br_2^-$ is analyzed, $k_3 = 1.1 \pm 0.1 \times 10^{10}\ M^{-1}\ sec^{-1}$ and $k_{-3} = 7 \pm 2 \times 10^5\ sec^{-1}$.

The absorption spectrum of iodine atoms in water has recently been reported,[1] the band with a maximum at 255 nm being assigned to a charge-transfer (CT) transition from a water molecule to an iodine atom. It follows then that bromine and chlorine atoms, which have higher electron affinities, are expected to display charge-transfer absorptions at longer wavelengths. For several aromatic donor molecules, however, the CT energy of the Cl complex is the highest.[2]

This possibility is examined in the present work. The transient absorption spectra of Br and Cl atoms in water are reported for the first time. Secondary fast reactions occur which shorten their lifetimes below the microsecond time scale and convert the X atoms to other transient species with overlapping absorption spectra. The single pulse laser photolysis technique with time resolution ~15 nsec was therefore used in this study.

The new results are used to explain the known, but rather puzzling, absorption spectra of OH and H in water.[3] The spectra, in particular that of the H atom, are much removed from the gas phase transitions, and until now no satisfactory interpretation has been provided. A correlation between $h\nu_{max}$ and the electron affinities of the Cl, Br, I, OH, and H radicals in water is presented. The kinetics of the reaction $Br + Br^- \rightleftharpoons Br_2^-$ has also been studied.

Experimental Section

A frequency-quadrupled neodymium laser (Holobeam, Inc.) emitting at 265 nm with single pulses of ~15 nsec duration and ~20 mJ was used. The monitoring light was at a right angle to the laser beam, and the output of a pulsed 250-W Osram xenon lamp was used. The reaction cell (10-mm optical path) was enclosed in a temperature-controlled jacket.

Bromine (Alfa, optronic grade), chlorine gas (Matheson, lecture bottle), and other chemicals were of the highest purity available commercially and were used without further purification. The solutions were freed from air by bubbling with argon before adding the volatile solutes.

Results

Bromine Atom. Photolysis of Br_2. Aqueous solutions of bromine (2.5 m*M*) containing 0.1-1.5 *M* $HClO_4$ to suppress hydrolysis were photolyzed. Immediately after the 15-nsec laser pulse, two transient absorptions were observed: one appearing as a shoulder at ~270 nm (Figure 1, curve 1) and decaying, while the oher with λ_{max} ~360 nm "growing-in" *after* the laser pulse, and then decaying on a much slower time scale. Both the decay of the 270-nm transient and the growth of the 360-nm transient follow first-order kinetics with equal rate constants.

On adding Br^- to the system, these absorptions were enhanced and the two rate constants, while still the same, increased linearly with the Br^- concentration (Figure 2).

The spectrum around 360 nm is identical with that of Br_2^- [4] and the results indicate that the 270 nm transient is the precursor of Br_2^-. The precursor was fully formed during the pulse duration and so it could not be produced by secondary reactions involving species present at concentrations below ~1 m*M* (e.g., Br^- or Br_3^-). The precursor could be a Br atom or its complex with water, Br_2, H^+, or ClO_4^-. Its exact nature will be discussed below. In the meantime it is designated as Br.

To obtain the correct spectrum of Br one must correct for absorption changes caused by depletion of the photolyzed solution and the formation of any products, up to the time of measurement (~35 nsec from the beginning of the pulse). This correction turned out to be relatively large.

Even with no Br^- initially added, the bromine solutions contained[5] 5-15 μM Br^- and 0.2-0.6 μM Br_3^-, and their absorbance at 265 nm was 0.1-0.2. Br_3^- has a very intense band maximum at 266 nm[6] with ϵ_{max} $3.8 \times 10^4\ M^{-1}\ cm^{-1}$. Part of the 265-nm light is, therefore, absorbed by Br_3^- to generate equimolar amounts of Br and Br_2^- via reaction 1[7]

$$Br_3^- \xrightarrow{h\nu} Br + Br_2^- \tag{1}$$

in parallel with reaction 2. This explains why Br_2^- was always formed in considerable amounts during the 15-nsec laser pulse.

