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The Effect of Temperature on the Formation of Benzyl Radical–Halide Ion Complexes in γ-Irradiated Organic Glassy Matrices

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Broad structureless charge-transfer (CT) bands of benzyl radical-halide ion ($\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-$) complexes have been observed in 3-methylhexane (3MHx) and 2-methyltetrahydrofuran (MTHF) matrices containing BzCl and BzBr irradiated with γ-rays at 4.2 K. 3MHx and ethanol matrices containing BzI also showed the CT band when warmed from the irradiation temperature to 77 K. These observations are in marked contrast with previous ones in which the CT band was found to be present only in alkane matrices when irradiated at 77 K. The CT band has been found to shift to the blue with increasing matrix polarity, as expected from a large contribution of the solvation of the ion to the CT transition energy of the radical–anion complex. The observed nature and behavior of the CT bands indicates that the dissociative electron attachment reaction in the matrices is a stepwise process: The formation of a $\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-$ complex and its dissociation. These steps proceed readily in more polar environments and for lighter ions. For the electron attachment to BzI at 4.2 K, an even earlier step, an ionic entity prior to the C–I bond dissociation, was indicated.

The dissociative electron attachment to benzyl halide in glassy matrices of nonpolar alkanes γ-irradiated at 77 K was previously found to give benzyl radical–halide ion complexes.[1,2] These complexes provided us with an interesting example of the charge-transfer (CT) interaction between a neutral open-shell free radical and a closed-shell anion. Their CT band, observed by means of the fluorescence spectrophotometric method, shifted depending on both the ionization energy of the electron donors (halide ions)[2] and the electron affinity of the electron acceptors (ring-substituted mono- and dimethylbenzyl radicals[3]). A similar CT band was also observed for the α-methylbenzyl radical formed from (2-chloroethyl)benzene[4] and the diphenylmethyl radical from diphenylmethyl halides[5] in glassy 3-methylhexane (3MHx) at 77 K. It is likely that a complex of this kind is generally formed as a transient intermediate state during the course of dissociative electron attachment reactions. A detailed study on the nature and behavior of this complex is expected to give a mechanistic insight into the reactions occurring in low temperature glassy matrices.

The CT excitation energy should depend significantly on the energy of solvation of the ions (both in the ground and excited states of the complex) for a neutral radical–anion complex. Actually, this has been proved by changing the ionic radius by using the different halide ions.[2] In this respect, it seems worthwhile studying the effect of the matrix polarity on the CT excitation energy. However, so far only the CT band for the benzyl radical–iodide ion complex in semipolar 2-methyltetrahydrofuran (MTHF) at 77 K,[6] apart from alkane matrices, has been observed. The failure in observing the CT band from polar matrices was attributed to ion solvation effects: polar matrix molecules weakening the interaction between the radical and the ion.

The 4.2 K-γ irradiation technique has proven useful in freezing chemical processes so that the early stages in the processes can be followed. This technique has, for example, enabled the spectrophotometric observations of the precursor of the carbon-halogen bond dissociation which resulted from the electron attachment to benzyl chloride[7] and halobenzenes,[8] and of the toluene anion which is the precursor of the methylcyclohexadienyl radical in a glassy toluene matrix.[9]

The present investigation was planned for observing the benzyl radical–halide ion CT band in organic glassy matrices of different polarity using the 4.2 K-γ irradiation technique. Another aim of the investigation was to elucidate the detailed mechanism of the dissociative electron attachment reaction in these matrices.

Experimental

Benzyl chloride (BzCl) of reagent grade was used without further purification. Benzyl bromide (BzBr) of reagent grade was distilled before use. Benzyl iodide (BzI) was synthesized from BrCl and NaI and purified by repeated recrystallization from methanol. 3MHx, MTHF, and ethanol were purified as described elsewhere.[6]

The solutions of the benzyl halides (10^{-2}—10^{-3} mol/dm^3) were deaerated by freeze-pump-thaw cycles to 1.4×10^{-3} Pa, sealed in Suprasil quartz tubes of 2 mm outer diameter, and rapidly frozen into the glassy state by immersion in liquid nitrogen. The samples were transferred into a liquid He dewar of quartz (originally for ESR measurement at 4.2 K), irradiated with ^{60}Co γ-rays to a dose of 5×10^4—4×10^5 rad at 4.2 K, after which excitation and emission spectra were measured with a Hitachi Model MPF-2A fluorescence spectrophotometer. The wavelength resolution of the measurements was 2 nm or less. Thermal annealing was carried out by rapidly transferring the irradiated samples into liquid nitrogen and keeping them there for a predetermined period.

