BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (1), 235—236 (1979)

Radical-Ion Interaction. Diphenylmethyl and Triphenylmethyl Radicals Generated by the Dissociative Electron Attachment to Halogenated Compounds in Rigid Matrices

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(Received July 21, 1978)

Synopsis. Dissociative electron attachment to diphenylmethyl halides and triphenylmethyl halides in a γ-irradiated 3-methylhexane matrix at 77 K generates free radicals temporarily associated with a counterpart halide ion. The association is indicated by changes in the fluorescence and excitation spectra of the radicals as well as the charge-transfer excitation band of the radical-ion complexes.

Temporary radical-ion association has been indicated by the fluorescence spectrophotometric method for benzyl radicals$^{1-3)}$ and the methyl-substituted derivatives (at the phenyl ring$^{2)}$ and at the methylene position$^{4)}$) generated by the dissociative electron attachment to the corresponding halogenated compounds such as benzyl halides in organic glassy matrices γ-irradiated at 77 K. The radical-ion interaction causes the wavelength shift and the change in the vibration band structure of the benzyl spectra as well as the decrease in the fluorescence lifetime. The interaction has also been indicated by the charge-transfer band of the benzyl radical-halide ion complexes in nonpolar hydrocarbon matrices. The interaction is absent in a polar ethanol matrix probably because of the solvation of the halide ions. The temporary radical-ion association before complete dissociation appears as a general feature in solid state radiation chemistry and adds a new aspect to the molecular spectroscopy of radical intermediates. The study was extended to diphenylmethyl and triphenylmethyl radicals, because they show a similar absorption character to that of the benzyl radicals.$^{5-8)}$ The triphenylmethyl radical shows an intense near-UV absorption due to the allowed $A_2'' \leftarrow E''$ transition and a weak visible absorption due to the forbidden $A_1'' \leftarrow E''$ transition. The assignment is based on the assumed D_{3h} symmetry of the radical. The forbidden transition is observable because of a slight deviation from the assumed planar configuration.$^{7)}$ A similar assignment may be applicable to the diphenylmethyl radical.

Experimental

Diphenylmethane, dephenylmethyl chloride (Ph_2CHCl) and bromide (Ph_2CHBr), and triphenylmethyl chloride (Ph_3CCl) and bromide (Ph_3CBr), of analytical grade, were used as received. The solvents, 3-methylhexane (3MHx) and ethanol (EtOH), were purified as described elsewhere.$^{2)}$ The solutions (10^{-2}—10^{-3} mol·dm^{-3}) were prepared under vacuum of *ca.* 10^{-5} Torr, sealed in quartz tubes (i.d. 4 mm), frozen by liquid nitrogen into the glassy state, and irradiated at 77 K with ^{60}Co γ-rays to a dose of *ca.* 5×10^4 rad or with unfiltered light from a high pressure mercury lamp. The fluorescence and fluorescence excitation spectra of the irradiated samples were recorded with a conventional fluorescence spectrophotometer (Hitachi, Model MPF-2A) at 77 K.

Results and Discussion

Diphenylmethyl Radical. When the diphenylmethyl (Ph_2CH) radical is generated by the dissociative electron attachment to Ph_2CHCl in the γ-irradiated EtOH matrix, the highest peak in the fluorescence spectrum is at 523 nm and the highest peak in the excitation spectrum is at 337 nm as shown in Fig. 1A. These spectra are essentially the same as those reported previously.$^{5-7)}$ The excitation spectrum in the visible region is however too weak to be recorded. Although the vibration band structure is not well resolved, as is usually the case for glassy matrix samples, the peaks mentioned above indicate the wavelength of the 0-0 band for the electronic transitions in the near-UV and visible regions. The photolysis of Ph_2CH_2 gives also