$$Br_2 \xrightarrow{h\nu} Br + Br \tag{2}$$

The scheme proposed above was further confirmed by comparing the absorbance produced at ~360 nm, 20 nsec after the pulse (A_i), with the equilibrium absorbance observed after the pulse (A_{eq}), when Br_2^- has just reached its equilibrium concentration via reaction 3. At this point in time no appreciable decay of Br_2^- occurred. The ratio A_{eq}/A_i was higher than 2 when no Br^- was initially added (A_{eq}/A_i ~ 4 for 2.5 m*M* Br_2 + 1.4 *M* $HClO_4$) but approached

$$Br + Br^- \rightleftharpoons Br_2^- \tag{3}$$

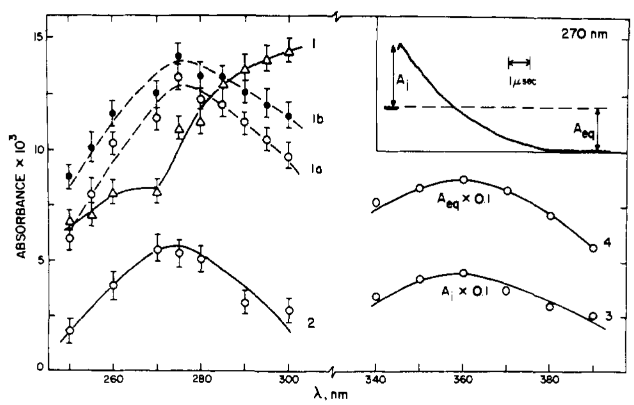

Figure 1. Transient absorption spectra produced from the laser photolysis of aqueous solutions of bromine-bromide and bromobenzene at 25°, at specified times after the pulse: curve 1, 2.5 m*M* Br_2, 1.4 *M* $HClO_4$, measured at 20 nsec after the laser pulse. The dashed curves are the stages in deriving the correct spectrum of B (see text); a typical oscilloscope trace is shown in the insert. Solutions containing 2.5 m*M* Br_2, 0.12 *M* $HClO_4$, 0.52 m*M* KBr were read at 20 nsec (curve 3) and 1 μsec (curve 4) after the pulse. Curve 2 shows the transient spectra from a 1.4 m*M* C_6H_5Br solution read at 20 nsec after the pulse.

this value on adding Br^-. When that happened (as in Figure 1, curves 3 and 4), only reactions 1 and 3 were taking place, with Br almost completely converted to Br_2^- (see below for the equilibrium constant K_3). This result provides direct evidence that reaction 1 is indeed the primary photochemical process for Br_3^-.

The spectrum of Br was corrected for the depletion of Br_3^- and Br_2 and for the production of Br_2^- by considering the various contributions to A_i and A_{eq}

$$A_i = A_i(\mathrm{Br}) + A_i(\mathrm{Br_2^-}) + \Delta A_i(\mathrm{Br_3^-}) + \Delta A_i(\mathrm{Br_2}) \tag{4a}$$

$$A_{eq} = A_{eq}(\mathrm{Br}) + A_{eq}(\mathrm{Br_2^-}) + \Delta A_i(\mathrm{Br_3^-}) + \Delta A_i(\mathrm{Br_2}) \tag{4b}$$

since Br_3^- and Br_2 could not be appreciably regenerated during the time required for reaction 3 to reach equilibrium. In terms of the oscilloscope trace, A_{eq} is the absorbance at which the trace first levels off. When no Br^- was initially added, A_{eq} was found to be positive at $\lambda > 280$ nm and negative at shorter wavelengths (see, e.g., Figure 1, insert). In all cases the solutions *finally* regained their original absorptions. Thus $(A_i - A_{eq})$ is simply the "initial" transient absorbance measured not relative to the base line but relative to the equilibrium value. A plot of $(A_i - A_{eq})$ is shown in Figure 1, curve 1a.

From expressions (4) we derive

$$A_i(\mathrm{Br}) - A_{eq}(\mathrm{Br}) = (A_i - A_{eq}) + [A_{eq}(\mathrm{Br_2^-}) - A_i(\mathrm{Br_2^-})] \tag{5}$$

The last term could be evaluated at any wavelength from its value at 360 nm (where the spectral changes are almost fully determined by Br_2^-) and the known spectrum of Br_2^- down to 250 nm.[4b] The correct spectrum of Br should have the same shape as $A_i(Br) - A_{eq}(Br)$; it is shown in Figure 1 (curve 1b), with λ_{max} 275 nm.

When only reactions 1 and 3 take place, and Br is fully converted to Br_2^-, the extinction coefficient of Br could be determined from the relation

$$\epsilon(\mathrm{Br}) = \epsilon(\mathrm{Br_2^-})_{360}\frac{A_i(\mathrm{Br})}{A_i(\mathrm{Br_2^-})_{360}} \tag{6}$$

with $A_i(Br)$ determined from eq 5, $A_{eq}(Br) = 0$. Using the value[4b] $\epsilon(Br_2^-)_{360} = 1.2 \times 10^4$ M^{-1} cm^{-1}, one thus obtains $\epsilon(Br)_{max} = 3500 \pm 500$ M^{-1} cm^{-1} (Br in bromobenzene[8] has ϵ 2800 ± 500 M^{-1} cm^{-1}). From the same experiments, the quantum yield of reaction 1 could be derived from the amount of light energy absorbed by Br_3^- at 265 nm and the amount of Br_2^- initially produced: $\phi_{Br} = 0.15$.

