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Charge-Transfer Complexes of Bromine Atoms with Haloalkanes and Alkanes

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Charge-transfer complexes of bromine atoms with haloalkanes and alkanes were produced by pulse radiolysis and by laser-flash photolysis in various organic solvents. Br atoms were produced by photolysis of Br_2 (at 351 or 248 nm), by photolysis of bromoalkanes (at 248 nm), or by radiolysis of bromoalkanes (either in liquid form or in cyclohexane solutions). The transient spectra, monitored within microseconds after the pulse, had absorption maxima that varied between 300 and 500 nm and are ascribed to complexes of Br atoms with the various solvents or other solutes present. The absorption maxima for Br atom complexes with alkanes and chloroalkanes correlate with the ionization potential of these molecules, suggesting the existence of charge-transfer complexes. The correlation for the bromoalkanes was more complex. $CBr_4 \cdot Br$ and $CHBr_3 \cdot Br$ were observed to react rapidly ($k = 10^8 - 10^9$ L mol^{-1} s^{-1}) with Br_2 and with HBr to transfer their Br atom to these latter molecules.

Introduction

Charge-transfer complexes of dihalogen molecules and halogen atoms with organic compounds have been studied for many years.[2] Most studies utilized arenes as donors and prepared the halogen atoms by pulse radiolysis or flash photolysis. For example, pulse radiolysis of CCl_4/arene mixtures gave transient spectra which were ascribed to charge-transfer complexes of Cl atoms with the various arenes, based on a reasonable linear correlation between the energies of the absorption maxima, $h\nu_{CT}$, and the vertical ionization potential of the arene.[3] A similarly reasonable correlation was observed for Br atom complexes with arenes produced in the radiolysis of bromoalkane/arene mixtures.[4] More recently, laser-flash photolysis was used to measure absorption spectra of charge-transfer complexes of halogen atoms with a long series of substituted benzenes,[5] and the results were compared to the spectra of the halogen–molecule complexes with the same arenes. The absorption maxima of the complexes with the halogen molecules gave a reasonable linear correlation with the ionization potential of the arene. The complexes with the atoms, however, gave a good correlation for I but showed considerable scatter for Br or Cl.[5]

Most of the earlier studies were carried out with aromatic donors. Recently, the UV absorption spectra of Cl atoms in several chloroalkane solvents were measured by laser-flash photolysis of Cl_2 dissolved in these solvents.[6] Linear correlation between the energies of the absorption maxima and the ionization potentials of the solvents was interpreted to suggest that the observed species were charge-transfer complexes.

In the pulse radiolysis of bromoalkanes, in liquid form or in cyclohexane solutions, transient absorption spectra were observed and ascribed to complexes of Br atoms with the parent compounds, $RBr \cdot Br$.[7] The complexes with C_2H_5Br, CH_2Br_2, $CHBr_3$, and CBr_4 exhibit absorption peaks at 370, 390, 425, and 480 nm, respectively. The last three compounds gave a reasonable correlation of $h\nu_{CT}$ with their ionization potentials, but the result for bromoethane deviated considerably. To examine the correlation of $h\nu_{CT}$ for Br atom complexes with a series of aliphatic molecules, we have determined the absorption spectra of Br atoms in different solutions. We have prepared the Br atoms both by pulse radiolysis as above and by laser flash photolysis of bromo compounds (at 248 nm) or of Br_2 (at 248 and 351 nm).

$$RBr + h\nu \rightarrow R^{\cdot} + Br^{\cdot} \qquad (1)$$

$$Br_2 + h\nu \rightarrow 2Br^{\cdot} \qquad (2)$$

We find reasonable linear correlations that are slightly different for the different groups of aliphatic compounds.