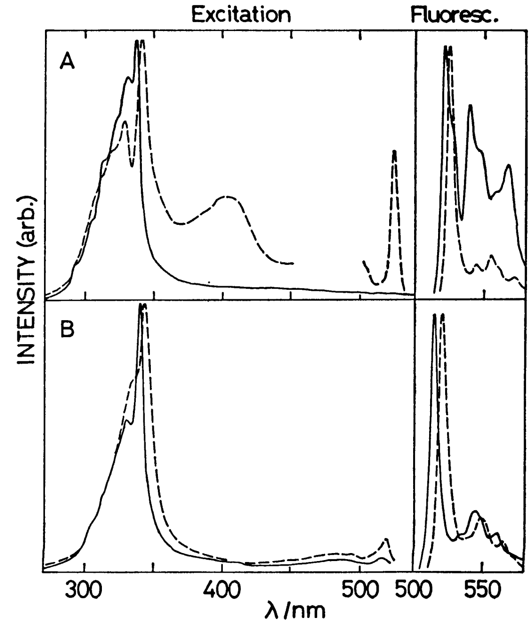

Fig. 1. Fluorescence and excitation spectra of (A) Ph_2CH radical generated from Ph_2CHCl and (B) Ph_3C radical generated from Ph_3CCl (——) in the EtOH matrix and (----) in the 3MHx γ-irradiated at 77 K. The spectral shape in the wavelength 460—500 nm shown by the dashed curve in A could not be determined because of the resonance lines of the Xe lamp used as a excitation source. Th excitation wavelengths and the monitoring one are generally at the highest peak of the fluorescence spectra and the excitation ones.

Table 1. Fluorescence and excitation spectra of diphenylmethyl and triphenylmethyl radicals generated by dissociative electron attachment to the corresponding halo-compounds in 3-methylhexane and ethanol matrices at 77 K

Radical	Source	Matrix	Wavelength (nm)		
			Fluorescence[a]	Excitation[b]	CT-band[c]
$\dot{\mathrm{C}}\mathrm{H(C_6H_5)_2}$	$\mathrm{CH(C_6H_5)_2Cl}$	3 MHx	526	342	405
		EtOH	523	337	—
	$\mathrm{CH(C_6H_5)_2Br}$	3 MHx	526	341	460[e]
		EtOH	523	336	—
$\dot{\mathrm{C}}\mathrm{(C_6H_5)_3}$	$\mathrm{C(C_6H_5)_3Cl}$	3 MHx	520 (515)[d]	344 (341)	—
		EtOH	514 (513)	341 (342)	—
	$\mathrm{C(C_6H_5)_3Br}$	3 MHx	519 (515)	345 (340)	—
		EtOH	514 (513)	341 (341)	—

a) The 0-0 band of the fluorescence spectrum. b) The 0-0 band of the near-UV excitation spectrum. c) The peak of the CT excitation spectrum. d) The figures in parentheses give the wavelength after melting and refreezing of the irradiated samples. e) A satellite peak was observed at 395 nm.

the same spectra except that they overlap with the spectra of the benzyl radical attributed to the loss of a phenyl ring from the parent molecule. The $\mathrm{Ph_2CH}$ radical generated from $\mathrm{Ph_2CHCl}$ in the γ-irradiated 3MHx matrix gives a different spectra from those observed from the EtOH matrix (Fig. 1A): the spectra shift to the red, and the vibration band structure so changes that the 0-0 band comparatively increases in intensity. The visible excitation spectrum becomes intense enough to be recorded. These features are the same as those observed for the benzyl radicals and have been interpreted as the effect of the proximity of the halide ions to the radicals.[2)] A similar phenomenon has been observed for the $\mathrm{Ph_2CH}$ radical from $\mathrm{Ph_2CHBr}$, as representatively shown for the spectral red-shift in Table 1. In the EtOH matrix, the halide counter-ion is solvated with polar matrix molecules, so that the radical-ion interaction no longer affects the spectra of the $\mathrm{Ph_2CH}$ radical.

