BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(12), 3167—3168 (1974)

Dissociative Electron Attachment to (Chloroethyl)benzenes in γ-Irradiated Organic Glassy Matrices

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(Received May 17, 1974)

Synopsis. Free radicals formed from (1- and 2-chloroethyl)benzene in γ-irradiated organic matrices were studied with a fluroescence spectrophotometer. The observed spectra suggest the transformation of phenetyl radical primarily formed from (2-chloroethyl)benzene to α-methylbenzyl radical and indicate interaction between the α-methylbenzyl radical, formed from both (1- and 2-chloroethyl)benzene, and chloride anion before complete dissociation.

There is a current interest in radiation chemistry in condensed media in studies of the relaxation process[1] before the formation of thermodynamically stable intermediates such as trapped electrons and anions. Recently, we have studied the formation of benzyl radical from benzyl derivatives and obtained spectroscopic evidence that the benzyl associates temporarily with fragment anion when formed through dissociative electron attachment in organic glassy matrices.[2] In order to see the generality of this behavior, the study was extended to (1- and 2- chloroethyl)benzene by means of a fluorescence spectrophotometric method. The method has great advantages in studying intermediates formed in γ-irradiated matrices on account of its high sensitivity, applicability to non-transparent specimens and the possibility to distinguish a spectrum from other overlapping ones. Prominent results are: (1) a temporary association is evidenced also between α-methylbenzyl radical and chloride anion and (2) phenetyl radical transforms readily to α-methylbenzyl radical in the matrices at 77 K.

3-Methylhexane was used as non-polar solvent after being purified several times by washing with a sulfuric acid–nitric acid mixture and then with water and drying with anhydrous calcium chloride and calcium hydride. Ethanol of spectro-grade was used without further purification as a polar solvent. Solutes of analytical grade, ethylbenzene, (1-chloroethyl)benzene and (2-chloroethyl)benzene, were used without further purification. The effect of purification was checked once for 2-chloroethylbenzene, no difference in results being found.

Solution of 10^{-1}—10^{-2} M concentration was prepared in a vacuum of about 10^{-6} Torr, for desired combination of solvent and solute, and sealed in tubes of pure quartz (originally for ESR). The samples were frozen into glassy state, irradiated with ^{60}Co γ-rays to a dose of about 3×10^5 rad or with UV light from a high pressure mercury lamp, and examined with a recording fluorescence spectrophotometer (Hitachi, Model MPS-2A) at 77 K.

Typical examples of emission and excitation spectra of α-methylbenzyl radicals generated in different ways are given in Fig. 1. The emission spectra are observed in visible region with a 0-0 band at about 470 nm. Excitation spectra are observed in visible, near-UV (at about 320 nm) and far-UV (at about 270 nm) regions. However, spectral lines of excitation source (Xe lamp) interfered accurate recording of the weak visible excitation spectra. The emission spectra were recorded by excitation at the peak of the near-UV excitation spectra, though the shape of the emission spectra was not affected by the excitation wavelength. The near-UV and far-UV spectra were recorded by observation at the maximum point of the emission spectra. Characteristics of the recorded spectra are summarized in Table 1.

Ethylbenzene. Free radicals generated from ethylbenzene were studied for comparison. The spectra obtained by photolysis in the non-polar matrix (Fig. 1A) are close to those of photolytically generated benzyl radicals,[2] except that the strong 0-0 band in the emission spectrum indicates a partial removal of the forbidden nature of this band by methyl substitution, and thus they are attributed to the α-methylbenzyl radical. Porter and Starachen reported the absorption spectrum in the near-UV region (maximum at 322.2 nm) of the α-methylbenzyl radical formed by the photolysis of ethylbenzene in ether–isopentane–ethanol mixed glass.[3] The present spectra are consistent with theirs.

The γ-irradiation gives the same spectra as those in Fig. 1A, irrespective of solvent (Table 1). This in-

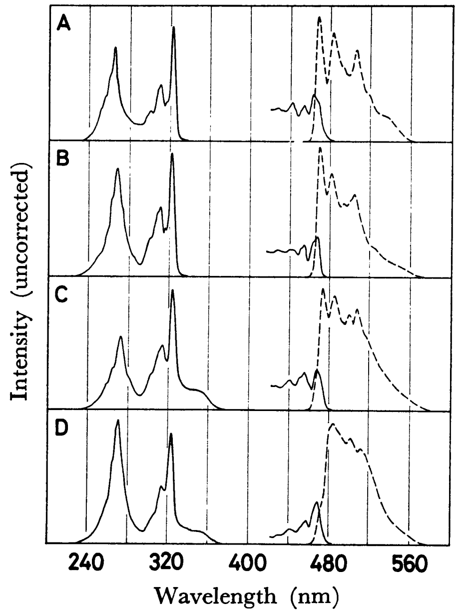

Fig. 1. Emission (----) and excitation (——) spectra of α-methylbenzyl radicals generated (A) from ethylbenzene by photolysis in 3-methylhexane, from (1-chloroethyl)benzene by γ-irradiation (B) in ethanol and (C) in 3-methylhexane, and (D) from (2-chloroethyl)benzene by γ-irradiation in 3-methylhexane.