Experimental Section[8]

The organic solvents were spectrophotometric, analytical, or HPLC grade from Mallinckrodt, Baker, or Aldrich and were used as received unless specified otherwise. Dibromomethane was obtained from Fluka (puriss.); bromoform from Fisher was purified by vacuum distillation and by passing through activated alumina; carbon tetrabromide from Eastman was recrystallized from acetone/water; and ethyl bromide from Fisher was purified by passing through a column of activated alumina. Dichloromethane (Aldrich, spectrograde) was treated with Br_2 and then washed with KOH/water and distilled. 2-Chloropropane (Fluka, purum) was passed through neutral activated alumina. 1-Chlorobutane (Fluka, purum) was refluxed with HCl, washed with $NaHCO_3$, treated with Br_2/KOH, distilled, and passed through activated alumina. Cyclohexane was analytical grade from Mallinckrodt and was purified by passing through activated alumina. Neohexane (Columbia) was refluxed with alkaline $KMnO_4$ and then distilled over metallic sodium. Cyclopentane (Aldrich, HPLC grade) was purified by treating with concentrated sulfuric acid and then distillation. Decalin (Merck, cis–trans mixture) was purified by passing through basic alumina, treating with $KMnO_4$/KOH and then with Br_2, passing again through alumina, and finally vacuum distilling (utilizing the difference between the boiling points of decalin and brominated decalin). The long term stability of Br_2 solutions in the various solvents was taken as a measure of purity for these experiments.

Fresh solutions were prepared before each experiment, and samples were transferred with a syringe to the irradiation cell and irradiated under air. The cell was filled with a fresh solution before each pulse. The pulse radiolysis apparatus was described before.[9] It utilizes 50-ns pulses of 2-MeV electrons from a Febetron 705 accelerator. The dose per pulse was between 10 and 30 Gy in most experiments, as determined by dosimetry with N_2O saturated aqueous KSCN solutions.[10] The laser flash photolysis system consisted of a Lambda Physik EMG 201 MSC excimer laser, utilizing either KrF for 248 nm or XeF for 351 nm, with a pulse duration of 20–40 ns and pulse energies of 150–500

TABLE I: Absorption Maxima of Br Atom Complexes with Bromoalkanes

| | laser-flash photolysis | | pulse radiolysis[7] | |
solute/solvent	λ_{ex}	λ_{max} (nm)	λ_{max} (nm)	I_D[8] (eV)
CBr_4/cyclohexane	248	480	480	10.31
$CHBr_3$/cyclohexane	248	430	425	10.48
CH_2Br_2			390	
CH_2Br_2/cyclohexane	248	390	390	
Br_2/CH_2Br_2	351	385	390	10.50
CH_3CH_2Br/cyclohexane			365	
Br_2/CH_3CH_2Br	351	370	370	10.28
$Br_2/ClCH_2Br$	351	365		10.77
Br_2/CF_2Br_2	351	360		11.07

mJ.[11] For both systems, the kinetic–spectrophotometric detection setup consisted of a Varian 300-W xenon lamp, a 2-cm optical path length irradiation cell, a Kratos high-intensity monochromator, an RCA 4840 photomultiplier, and the appropriate shutters, lenses, and optical filters. The signals were digitized with a Tektronix 7612 transient recorder and analyzed with a PC. All experiments were carried out at room temperature, 22 ± 2 °C.

Results and Discussion

Bromoalkanes. The spectra of RBr·Br complexes for CBr_4, $CHBr_3$, CH_2Br_2, and CH_3CH_2Br have been measured previously by the pulse radiolysis of neat liquid bromoalkanes or their solutions in cyclohexane.[7] In the present study these complexes were produced by laser-flash photolysis of either the bromoalkane (dissolved in cyclohexane) at 248 nm or Br_2 (dissolved in the bromoalkane) at 351 nm. The spectra monitored by the two techniques were very similar; the peak positions are summarized in Table I.

Chloroalkanes. Radiolysis of chloroalkanes leads to the formation of radical cations and Cl atoms, and thus chloroalkanes are not suitable solvents for the radiolytic formation of Br atoms either from Br_2 or from RBr. Therefore, the behavior of bromine atoms in these solvents was studied by laser photolysis, using 248- or 351-nm excitation to form Br from Br_2. The concentration of Br_2 was adjusted to give an absorbance at the excitation wavelength between 0.2 and 0.5 (for 351-nm excitation, the concentration of Br_2 was several millimoles per liter; for 248-nm excitation, the concentration was 0.2–0.5 mmol L^{-1}). Representative spectra, taken immediately (<100 ns) after the laser pulse, are shown in Figure 1, and the peak positions are summarized in Table II. The peaks are found at lower wavelengths and cover a narrower range than for the bromoalkane complexes.