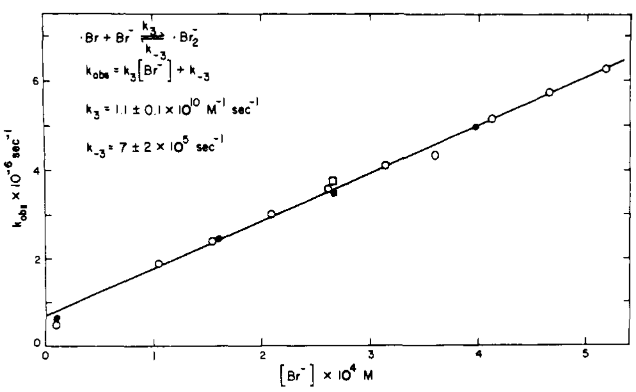

Figure 2. The kinetics of the reaction $Br + Br^- \rightleftharpoons Br_2^-$ at 25°. The dependence of the observed first-order rate constant upon the concentration of Br^-: buildup of Br_2^- (open symbols) and decay of Br (dark symbols) (2.5 m*M* Br_2, 0.12 *M* $HClO_4$ (○); 1.4 m*M* C_6H_5Br (□)).

Air was found to have no effect on the results reported here. We could not confirm the production of BrO_2 as previously reported,[9] but this failure could be the outcome of its low extinction coefficients.

Photolysis of Bromobenzene. Aqueous solutions of bromobenzene (1.4 m*M*) were laser photolyzed. Immediately after the pulse a transient was observed with λ_{max} 275 nm (Figure 1, curve 2), formed within the pulse duration. In the presence of Br^- the formation of Br_2^- was observed, and again its rate was equal to the decay rate of the 275-nm transient (Figure 2). Air did not affect these results.

The new spectrum is very similar to the spectrum assigned to Br (curve 1b, Figure 1). This excludes, therefore, the possibility that it is due to a complex of Br with Br_2, H^+, or ClO_4^-. In analogy with C_6H_5I, bromine atoms are produced via reaction 7.[10]

$$\mathrm{C_6H_5Br} \xrightarrow{h\nu} \mathrm{C_6H_5} + \mathrm{Br} \tag{7}$$

The Br spectrum should be corrected for that of the phenyl radical, as well as any possible contribution from the triplet absorption of C_6H_5Br. The latter is not known. The spectrum of $C_6H_5\cdot$ is known,[11] its extinction coefficient is relatively weak in this wavelength region. The correction cannot significantly affect the band shape.

As in the previous case, the yield of Br could be determined by converting all the Br atoms to Br_2^-. Here, at equilibrium, 1 mol of Br corresponds to only 1 mol of Br_2^- (reactions 7 and 3; compare with reactions 1 and 3). This enables one to derive: $\epsilon_{max}(Br)$ ~4500 M^{-1} cm^{-1} and $\phi(Br)$ ~ 0.03. Taking the value 400 M^{-1} cm^{-1} for ϵ of the phenyl radical at 280 nm,[11b] the corrected value of ϵ_{max} comes closer to 4000 M^{-1} cm^{-1}. This is in good agreement with the value derived above from the Br_2-Br^- system. The low $\phi(Br)$ value supports the conclusion[10] that the yield for the photodissociation of C-X decreases steeply on going from C_6H_5I to C_6H_5Cl (see also below).

The Br absorption was found to be replaced by a long-lived absorption, probably resulting from the reactions of Br and C_6H_5 with C_6H_5Br.[12] On adding Br^-, this effect became less pronounced due to the removal of Br (reaction 3).

Photolysis of Bromoform. A transient optical absorption was observed with λ_{max} ~275 nm, produced during the laser pulse. The spectrum of the $CHBr_2$ radical formed is, however, not known. This system deserves further investigation.

Kinetics. When $[Br^-] \gg [Br]$, the conditions present in

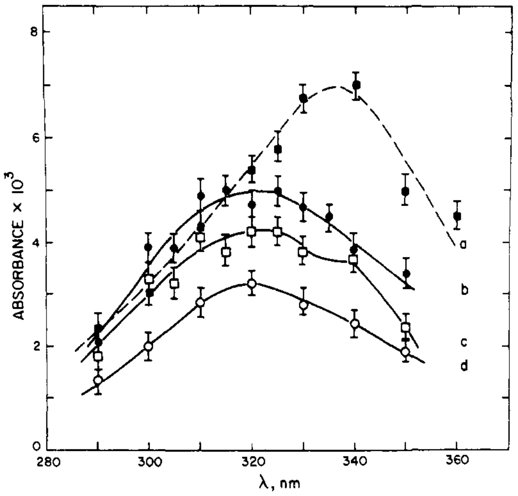

Figure 3. Transient absorption spectra produced from the laser photolysis of aqueous solutions of chlorine and choroacetone at specified times after the pulse: 7 mM Cl_2, 4 N $HClO_4$, 12°, 20 nsec (curve c) and 1 μsec (curve a); 7 mM Cl_2, 6 N $HClO_4$, 25°, 20 nsec (curved); 28 mM $ClCH_2COCH_3$, 12°, 20 nsec (curve b).