Occasionally, optical absorption measurements were made with a Shimadzu MPS-5000 spectrophotometer and sample solutions sealed in an optical absorption cell of quartz (optical path length: 2 mm), as has been described before.[9]

Results

The fluorescence and excitation spectra recorded from the 3MHx containing BzCl or BzBr irradiated at 4.2 K are essentially the same as the spectra ob-

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Table 1. The charge-transfer excitation band (energy) of benzyl radical–halide ion complexes

Halide ion	Matrix	λ_{max}/nm (Transition energy/eV) 4.2 K	λ_{max}/nm (Transition energy/eV) 77 K
Cl$^-$	3MHx	364 (3.41)	366[a] (3.39)
	MTHF	340 (3.65)	Unobserved
	EtOH	Unobserved	Unobserved
Br$^-$	3MHx	413 (3.00)	413[a] (3.00)
	MTHF	370 (3.35)	Unobserved
I$^-$	3MHx	500[b] (2.48)	500[a] (2.48)
	MTHF	No measurement	420[c] (2.95)
	EtOH	345[b] (3.59)	Unobserved

a) Ref. 2. The previously reported 362 nm of Cl$^-$ has been corrected, based on a careful reexamination in this investigation. b) The band appeared when the samples irradiated at 4.2 K were warmed to 77 K. c) Ref. 6.

served after the irradiation at 77 K.[2] The excitation spectra are comprised of three bands, in the visible (around 460 nm), near-UV (around 320 nm), and far-UV (around 260 nm) regions due respectively to the $1^2A_2 \leftarrow 1^2B_2$, $2^2A_2 \leftarrow 1^2B_2$, and $4^2B_2 \leftarrow 1^2B_2$ electronic transitions in a benzyl radical of C_{2v} symmetry[10] which has been generated by dissociative electron attachment to BzX. In addition, a structureless broad excitation band was observed with a band maximum at 364 nm for BzCl and at 413 nm for BzBr. This band has previously been attributed to the CT band of the $\dot{\mathrm{B}}\mathrm{z}$---X$^-$ complex.[1,2,6] All these excitations induce the fluorescence from the benzyl radical in the wavelength region 460—530 nm.

The main concern of the present investigation was the CT excitation band of the complexes. Upon warming the 3MHx matrices containing BzCl or BzBr to 77 K, no change in the CT band was observed. The CT excitation energy is independent of the irradiation temperature, as can be seen in Table 1. The wavelength difference of 2 nm between 4.2 and 77 K for BzCl/3MHx is within the experimental uncertainty caused by the broad peak of the bands.

The effect of irradiation temperature is significant for the MTHF matrix. CT bands with maximum at 340 nm and 370 nm were observed for BzCl and BzBr after irradiation at 4.2 K. This is in contrast with irradiation at 77 K[2,6] where CT bands were not observed. The CT bands disappeared readily on warming the samples irradiated at 4.2 K to 77 K. The CT band could not be observed for a BzCl/ethanol solution either by irradiation at 77 or at 4.2 K.

The effect of irradiation temperature is more prominent when BzI is the source of benzyl radicals. Immediately after irradiation at 4.2 K, no emission at all was observed from the 3MHx and ethanol matrices. However, the excitation band of the benzyl radical as well as the CT excitation band of the $\dot{\mathrm{B}}\mathrm{z}$---I$^-$ complex could be recorded after warming the samples to 77 K. For BzI/3MHx, the CT band was found to have its maximum at about 500 nm, equal to that observed previously for irradiation at 77 K.[2,6] The CT excited state is lower than the first excited state of the benzyl radical and, therefore, the fluorescent state of the $\dot{\mathrm{B}}\mathrm{z}$---I$^-$ complex, so that a broad structureless CT fluorescence with the maximum at 548 nm was observed. For BzI/ethanol, the CT excitation band was unstable at 77 K: It disappeared within 40 min after its appearance (see Fig. 1).