Alkanes. The spectra obtained by laser-flash photolysis of Br_2 in alkanes were slightly different for the different solvents, indicating an interaction between the Br atom and the solvent. Representative spectra are shown in Figure 2, and the peak positions are summarized in Table II. These peaks are broader and less well defined than those obtained with the haloalkanes. The spectra were taken <100 ns after the laser pulse and decayed within several microseconds.

Reaction of RBr·Br with Br_2. The decay of CBr_4·Br and $CHBr_3$·Br, monitored by pulse radiolysis in cyclohexane solutions, was found to be accelerated in the presence of added Br_2. From the dependence of the first-order decay rate constant (monitored at 480 and 430 nm, respectively) on the concentration of Br_2 (Figure 3), we derived second-order rate constants of (2.2 ± 0.5) × 10^8 L mol^{-1} s^{-1} for CBr_4·Br and (4.0 ± 1.0) × 10^9 L mol^{-1} s^{-1} for $CHBr_3$·Br, for the reaction of these complexes with Br_2. The higher rate constant for the $CHBr_3$·Br complex as compared with that for the CBr_4·Br complex is in agreement with trends in rate constants measured previously for the reactions of these species with organic compounds and are due to the difference in stability of the two complexes.[7] As in the previous cases, the reactions are
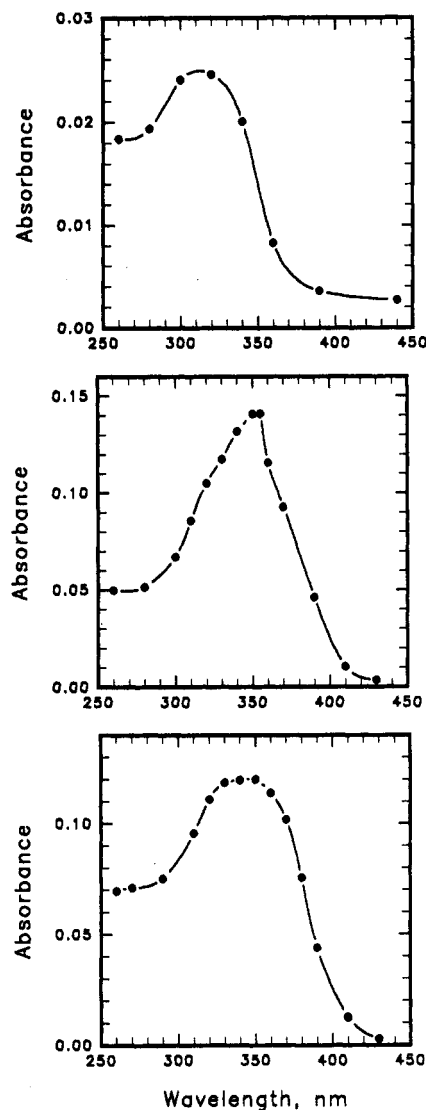

Figure 1. Transient absorption spectra monitored upon laser-flash photolysis of Br_2 solutions in dichloromethane (top), 2-chloropropane (center), and 1-chlorobutane (bottom).

TABLE II: Absorption Maxima of Br Atoms in Chloroalkanes and Alkanes[a]

solvent	λ_{max} (nm)	I_D (eV)
$2\text{-}C_4H_9Cl$	345	10.53
$1\text{-}C_4H_9Cl$	345	10.67
$2\text{-}C_3H_7Cl$	350	10.78
$ClCH_2CH_2Cl$	325	11.04
CH_2Cl_2	315	11.32
CCl_4	305	11.47
decalin	395	9.25; 9.41
cyclohexane	370	9.86
n-hexane	350	10.13
neohexane	340	10.06
n-pentane	344	10.35
cyclopentane	335	10.51
methanol	360	10.84
benzene[7]	540	9.25

[a] The Br atoms were produced by laser-flash photolysis of Br_2 in the solvent listed, using 248 nm as the excitation wavelength in most cases; dichloromethane and dichloroethane solutions were excited at 248 and at 351 nm and gave the same results; and carbon tetrachloride solutions were excited only at 351 because the solvent absorbs the 248 nm light. For comparison we also list the results for methanol, by 248-nm excitation, and for benzene, by pulse radiolysis of Br_2 or CBr_4 in benzene.