The radical-ion interaction has also been indicated by the presence of a broad unstructured excitation band at 405 nm observed from $\mathrm{Ph_2CHCl}$ in the 3MHx matrix (Fig. 1A). A similar band has been recorded for $\mathrm{Ph_2CHBr}$ at 460 nm with a satellite peak at 395 nm. Assignment has been made to the CT band of the $\mathrm{Ph_2CH}$ radical-halide ion complexes; the former having a large electron affinity acts as an electron acceptor, and the latter with a small ionization energy (the electron affinity of Cl and Br atom is 3.61 and 3.36 eV[9)]) as an electron donor. The CT transition energy approximates to $h\nu_{\mathrm{CT}}=IP(\mathrm{X}^-)-EA(\mathrm{R}\cdot)+E_{\mathrm{s}}(\mathrm{R}\cdot\text{--}\mathrm{X}^-)-E_{\mathrm{s}}(\mathrm{R}^-\text{--}\mathrm{X})$, where IP and EA represent the ionization energy and the electron affinity, and E_{s} is the solvation energy before and after the transition. $E_{\mathrm{s}}(\mathrm{R}\cdot\text{--}\mathrm{X}^-)$ can be expressed approximately by Born's formula, $E_{\mathrm{s}}(\mathrm{X}^-)=(e^2/2r)(1-1/D)$, where r is the effective radius of the halide ion and D is the dielectric constant of the matrix. The difference in the CT transition energy between 3.1 eV (405 nm) and 2.7 eV (460 nm) of 0.4 eV for $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ as a counter-ion agrees well with 0.45 eV, the difference of $IP(\mathrm{X}^-)+E_{\mathrm{s}}(\mathrm{X}^-)$ calculated from the dielectric constant, 2.0, for 3MHx[10)] and the ionic radius, 0.164 and 0.180 nm for $\mathrm{Cl^-}$ and $\mathrm{Br^-}$.[11)] The energy difference between the main peak and the satellite one, 0.44 eV, observed for the $\mathrm{Ph_2CH\text{--}Br^-}$ complex may be interpreted as being due to the splitting of the CT excited state caused by the large separation between the $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$ states of the bromine atom, 0.459 eV.

Triphenylmethyl Radical. Triphenylmethyl ($\mathrm{Ph_3C}$) radicals generated from $\mathrm{Ph_3CCl}$ and $\mathrm{Ph_3CBr}$ in the γ-irradiated EtOH and 3MHx matrices give the spectra, as shown in Fig. 1B, of which the spectroscopic parameters are given in Table 1. The "free" $\mathrm{Ph_3C}$ radical in the EtOH matrix shows a visible fluorescence spectrum as well as a weak excitation spectrum in the visible region and an intense one in the near UV region. The $\mathrm{Ph_3C}$ radical in the 3MHx matrix shows a red-shift of the spectra (see Table 1) and an increase in spectral intensity in the visible region. The above observations indicate a radical-ion interaction for the $\mathrm{Ph_3C}$ radical.

Removal of the halide counter-ion produces further evidence for the interaction. The $\mathrm{Ph_3C}$ radical is so stable that it persists on melting the irradiated samples. The spectra of the $\mathrm{Ph_3C}$ radical in the 3MHx matrix changes and becomes identical with the spectra observed from the EtOH matrix, when examined after melting and refreezing. This change has been attributed to the removal of the counter-ion. The spectra observed from the EtOH matrix show no change upon melting and refreezing, since the radical is initially "effectively free" from the counter-ion in the matrix.

No CT band was recorded for the $\mathrm{Ph_3C}$ radical-halide ion complex in the 3MHx matrix. The intermolecular conformation adequate to the CT interaction is sterically inhibited for the bulky $\mathrm{Ph_3C}$ radical. However, the present investigation gives spectroscopic evidence for the temporary radical-ion association for the $\mathrm{Ph_3C}$ radical, as well as for the $\mathrm{Ph_2CH}$ radical, generated by the dissociative electron attachment in the irradiated nonpolar 3MHx matrix at 77 K.

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