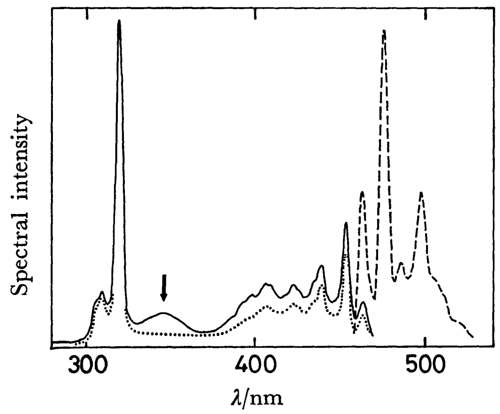

Fig. 1. Fluorescence (dashed curve) and excitation (solid curve) spectra of benzyl radicals generated by irradiating an ethanol matrix containing BzI with γ-rays at 4.2 K and observed immediately after warming to 77 K. Excitation and monitoring were made at 320 nm and 463 nm, respectively. The excitation spectrum changed to that of the dotted curve after 40 min annealing at 77 K. The arrow indicates the CT excitation band of the $\dot{\mathrm{B}}\mathrm{z}$---I$^-$ complex.

Table 1 summarizes all the data on the CT excitation band obtained in the present investigation as well as in the previous ones.[2,6]

The absence of a CT band from BzI at 4.2 K raises the question of what the precursor of the $\dot{\mathrm{B}}\mathrm{z}$---I$^-$ complex is. As the precursor does not fluoresce, optical absorption measurements were made for 3MHx, MTHF, and ethanol matrices containing BzI at 4.2 K. Although the shape of the absorption spectra observed varied from sample to sample, typical examples of observed spectra can be seen in Fig. 2. The spectra are generally composed of a sharp line at *ca.* 320 nm (with a satellite line at 310 nm) and a broad component in the longer wavelength region. The latter showed broad peaks whose position is dependent on the matrix. This broad component disappeared upon warming to 77 K. It does not correspond to the CT excitation band. The sharp line has almost the same wavelength position as that of the intense near-UV excitation due to the $2^2A_2 \leftarrow 1^2B_2$ transition of the benzyl radical. The lines seemed to increase in peak intensity and to shift a few nm to the blue side on warming to 77 K. On the whole the observed absorption spectra shows no similarity to the spectrum of the toluene anion generated in the γ-irradiated MTHF matrix.[9] The absorption spectra are very much like the spectrum observed by Higashimura *et al.* from BzCl/ethanol irradiated at 4.2 K.[7] They have attributed the broad component to the precursor of the benzyl radical.

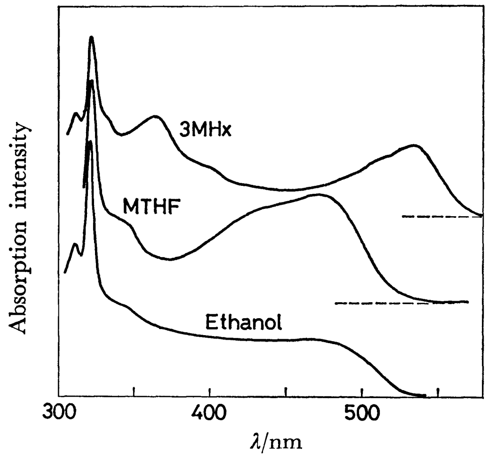

Fig. 2. Optical absorption spectra observed from glassy organic matrices containing BzI irradiated with γ-rays and measured at 4.2 K. Correction has been made for background absorption. The dashed line indicates the zero-absorption level of each spectrum.

Although further studies are evidently needed to attain a definite assignment, the absorption spectra observed here are tentatively assigned to a BzI molecular anion with a partially broken C–I bond (a tightly correlated benzyl radical–iodide ion pair). The absence of fluorescence at 4.2 K seems to indicate that the sharp lines are not due to the (normal) benzyl radicals.