expected to take place by transfer of the Br atom from the RBr complex to the added reactant to form initially the complex with

Figure 4. Transient absorption spectrum monitored upon pulse radiolysis of HBr solutions (0.018 mol L^{-1}) in cyclohexane.
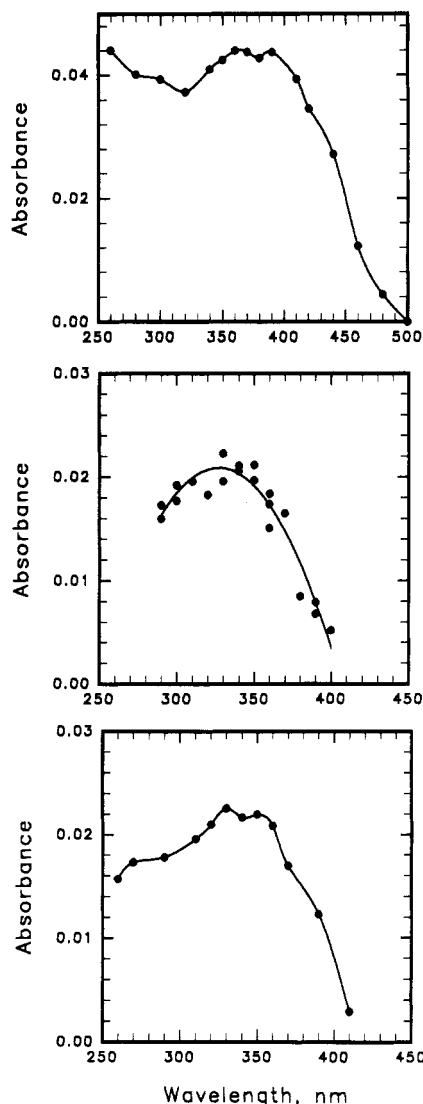

Figure 2. Transient absorption spectra monitored upon laser-flash photolysis of Br$_2$ solutions in cyclohexane (top), cyclopentane (center), and neohexane (bottom).
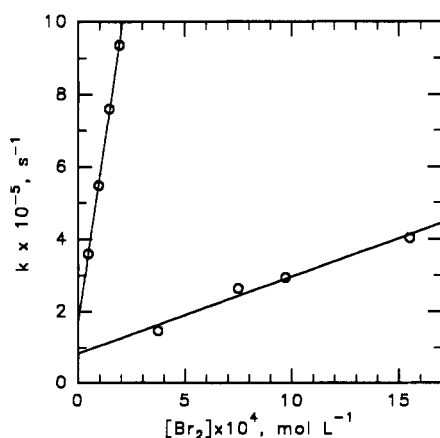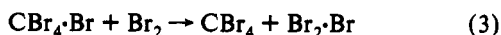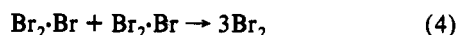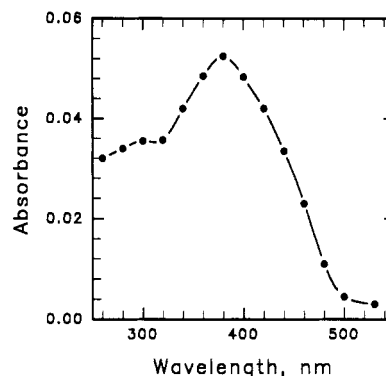

Figure 3. Rate of decay of CBr$_4$·Br (low line) and CHBr$_3$·Br (steep line) as a function of Br$_2$ concentration.

this reactant, e.g.,

$$CBr_4 \cdot Br + Br_2 \rightarrow CBr_4 + Br_2 \cdot Br \qquad (3)$$

This probably is followed by rapid combination to form Br$_2$, e.g.,

$$Br_2 \cdot Br + Br_2 \cdot Br \rightarrow 3Br_2 \qquad (4)$$

In an attempt to monitor the absorption spectrum of Br$_2$·Br, we

recorded the spectra at different times after the pulse with solutions containing 2% bromoform in cyclohexane and various concentrations of Br$_2$ (0–1.6 × 10^{-3} mol L^{-1}). The absorption below 370 nm increased with time and with Br$_2$ concentration. The results point to a peak below 330 nm, which could not be observed directly due to light absorption by the starting solution.