all our experiments, the general solution of the kinetics of reaction 3 is

$$t = \frac{1}{k_3[\mathrm{Br}^-] + k_{-3}} \ln \frac{A_{eq} - A_i}{A_{eq} - A} \qquad (8)$$

where A_i, A, and A_{eq} denote the absorbance of Br_2^- at time $t = 0$, t, and equilibrium. Thus the growth of Br_2^- should follow a first-order kinetics with

$$k_{obsd} = k_3[\mathrm{Br}^-] + k_{-3} \qquad (9)$$

As already stated, all the systems examined showed this behavior. From the plot of k_{obsd} against $[Br^-]$ (Figure 2) one can derive: $k_3 = (1.1 \pm 0.1) \times 10^{10}\ M^{-1}\ sec^{-1}$, $k_{-3} = (7 + 2) \times 10^5\ sec^{-1}$, and $K_{eq} = (1.7 \pm 0.7) \times 10^4\ M^{-1}$. The values of k_{-3} and K_{eq} are considerably different from these derived from indirect measurements.[13] The rate $k(I + I^- \rightarrow I_2^-) = 1.3 \times 10^{10}\ M^{-1}\ sec^{-1}$ (ref 14) is also diffusion controlled and nearly the same as k_3. The dissociation of I_2^- is, however, slower than for Br_2^-.

Chlorine Atom. Photolysis of Chlorine. Aqueous solutions of 7 mM Cl_2 in 4 N $HClO_4$ were photolyzed. Figure 3 (curves c and a) shows the transient absorption observed immediately after the 15-nsec laser pulse and 1 μsec later. The former spectrum has λ_{max} ~320 nm and is later replaced by a transient with λ_{max} ~340 nm, close to that of Cl_2^-.[4a,15] The formation of Cl_2^- was too fast for kinetic study. It is, in part, produced during the pulse (note the "shoulder" on curve c, Figure 3). Since its absorption was always higher than that of the 320-nm transient, the decay of the latter could not be followed. The whole absorption decreased on raising the $HClO_4$ concentration.

We believe that the main contribution to the 320-nm band is due to Cl atoms (or their complex with water) for the following reasons. (a) Its rise time is equal to the pulse duration. (b) Other possible chlorine species have different λ_{max}: Cl_2^- (340 nm[15]), $ClOH^-$ (350 nm[15]), ClO (280 nm[16]). ClO and $ClOH^-$ could result from the photolysis of ClOH (see below). (c) A similar absorption was produced from the laser photolysis of chloroacetone (Figure 3, curve b). This rules out the possibility of the transient being Cl_3, Cl_2OH (from OH produced by reaction 10 and Cl_2), or a complex of Cl with H^+, ClO_4^-.

Owing to the strong hydrolysis of Cl_2, the Cl_2 solutions contained[17] ~1 mM Cl^-, 1 mM ClOH, and 1 μM Cl_3^-. Considering the spectra of these species,[17] most of the 265-nm light was absorbed by ClOH which, like other hypohalites,[18] most probably undergoes reaction 10. Increasing

$$\mathrm{ClOH} \xrightarrow{h\nu} \mathrm{Cl} + \mathrm{OH} \qquad (10)$$

$[HClO_4]$ to 6 N somewhat reduces the hydrolysis (less Cl_2^- is produced during the pulse; compare curves c and d), but the features are essentially the same.

The new spectrum should be corrected for the depletion of ClOH and the production of Cl_2^- and possibly $ClOH^-$, produced by reactions 10 and 11.[15] The first correction

$$\mathrm{Cl}^- + \mathrm{OH} \longrightarrow \mathrm{ClOH}^- \qquad (11)$$

should be small, owing to the low extinction coefficients of ClOH in this region (the same applies to any possible depletion of Cl_2 or Cl_3^-),[17] but the correction for Cl_2^- may be very significant, owing to the high values of $k(Cl + Cl^-)$, $\epsilon(Cl_2^-)$,[15] and the considerable concentration of Cl^- in the system. The correction of $ClOH^-$ should be smaller because $k(OH + Cl^-)$ and $\epsilon(ClOH^-)$ are considerable lower.[15] Any estimate of these corrections is risky. However, Cl_2^- and $ClOH^-$ could not be the major contributors to the observed absorptions because the peak at 320 nm is distinctly removed from their maxima (340 and 350 nm, respectively[15]). Therefore, we believe that λ_{max} of the new transient must be somewhere between 310 and 320 nm, i.e., 315 ± 5 nm.