Discussion

The broad structureless excitation band was previously assigned to the CT transition of the transient $\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-$ complexes which are generated by the dissociative electron attachment to BzX in rigid matrices. This assignment was based on the observed dependence of the transition energy on the ionization energy of the electron donors, the halide ions,[2] or on the electron affinity of the electron acceptors, that is benzyl or methyl-substituted benzyl radicals.[2,3]

Following Mulliken's CT resonance model,[11] the CT transition energy, $h\nu_{\mathrm{CT}}$, of a weak electron donor-acceptor complex is written as

$$h\nu_{\mathrm{CT}} = W_1 - W_0 + \frac{(H_{01}-W_0S_{01})^2+(H_{01}-W_1S_{01})^2}{W_1-W_0}, \tag{1}$$

where W_0 is the eigenvalue of the no-bond wave function $\phi_0(\mathrm{A,D})$ and W_1 the eigenvalue of the dative wave function $\phi_1(\mathrm{A^-{-}D^+})$. H_{01} and S_{01} are defined as $\langle\phi_0|H|\phi_1\rangle$ and $\langle\phi_0|\phi_1\rangle$, respectively. The third term on the right hand side cannot be estimated without knowledge of the exact conformation of the complex, but for the $\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-$ case studied here it is small and can be neglected, as will be mentioned below. The main contribution to W_1-W_0 comes from the ionization energy of X^-, $IP(\mathrm{X}^-)$, the electron affinity of $\dot{\mathrm{B}}\mathrm{z}$, $EA(\dot{\mathrm{B}}\mathrm{z})$, and the difference in solvation energy between the excited and ground states of the complex, $E_{\mathrm{s}}(\mathrm{Bz^-}$---$\mathrm{X})-E_{\mathrm{s}}(\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-)$. The solvation energies can however be approximated to those of Bz^- and X^- and are then given by Born's formula:

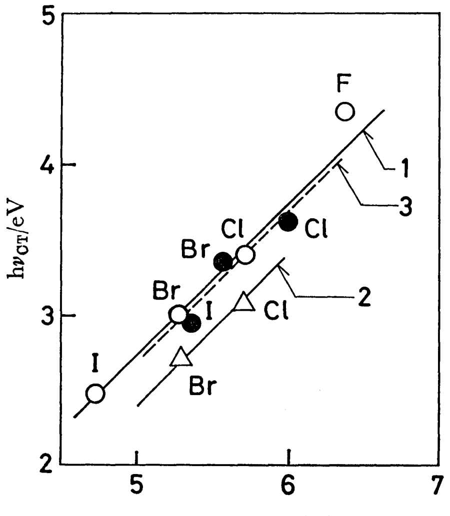

Fig. 3. The dependence of the observed CT transition energy on the calculated sum of the ionization energy and the solvation energy of the halide ion, $IP(\mathrm{X}^-)+E_{\mathrm{s}}(\mathrm{X}^-)$. ○: $\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-$ complexes in the 3MHx matrix cited from Ref. 2. Line 1 gives 0.263 nm for the effective radius of Bz^-. ●: $\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-$ complexes in the MTHF, for which the dependence expected from an equal effective radius of Bz^- is shown by line 3. △: Dephenylmethyl radical---X^- complex in the 3MHx matrix, cited from Ref. 5, for which a linear dependence with a slope of unity is shown by line 2.

$$E_{\mathrm{s}} = \frac{e^2}{2r}\left(1-\frac{1}{D}\right), \tag{2}$$

where r is the radius of the solvated species. The Franck-Condon principle requires the usage of the static dielectric constant, D_{s}, and the optical dielectric constant, D_{op}, for the ground and excited states respectively. Thus, Eq. 1 is reduced to

$$h\nu_{\mathrm{CT}} = IP(\mathrm{X}^-) + E_{\mathrm{s}}(\mathrm{X}^-) - \{EA(\dot{\mathrm{B}}\mathrm{z})+E_{\mathrm{s}}(\mathrm{Bz}^-)\}. \tag{3}$$

A linear relationship between $h\nu_{\mathrm{CT}}$ and $IP(\mathrm{X}^-)+E_{\mathrm{s}}(\mathrm{X}^-)$ was indeed observed for the $\dot{\mathrm{B}}\mathrm{z}$----$\mathrm{X}^-$ complexes in the 3MHx matrix[2] as is shown by the solid line in Fig. 3. From the intercept and the reported $EA(\dot{\mathrm{B}}\mathrm{z})$ value, 0.90 eV,[12] the effective radius of the Bz^- anion can be calculated as 0.263 nm. The linear relationship (3) holds also for diphenylmethyl radical–halide ion complexes.[5]