Because of the increased decay rate of Br atom complexes in the presence of Br$_2$, the complexes formed upon laser-flash photolysis of Br$_2$ solutions were relatively short-lived, and, therefore, their spectra were monitored immediately (<100 ns) at the end of the laser pulse.

Reaction of RBr·Br with HBr. In parallel with the above experiments, addition of HBr increased the rate of decay of the RBr·Br complexes. From the concentration dependence we derived second-order rate constants of (7 ± 2) × 10^7 L mol^{-1} s^{-1} for the reaction of CBr$_4$·Br with HBr and (1.3 ± 0.4) × 10^9 L mol^{-1} s^{-1} for CHBr$_3$·Br. Again, the bromoform complex reacts with a higher rate constant, and, as discussed above, the reactions involve a Br atom transfer, e.g.,

$$CBr_4 \cdot Br + HBr \rightarrow CBr_4 + HBr \cdot Br \qquad (5)$$

HBr$_2$ is the protonated form of Br$_2$·$^-$, extensively studied in aqueous solutions, but appears to be much shorter lived, probably decaying to give bromine.

$$HBr \cdot Br + HBr \cdot Br \rightarrow 2HBr + Br_2 \qquad (6)$$
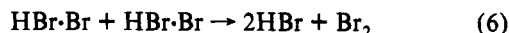
We attempted to produce HBr·Br by pulse radiolysis of HBr (1.8 × 10^{-2} mol L^{-1}) in cyclohexane, assuming similar formation reactions to those for RBr solutions. The absorption spectrum (Figure 4) has a peak at 380 nm, which is close to that for Br$_2$·$^-$ in aqueous solutions (360 nm). Although the peak is also close to the absorption maximum for RH·Br produced by photolysis of Br$_2$ in cyclohexane (Figure 2), the shapes of the two spectra are different. Furthermore, the Br atom complex with cyclohexane should be much less stable than the complex with HBr, and we ascribe the observed absorption (Figure 4) to the latter species, HBr·Br. This species decayed in a second-order process with a first half-life of about 3 μs, nearly 5 times more slowly than the decay of RH·Br in cyclohexane (the values of the second-order rate constants cannot be derived due to unknown molar absorptivities or concentrations of the Br atom complexes).

Correlation of the Absorption Maxima. The absorption bands of the Br atom complexes with various compounds (Tables I and II) probably arise from an excitation to a charge-transfer state. Therefore, the energies of the absorption maxima, $h\nu_{CT}$, may be correlated with the ionization potentials of the donors, I_D, according to the equation of Mulliken,[2,12]