An upper limit, $\epsilon_{max} \leq 5000\ M^{-1}\ cm^{-1}$, was derived for the Cl atom from the relation $A_{eq}(Cl_2^-)_{340}/A_{i320} \leq \epsilon(Cl_2^-)_{340}/\epsilon(Cl)_{max}$, taking $\epsilon(Cl_2^-)_{340}$ $8.8 \times 10^3\ M^{-1}\ cm^{-1}$.[15] The CT complex of Cl with benzene in CCl_4 has ϵ_{max} ~2000 $M^{-1}\ cm^{-1}$.[19]

Photolysis of Chloroacetone. Chlorine atoms are produced by reaction 12.[20] The correction for the depletion of

$$\mathrm{ClCH_2COCH_3} \xrightarrow{h\nu} \mathrm{Cl} + \cdot\mathrm{CH_2COCH_3} \qquad (12)$$

$ClCH_2COCH_3$ should be negligible owing to its low ϵ in this wavelength region.[21] The absorptions due to radical $\cdot CH_2COCH_3$ and the triplet chloroacetone require more consideration. The spectrum of $\cdot CH_2COCH_3$ is relatively weak above 300 nm,[22] but it may still contribute significantly to the short wavelength end of the transient absorption shown in Figure 3 (curve b). The same probably applies to the triplet absorption if it is assumed to resemble that of acetone.[23] A more significant contribution to the initial transient absorption may be due to Cl_2^- (from the reaction $Cl + Cl^- \rightleftharpoons Cl_2^-$, Cl^- being produced from the hydrolysis of chloroacetone) and the products of any other reactions between the radicals and chloroacetone. We cannot even estimate these contributions, but the close resemblance between the 320-nm bands displayed by the two different systems (Figure 3 curves b and d) strongly supports the view that in both cases this band is mainly due to Cl atoms.

Photolysis of ClO^- + Cl^-. Alkaline solutions of Cl_2 (which consist of equimolar amounts of ClO^- and Cl^-) gave rise after the pulse to a broad absorption around 330 nm. It could result from the overlap of the 320- and 340-nm bands of Cl and Cl_2^-, respectively.

Photolysis of Benzyl Chloride. The transient absorption observed showed at least two types of decay, the slowest one closely resembling that of the benzyl radical.[24] The fast-decaying absorption had a rather complex appearance, but a band could be discerned around 320 nm.

Photolysis of Chlorobenzene. A fast decaying transient was produced with λ_{max} 310 nm, $\tau_{1/2}$ ~50 nsec independent of $[C_6H_5Cl]$. These results were also unaffected by the presence of 0.1 M KCl. Therefore the transient species observed cannot be Cl. It is probably the triplet absorption of

Table I. Charge-Transfer Spectra of Cl, Br, I, OH, and H in Water. Comparison between Calculated and Experimental Values for $h\nu_{\max}$

A	E_A,[a] eV	$h\nu_A$,[b] eV (gas)	r_{OA},[c] Å	$h\nu_{CT}$(calcd) (gas),[d] eV	r_{A^-},[e] Å	C_{calcd},[f] eV	$h\nu_{CT}$(calcd),[g] eV	$h\nu_{CT}$(exptl), eV	ϵ_{max}, M^{-1} cm^{-1}
Cl	3.61	8.92	3.20	5.3	2.26	9.3	4.3	3.95	<5000
Br	3.36	7.87	3.35	5.7	2.44	8.9 (9.4)	4.6 (4.2)	4.50	3500
I	3.06	6.77	3.55	6.3	2.70	8.3 (8.8)	5.1 (4.8)	4.85[h]	1040[h]
OH	1.83	4.02	2.80	6.4	1.75	8.3	5.1	5.40[i]	540[i]
H	0.76	10.20	2.60	7.0	2.60	6.9	6.5	>6.20[i]	>900[i]

[a] R. S. Berry, *Chem. Rev.*, 69, 533 (1969). For OH the difference between the vertical and adiabatic electron affinities was ignored. [b] The first allowed electronic transitions of A in the gas phase. Data for the atoms: C. E. Moore, *Nat. Bur. Stand. (U.S.), Circ.*, 467 (1949). For OH, the strongest (O–O) transition is recorded: G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, New York, N.Y., 1950. [c] The van der Waals radii, from ref 32. The OH complex was assumed to be $HO{-}O{-}H_2$ and the negative charge transfer to the center of O. [d] From eq 13 with $C = E_A + e^2/r_{OA}$. [e] $r_{A^-} = 1.25r_{A^-}$(cryst), where r_{A^-}(cryst) is Pauling's crystallographic radius. [f] From eq 20, the values in parentheses are calculated with r_{OA} as in the solid state (ref 2, 26, 30). [g] From eq 20 and 13, for the values in parentheses see footnote [f] above. [h] Reference 1. [i] Reference 3.