Table 1. Excitation and emission spectra observed at 77 K of α-methylbenzyl radicals generated photolytically or radiolytically in organic glassy matrices

Parent molecules	Matrices	Generation method	Excitation spectra		Emission spectra λ_{max} (nm)
			Near-UV band λ_{max} (nm)	350 nm band	
$C_6H_5CH_2CH_3$	3MHx$^{a)}$	Photolysis	322	—	$467._5$
	3MHx	Radiolysis	$322._5$	—	468
	EtOH$^{b)}$	Radiolysis	323	—	468
$C_6H_5CHClCH_3$	3MHx	Radiolysis	$323._5$	Observed	473
	EtOH	Radiolysis	322	—	469
$C_6H_5CH_2CH_2Cl$	3MHx	Photolysis	$323._5$	—	469
	3MHx	Radiolysis	$323._5$	Observed	483$^{c)}$
	EtOH	Radiolysis	$323._5$	—	$469._5$

a) 3-methylhexane. b) Ethanol. c) Does not apparently correspond to the 0—0 band of the spectrum.

dicates the formation of α-methylbenzyl radicals also by radiolysis. Although radiation chemical processes involved are not known in detail, it is unconceivable that the methylbenzyl radical is formed through the electron attachment to ethylbenzene. A hydrogen atom or some other radical might be formed as a counterpart of the methylbenzyl radical by the homolytic C–H bond rapture. Radical formation may be possible by energy transfer from solvent to solute.4) An alternative may be charge neutralization between ethylbenzene cation and electron to form excited ethylbenzene, as proposed for the formation of benzyl radical from toluene in aqueous solution.5)

(1-Chloroethyl)benzene. When α-methylbenzyl radicals are generated from (1-chloroethyl)benzene by γ-irradiation, the spectra differ depending on the nature of matrices, polar or non-polar. The spectra in the polar matrix are the same as those of normal methylbenzyl radicals (compare Fig. 1B with Fig. 1A), whereas the spectra in the non-polar matrix (Fig. 1C) differ in the following way. (1) The visible emission and near-UV excitation spectra are more or less red-shifted. Although the band structure in the far-UV spectrum is not resolved, its peak also red-shifts from $267._5$ to $272._5$ nm. (2) The band width of the spectra becomes broader in the non-polar matrix, as seen clearly in the visible emission spectra. (3) A new broad excitation spectrum is observed around 350 nm. These observations are completely analogous to those for benzyl radicals formed from benzyl chloride.2) The methylbenzyl radical is generated with chloride anion as a counterpart through dissociative electron attachment to (1-chloroethyl)benzene. The first two observations are qualitatively interpreted to be due to the local Coulombic effect of nearby anion, as in the case of radical cation spectra perturbed by counter anions.6) The effect of the counter anion is dominant in the non-polar matrix but almost absent in the polar matrix because of the solvent polarization and anion solvation. According to the assignment of electronic transitions given to benzyl-type radicals,7) the new spectrum may possibly be due to the $2^2B_2 \rightarrow 1^2B_2$ transition, hidden by the intense near-UV spectrum of the $2^2A_2 \rightarrow 1^2B_2$ transition in the absence of the effect of nearby anion.2) The association between the α-methylbenzyl radical and the anion temporarily occurs after the dissociative electron attachment to (1-chloroethyl)benzene in the glassy matrix. The efficiency of methylbenzyl radical formation by photolysis is too low to record spectra.

(2-Chloroethyl)benzene. The dissociative electron attachment to (2-chloroethyl)benzene results in the formation of phenethyl radical as a primary intermediate. However, the spectra observed after γ-irradiation indicate that α-methylbenzyl radicals are trapped in the irradiated matrices. The phenethyl radical is unstable even in rigid matrices and readily transforms to the methylbenzyl radical, $\dot{C}_6H_5CH_2CH_2 \rightarrow C_6H_5\dot{C}HCH_3$. In this case also, the methylbenzyl radicals formed by γ-irradiation show spectra dependent on the polarity of the matrix. In the polar matrix, the spectra are the same as those of the "free" methylbenzyl radical (Fig. 1B). In the non-polar matrix, the effect of a nearby anion is seen in the excitation spectra (Fig. 1D). Although the 0-0 band of the emission spectrum is not resolved in this case, it is evident that the spectrum is also red-shifted and the band width is extremely large.

When (2-chloroethyl)benzene is photolyzed, the counterpart of the methylbenzyl radical is necessarily a chlorine atom rather than a chloride anion. In fact, photolysis in the non-polar matrix gives spectra typical of the "free" methylbenzyl radical (Table 1). This observation strongly supports the view that the perturbed spectra of the α-methylbenzyl radical formed by dissociative electron attachment are attributed to the temporary radical-anion pair before complete dissociation.

References

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