The present observations of the $\dot{\mathrm{B}}\mathrm{z}$---$\mathrm{X}^-$ complex in three different matrices enables us to examine the effect of matrix polarity on the CT excitation energy, as expressed by Eq. 3. Qualitatively speaking, D_{op} is close to 2.0 for all the matrices examined, which means that $E_{\mathrm{s}}(\mathrm{Bz}^-)$ will be almost constant. The effect of polarity will come mainly from $E_{\mathrm{s}}(\mathrm{X}^-)$, which is dependent on D_{s}. For more polar matrices, $E_{\mathrm{s}}(\mathrm{X}^-)$ will become larger and this will lead to larger $h\nu_{\mathrm{CT}}$. Actually, the blue-shift of the CT band was followed by changing the matrix from 3MHx to MTHF,

Table 2. Observed and calculated charge-transfer transition energies of the benzyl radical-halide ion complexes

Matrix	Halide ion	Ionization energy of halide ion[a)] $IP(\mathrm{X}^-)$	Dielectric const.[b)]		Solvation energy[d)]		CT excitation energy, $h\nu_{\mathrm{CT}}$	
			D_s	D_{op}	$E_s(\mathrm{X}^-)$	$E_s(\mathrm{Bz}^-)$	Calcd	Exptl
MTHF	Cl⁻	3.61	2.2[c)]	2.0	2.39	1.37	3.73	3.61
	Br⁻	3.36	2.2[c)]	2.0	2.18	1.37	3.27	3.36
	I⁻	3.06	2.88	2.0	2.29	1.37	3.08	2.95
EtOH	I⁻	3.06	3.0	1.853	2.34	1.26	3.25	3.59

Energies are given in eV units. a) Ref. 15. b) Ref. 13. c) D_s at 4.2 K is assumed in the present investigation. See text. d) The calculation is based on Born's formula: $E_s=(e^2/2r)(1-1/D)$. $E_s(\mathrm{Bz}^-)$ from D_{op} and $r=0.263$ nm, which is assumed to be independent of the solvent. See also Refs. 2 and 6.

for the Cl⁻ and Br⁻ series, as shown in Table 1. Combining the new data (the third column) with the previous data (the last column), it can be seen that the CT band for the I⁻ ion is increasingly blue-shifted in the order 3MHx, MTHF, and ethanol.

The D_s and D_{op} values at 77 and 4.2 K for MTHF and ethanol are needed in order to apply equation (3) for an quantitative examination of the effect of the matrix polarity as observed in the present experiment. From an extrapolation of high temperature data, Kevan has proposed that for MTHF at 77 K, $D_s=2.88$ and $D_{\mathrm{op}}=2.0$.[13)] Using these values and the reported ionic radii[14)] (0.164, 0.180, and 0.205 nm for Cl⁻, Br⁻, and I⁻) and assuming that the $\dot{\mathrm{B}}\mathrm{z}^-$ ion has a constant radius (0.263 nm, irrespective of the matrix), $h\nu_{\mathrm{CT}}$ for the $\dot{\mathrm{B}}\mathrm{z}$---I⁻ complex in the MTHF matrix has been calculated as 3.08 eV (see Table 2). This is close to the observed value of 2.95 eV at 77 K. The dashed line in Fig. 3 shows the linear relationship between $h\nu_{\mathrm{CT}}$ and $IP(\mathrm{X}^-)+E_s(\mathrm{X}^-)$ calculated for the $\dot{\mathrm{B}}\mathrm{z}$---X⁻ complexes in a MTHF matrix with $D_{\mathrm{op}}=2.0$. The observed $h\nu_{\mathrm{TC}}$ at 4.2 K for the $\dot{\mathrm{B}}\mathrm{z}$---Cl⁻ and $\dot{\mathrm{B}}\mathrm{z}$---Br⁻ complexes fall on the predicted line, if one assumes that $D_s=2.2$ at 4.2 K. The smaller D_s indicates that the MTHF matrix is similar to nonpolar alkane matrices at 4.2 K. This can be attributed to an inhibition of the rotational relaxation of the polar MTHF molecules surrounding the ions at 4.2 K. Such an inhibition of the rotational relaxation has been verified by observing the evolution of the absorption spectrum of the trapped electrons in a MTHF matrix upon warming from the γ-irradiation temperature 4.2 K to 77 K.[16,17)]