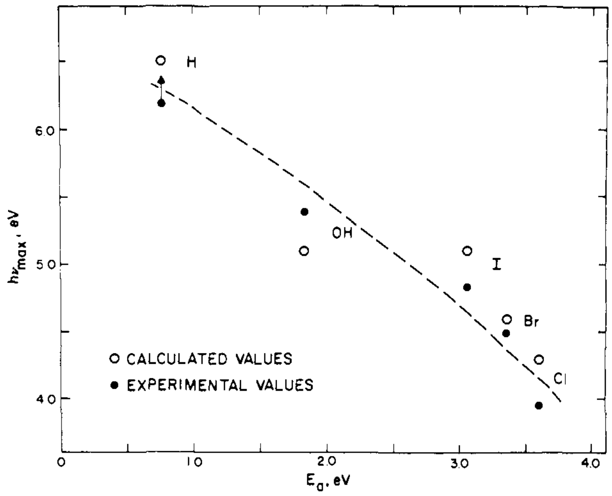

Figure 4. Correlation between the electronic transition energies (uv bands) of Cl, Br, I, OH, and H in water and their electron affinities.

C_6H_5Cl. We confirm[10] that the C–X bond scission is not a significant process in the photochemistry of chlorobenzene.

Discussion

Table I summarizes the spectral properties of the new halogen bands, together with previous data on the absorption spectra of I, OH, and H in water. In all these cases the transition energies are quite different from those of the free radicals in the gas phase (Table I), an effect which is too large to be attributed to simple solvent perturbation. The smallest difference is shown by OH, for which $h\nu$ in the gas phase transition is *lower* than that in solutions. Still, the spectral shift (1.4 eV) is higher than expected for a medium effect. (The blue shift shown by H_2O on condensation[25] is ~0.9 eV, which is exceptionally high). The intrinsic absorption of OH may contribute to the broad low-energy branch of its spectrum in water.[3] $h\nu_{max}$ in water increases with decrease in the electron affinity of the radical (Figure 4), and for the same halogen atom it increases with the ionization potential of the donor (Figure 5). This suggests that they are all charge-transfer (CT) spectra with the radical X and the solvent molecule acting as acceptor and donor, respectively. Such an interpretation was first proposed for the spectrum of I in water,[1] but that of the H atom was previously interpreted[3] as "a comparatively small red shift of the first water absorption continuum beginning at 1860 Å." However, a possible role of CT was also suggested: some negative charge was assumed[3] to be partially transferred from an *excited* water molecule to the H atom.

In support of the assignment of the bands in Table I to a charge-transfer origin, the transition energies of such bands were calculated, using expression 13[26]

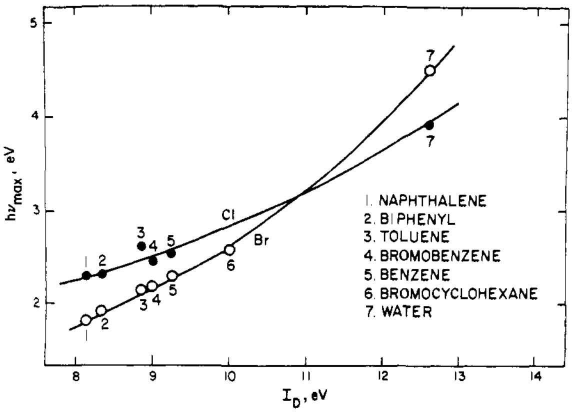

Figure 5. Correlation between the transition energies of the CT complexes of Cl and Br with the ionization potentials of the donors.

$$h\nu_{CT} = \frac{1}{1 - S^2}[(I_D - C)^2 + 4\beta_0\beta_1]^{1/2} \qquad (13)$$

I_D is the vertical ionization potential of the donor (12.6 eV for H_2O), S is the overlap integral, and β_0 and β_1 are the resonance integrals which are related through

$$\beta_1 = \beta_0 - S(I_D - C) \qquad (14)$$

The term C is given by relation 15 where E_A is the vertical

$$C = E_A + G_1 - G_0 \qquad (15)$$

electron affinity of the acceptor A and G_0 and G_1 are the dissociation energies of the complex in its pure "no-bond" and dative structures, respectively. G_0 is relatively small and the major contribution to G_1 is the electrostatic interaction of the ions, which must depend on the dielectric properties of the medium. However, previous calculations of $G_1 - G_0$ paid much attention to some of the minor contributions but either ignored the solvent effects or assumed them to be small.[2,27]

In recent years much experimental work has been done on CT spectra in the gas phase, including that of some I and Br complexes.[28] The problem of solvent effects[29] has become an important one. The theory of these effects is far from being able to even approximately predict the spectral shifts involved. This is partly due to the use of some physical parameters that are chosen somewhat arbitrarily, a difficulty which is also encountered in calculating $h\nu$ for the gas phase. In this respect, the halogen atoms have the advantage of having well-known electron affinities, and their ions have spherical symmetry (i.e., in the calculation they can be replaced by point charges situated at their centers) and known crystallographic radii. Furthermore, the common approximation of considering the positive ion as a point charge is probably better for H_2O than for larger and more complicated donor molecules.