$$h\nu_{CT} = I_D - E_A - W \qquad (7)$$

where I_D is the vertical ionization potential of the donor, E_A the electron affinity of the acceptor, and W the work required for the
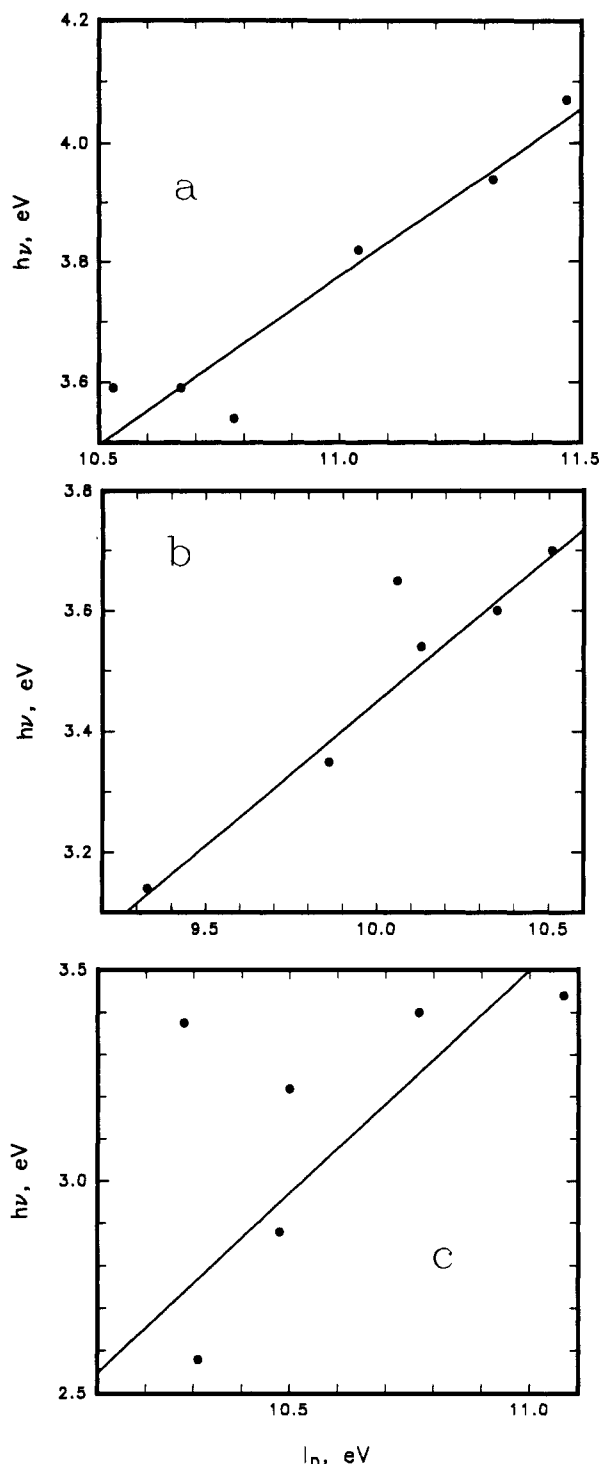
Figure 5. Correlation of $h\nu_{CT}$ with I_D for RCl (a), RH (b), and RBr (c).

because the distance between the donor and acceptor, r_{AD}, varies for the different groups, i.e., RBr–Br vs RCl–Br vs RH–Br. However, the separate plots for the chloroalkanes (Figure 5a) and alkanes (Figure 5b) show reasonable linear correlations with slightly different slopes. Only the highly branched neohexane deviates considerably from the line, probably due to steric factors as argued previously.[5] The complexes of Br atoms with the alkanes have a different structure than those with the haloalkanes since alkanes have no lone pair electrons to form a π-complex. Probably, the complex has a weak three-electron bond among three atoms, as is usually envisaged for a transition state in H-abstraction reactions, [R···H···Br]*.

In the bromo compounds, the point for bromoethane deviates very strongly from the line drawn through the rest of the data (Figure 5c). This may indicate that the ionization potential is not the only factor that governs $h\nu_{CT}$. It may be that the C–Br bond dissociation energy also plays a role in this case. The C–Br bond dissociation energies in C_2H_5Br, CH_2Br_2, $CHBr_3$, and CBr_4 have been reported[16] to be 272, 261, 238, and 218 kJ mol^{-1}, respectively, which follows the order of the $h\nu_{CT}$ values. The weakest of these C–Br bonds is only slightly stronger than the Br–Br bond (190 kJ mol^{-1}). Therefore, we may expect some contribution from structures similar to the transition state expected for Br atom abstraction (C···Br···Br).

References and Notes

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dissociation of the charge-transfer excited state (i.e. e^2/r_{AD}, where r_{AD} is the distance between the donor, D, and acceptor, A). Equation 7 holds for the gas phase, whereas in the liquid phase $h\nu_{CT}$ may be shifted somewhat due to differences in solvation energy of the complex in its ground and excited state.[13] By assuming r_{AD} to be constant and using the same acceptor (constant E_A) and the same solvent, one expects a linear correlation between $h\nu_{CT}$ and I_D with a unit slope. The slopes of such plots for the complexes of I, Br, and Cl atoms with arenes, however, were 0.51, 0.37, and 0.29, respectively.[3,4,14] Slopes less than unity were suggested to result from variations in the mean separation, r_{AD}, for the various donors.[2,15]

If we correlate all the $h\nu_{CT}$ values from the λ_{max} results of Tables I and II with I_D alone, we find a very poor fit, probably