By using Kevan's estimates of D_s and D_{op} for ethanol at 77 K,[13)] $h\nu_{\mathrm{CT}}$ for the $\dot{\mathrm{B}}\mathrm{z}$---I⁻ complex can be calculated as 3.24 eV, which is somewhat too small in comparison with the observed value of 3.59 eV (see Table 2). This discrepancy is partly due to the fact that Born's formula, used to calculate the solvation energies, is strictly valid only for the case of continuous matrix media. The main contribution to the solvation, however, will be the rotational relaxation of the polar ethanol molecules in the close vicinity of the I⁻ ion. In addition, it is possible that the rotational relaxation has not gone to completion after warming the sample to 77 K before the measurement of the CT band. The previous study on the evolution of the spectrum of the trapped electron indicates that the rotational relaxation in the ethanol matrix took about 30 min to be completed at 77 K.[18)]

Table 1 shows the general trend in the formation of $\dot{\mathrm{B}}\mathrm{z}$---X⁻ complexes. Experimental conditions favor observations of these complexes: (1) When the irradiation temperature is low, (2) when the X⁻ ion is bulky, and/or (3) when the matrix is nonpolar. Conditions (1) and (2) prevent the ion from escaping from the $\dot{\mathrm{B}}\mathrm{z}$ radical (cage effect). Condition (3) is somewhat more complex. An increase in matrix polarity will have two effects. The first effect is a solvation effect. The orientational rearrangement of the polar matrix molecules around the X⁻ ion of the ground state complex increases $E_s(\mathrm{X}^-)$ and is the cause of the blue-shift of the CT band. The varying extent of the solvation effect will broaden the band, so that its apparent intensity becomes weaker. The second effect is a separation effect. The molecular reorientation in the immediate vicinity of the X⁻ ion will push it away from the $\dot{\mathrm{B}}\mathrm{z}$ radical. A slight increase in the interdistance between X⁻ and $\dot{\mathrm{B}}\mathrm{z}$ will significantly reduce the overlap between the electron-donating orbital and the electron-accepting orbital, so that the transition moment of the CT excitation will decrease in magnitude. Neither a blue-shift nor a broadening of the line could be observed during the gradual decay of the $\dot{\mathrm{B}}\mathrm{z}$---I⁻ CT band after warming the ethanol matrix to 77 K. This is an indication that the separation effect is more important than the solvation effect in polar matrices.

The absence of both benzyl spectrum or the CT band immediately after 4.2 K irradiation of the matrices containing BzI gives an interesting example of the detailed reaction steps involved in the dissociative electron attachment. A gas phase study has shown that the dissociative attachment of thermal electrons to aromatic halides having low-energy vacant π orbitals occurs according to a mechanism involving an intermediate molecular negative ion as a precursor of the dissociation into a halide ion and a free radical.[19)] Although such a precursor is expected to be easily trapped in the solid state, spectroscopic observations of it have been very few.[8,9)] In the present case, the precursor was observed at 4.2 K (see Fig. 2). It unquestionably dissociated into $\dot{\text{Bz}}$ and I^-, as is evidenced by the excitation spectra after warming BzI/ethanol or 3MHx to 77 K (see, for example, Fig. 1). The cage effect is so prominent at 4.2 K for the most bulky I^- ion that the elongation of the C–I bond distance and/or the change of the $-\text{CH}_2$ group from sp^3 to sp^2 conformation is inhibited.

In conclusion, the following reaction steps have been revealed by the present investigation:

$$\text{BzI} \xrightarrow{e^-} \underset{\text{precursor}}{\text{BzI}^-} \longrightarrow \underset{\text{complex}}{(\dot{\text{Bz}}\text{---I}^-)} \longrightarrow \dot{\text{Bz}} + \text{I}^-.$$

The question whether the precursor observed by the optical absorption measurements is the molecular anion or an intermediate state between the molecular anion and the complex still remains. The precursor dissociates into the complex even at 4.2 K for BzBr and BzCl. The complex is stably trapped at 77 K in the nonpolar 3MHx matrix for all the BzX's examined, but it is unstable in the polar ethanol matrix. The dissociation of the complex could be followed by observing the gradual decay of the CT excitation band for $\dot{\text{Bz}}\text{---I}^-$ in the ethanol matrix at 77 K. The MTHF matrix is intermediate as concerns the stability of the complex.

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