In the following discussion we will show that a simple calculation, which considers the ions as point charges at the centers of solvent cavities in a continuous dielectric, can account for all the transition energies summarized in Table I and can be used to predict $h\nu$ of other similar charge-transfer spectra.

Calculation of C. Consider the following process

$$\text{D}\cdot\text{A(sol)} \xrightarrow{1} \text{D(g)} + \text{A(g)} \xrightarrow{2} \text{D}^+\text{(g)} + \text{A}^-\text{(g)} \xrightarrow{3} \text{D}^+\text{(sol)} + \text{A}^-\text{(sol)} \xrightarrow{4} \text{D}^+\cdot\text{A}^-\text{(sol)} \quad (16)$$

D·A and $D^+{\cdot}A^-$ denote the complex in its pure "no-bond" and dative structures, respectively, both with the same geometry as in the ground state, (g) denotes the gas phase, and (sol) denotes the solvent with all the atomic nuclei keeping their positions as in the ground state (Franck–Condon principle). At the end of stages 1, 2, and 3, the two former partners are considered to be far apart and not interacting with each other.

The energy $I_D - C$ (eq 13) is the sum of all the energy changes involved in the hypothetical process (16), i.e.

$$I_D - C = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 \quad (17)$$

where the term ΔE_2 is simply $I_D - E_A$.

Like other CT complexes of the type O-X,[26] these complexes are assumed to be weak, and the term ΔE_1 is most probably by far the smallest. Owing to the higher I_D of water, its CT complexes are expected to be even weaker than those of alcohols. ΔE_1 consists of the "no-bond" interaction and the solvation energies of D and A; both contributions are primarily due to van der Waals forces and are probably somewhat canceled by similar contributions to ΔE_3 and ΔE_4 (eq 17). However, the unpaired electron may cause a considerable binding effect. (In the extreme case, the "no-bond" may come close to a three-electron bond O:·X, with bond order ½). On the other hand, since the dative structure D^+A^- also has only one unpaired electron, the corresponding correction for valence energy should be much less than that previously calculated.[2] Again, the two valence bond corrections (for ground and excited states) may well cancel each other in expression 17.

In conclusion, in our calculation we ignored ΔE_1 and considered only the simple electrostatic contributions to ΔE_3 and ΔE_4.

$$-\Delta E_3 = \frac{e^2}{2r_{D^+}}\left(1 - \frac{1}{\epsilon_{op}}\right) + \frac{e^2}{2r_{A^-}}\left(1 - \frac{1}{\epsilon_{op}}\right) \quad (18)$$

$$-\Delta E_4 = \frac{e^2}{r_{DA}\epsilon_{op}} \quad (19)$$

where r_{D^+} and r_{A^-} are the radii of the solvent cavities occupied by D^+ and A^-, respectively; r_{DA} is the charge separation in $D^+{\cdot}A^-$; ϵ_{op} is the optical dielectric constant of the solvent, $\epsilon_{op} = n^2 = 1.77$. Expressions 18 and 19 represent, respectively, the electronic polarization energy of the ions in the solvent and their coulombic interaction with each other.

The use of the optical dielectric constant is dictated by the Franck–Condon principle, since only the electronic polarization can develop during the excitation process. Using eq 17 and summing up all the contributions one finally obtains

$$C = E_A + (e^2/2)(1 - 1/\epsilon_{op})(1/r_{D^+} + 1/r_{A^-}) + e^2/(r_{AD}\epsilon_{op}) \quad (20)$$

The geometry parameters were chosen as follows. (a) The structure of the complex was assumed to resemble that of the alcohol-molecular halogen complexes,[26] $X \cdots O\text{-}H_2$, and the positive charge was assumed to be centered on the oxygen atom. (Some shift toward the H atoms is expected but this can only have a small affect on the value of r_{DA}). (b) As in the case of other weak complexes,[26] r_{AD} was taken as the van der Waals distance $X \cdots O$. Some data are available on the distance $I \cdots O$ and $Br \cdots O$ in the solid state,[2,26,30] and in these cases they were also used to calculate C (Table I). (c) In the theory of charge-transfer-to-solvent (CTTS) spectra of ions in solutions, it was shown[31] that the ions can be considered to occupy cavities in a continuous medium, with radii which are larger than their crystallographic radii by a factor of 1.25. These cavity radii were also calculated from the partial molar volumes of the ions in water.[31] (The "packing factor" 1.25 applies to X^- ions in equilibrium. However, except for the H atom the crystallographic radius of X^- and the van der Waals radius of X are almost the same[32]). The same factor was applied to H_2O^+. Its crystallographic radius was assumed to be 1.38 Å as that of H_2O,[33] since the missing electron is nonbonding.

This treatment of the solvent effect is in principle similar to that previously presented for weak CT complexes,[34] but in that work the choice of the dielectric constant and cavity parameters was arbitrary. Since the calculated values are very sensitive to these parameters, the theory has no practical use unless methods for their evaluation are provided. In polar solvents, in particular, where the static and optical dielectric constants are very different, the role of the Franck–Condon principle must be fully understood.

The results of the present calculations are recorded in Table I. The value $C = 8.3$ eV for I is identical with that previously determined to best fit the available data for many complexes of I, including ROH, R_2O, RX, RCN, and some aromatic donors.[35] These solvents display a large variation in the static dielectric constants but all have $\epsilon_{op} \sim 2$. The alcohols and ethers also form weak O-X complexes and the geometry parameters may be similar to that of water. However, one should have more refined information on the geometry and charge distribution in these cases.

Calculation of $h\nu_{CT}$. The values of β_0 and S, which are required for calculating $h\nu_{max}$ (eq 13), were assumed to be the same as those found to represent the iodine atom complexes: $S = 0.1$, $\beta_0 = -1.2$ eV.[14,35] Small variation in β_0 (within 20%) as previously reported for some halogen atom complexes,[2] would have a small effect on the calculation owing to the high ionization potential of water (the term $(I_D - C)^2$ outweighs $4\beta_0\beta_1$). The effect of such a variation should be most pronounced when I_D is close to C (see eq 13), as in the case of the aromatic donors, and may account for the unexpected order $h\nu(\text{Cl}) > h\nu(\text{Br})$ shown by their complexes (Figure 5).

The agreement between the calculated and experimental values of $h\nu_{max}$ (Table I) is better than could be expected considering the approximations involved, e.g., the choice of r_{AD} as the van der Waals distance. However, $h\nu_{cal}$ is not very sensitive to this parameter: reducing r_{AD} by 20% brings about ~10% reduction in $h\nu_{max}$ (Table I).

For H atoms in water the theory predicts $\lambda_{max} \sim 190$ nm. Since ϵ 900 M^{-1} cm^{-1} at 200 nm,[3] in view of the moderate intensities of these CT bands (Table I) the prediction seems quite reasonable.

Solvent Effect. In the gas phase, the electrostatic energy is simply e^2/r_{AD} and $C = E_A + e^2/r_{AD}$. (Equation 20 reduces to this expression in the hypothetical case when $r_{AD} = r_{D^+} = r_{A^-}$). Assuming that r_{AD} is the same in both phases (which is not necessarily so[34]), we derive

$$\Delta(h\nu)_{CT} = h\nu_{CT}(\text{sol}) - h\nu_{CT}(\text{gas}) = (e^2/2)(1 - 1/\epsilon_{op})(1/r_{D^+} + 1/r_{A^-} - 2/r_{AD}) \quad (21)$$

The calculated values of $\Delta(h\nu)$ are all negative (Table I) (i.e., the dative structure is stabilized by the solvent more than the ground state) and are in the order of 1 eV. The shifts recently reported for I–benzene and I–cyclohexane complexes are −0.37 and −0.24 eV, respectively.[28]

Relation to CTTS Spectra. The CT spectra discussed here involve a flow of negative charge from the solvent to the radical X, which is in the opposite direction to that displayed by the charge-transfer-to-solvent (CTTS) bands of the anions X^-. There are two other major differences. (a) In CTTS transitions the acceptor is not a single solvent molecule but rather the cooperative function of many solvent molecules. (b) Although $h\nu_{max}$ of the halide ions increases with the electron affinity of X (i.e., in opposite direction to the CT spectra of X·sol), the CTTS spectra of OH^- and some other anions show marked departure from this regularity. On the basis of this behavior a model was presented for CTTS spectra using the theory of CT complexes.[36] However, the reason for this irregularity is simple and emphasizes the difference between these two types of transition. The polarized medium is organized around the ion when it is in its ground equilibrium state. Thus nuclear and dipolar polarizations play an important role in CTTS transitions, since on excitation there is a sharp change in interaction with these polarizations. Therefore in CTTS transitions $h\nu_{max}$ follows the order of $E_{A^-} + L_{A^-}$, where L_{A^-} is the solvation energy of the ion.[31] On the other hand, the dipolar and nuclear polarizations play no role in the CT transitions discussed here because these polarizations have no time to develop during excitation (Franck–Condon principle).

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