Ultraviolet Absorption Spectrum of the Benzyl Cation observed by the Pulse Radiolysis of Benzyl Chloride

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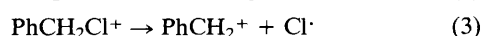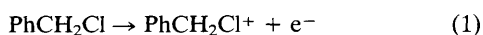
The absorption spectrum of the benzyl cation has been found to have a strong band at 303 ± 2 nm and a weak broad band near 500 nm by comparing the transient spectrum for benzyl chloride saturated with oxygen with those for the solutions of 0.5 mol dm^{-3} ethanol in benzyl chloride saturated with oxygen.

Numerous attempts have been made to observe the UV–VIS absorption spectrum of the benzyl cation. The methods employed include the use of strongly acidic solutions,[1–3] pulse radiolysis,[4] photoionisation in an argon matrix,[5] photodissociation in a mass spectrometer[6] and laser flash photolysis.[7] The reported spectra, however, do not necessarily agree well with each other. The question of the spectrum of the benzyl cation seems not to have been settled.

In the present work, we have tried to observe the spectrum of the benzyl cation by the pulse radiolysis of liquid benzyl chloride at room temperature. Benzyl chloride was purified at 60 °C by preparative gas chromatography. The sample (*ca.* 3 ml) was put in a Suprasil cell of optical path length 1.0 cm and either argon or oxygen bubbled through it. The samples were irradiated with 0.50 μs pulses of 3 MeV electrons from a van de Graaff accelerator.[8]

Fig. 1(*a*) shows the transient absorption spectra observed in the pulse radiolysis of neat benzyl chloride, benzyl chloride saturated with one atmosphere of oxygen, and the solutions of 0.5 mol dm^{-3} ethanol in benzyl chloride saturated with oxygen. Fig. 1(*a*) shows also the transitory spectrum recorded 1.5 μs after the end of electron pulse for the O$_2$-saturated benzyl chloride. The insert (*b*) in Fig. 1 displays the oscilloscope trace obtained in the pulse radiolysis of O$_2$-saturated benzyl chloride.

Our results are interpreted in terms of the processes eqn. (1)–(3).

$$PhCH_2Cl \rightarrow PhCH_2Cl^+ + e^- \qquad (1)$$

$$PhCH_2Cl + e^- \rightarrow PhCH_2{}^{\boldsymbol\cdot} + Cl^- \qquad (2)$$

$$PhCH_2Cl^+ \rightarrow PhCH_2{}^+ + Cl^{\boldsymbol\cdot} \qquad (3)$$

The transient spectrum for pure benzyl chloride shown in Fig. 1(*a*) is similar to, but does not correspond exactly to the spectrum of the benzyl radical.[9] As will be shown below, the transient spectrum in neat benzyl chloride is a superposition of the spectra of benzyl radical and benzyl cation.
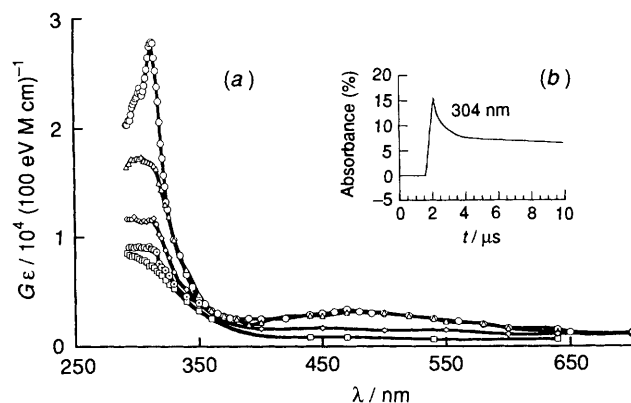

Fig. 1(*a*) End of pulse transient spectra observed in the pulse radiolysis of pure benzyl chloride (O), benzyl chloride bubbled with one atm. oxygen (△), 0.5 mol dm^{-3} solutions of ethanol (◇), and 0.05 mol dm^{-3} solutions of pyrrole (⊙) in benzyl chloride saturated with oxygen. The spectrum for the O$_2$-saturated benzyl chloride solutions determined 1.5 μs after the pulse (□). (*b*) The decay of absorption monitored at 304 nm in the pulse radiolysis of O$_2$-saturated benzyl chloride. Dose per pulse, 35 Gy; pulse length, 0.50 μs; irradiation temperature, 22 °C.
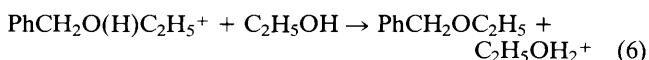
The oxygen added to benzyl chloride scavenges the benzyl radical formed by reaction (2) and other processes:

$$PhCH_2{\cdot} + O_2 \rightarrow PhCH_2O_2{\cdot} \qquad (4)$$

As expected, the characteristic doublet absorption of the benzyl radical disappeared to a large extent in the presence of O_2.

In the presence of O_2, however, the residual UV absorption is still conspicuous. The decay of the residual UV absorption consists of two portions as shown in Fig. 1(b). A short-lived species decays with a halflife of less than 1 μs. On the other hand, a long-lived species shows no significant decay over a few μs. Since the short-lived species disappears essentially within 1.5 μs, the spectrum determined 1.5 μs after the pulse corresponds to the spectrum of the long-lived species. The UV spectrum recorded 1.5 μs after the pulse is shown in Fig. 1(a). It agrees well with the spectrum of the benzyl peroxyl radical.[10] Thus, the long-lived species in O_2-saturated benzyl chloride is assigned to the benzyl peroxyl radical produced by reaction (4).

To investigate the nature of the short-lived species, ethanol, a typical carbocation scavenger, was added to O_2-saturated benzyl chloride. The addition of 0.5 mol dm^{-3} ethanol resulted in the appreciable decrease in the $G\varepsilon$ values as shown in Fig. 1(a). Since benzyl chloride has a weak benzylic C–Cl bond, fragmentation of the parent ion is inferred to give predominantly the benzyl cation. The reaction between ethanol and the benzyl cation may be written as in eqns. (5) and (6).

$$PhCH_2{}^+ + C_2H_5OH \rightarrow PhCH_2O(H)C_2H_5{}^+ \qquad (5)$$

$$PhCH_2O(H)C_2H_5{}^+ + C_2H_5OH \rightarrow PhCH_2OC_2H_5 + \\ C_2H_5OH_2{}^+ \qquad (6)$$

The difference in the $G\varepsilon$ values for O_2-saturated benzyl chloride and the 0.5 mol dm^{-3} solutions of ethanol in benzyl chloride saturated with O_2 is taken to correspond to the spectrum of the benzyl cation. The spectrum obtained in this way has a strong absorption peak at 303 ± 2 nm and a diffuse band near 500 nm as shown in Fig. 2. The weak visible absorption in the wavelength 400–600 nm shows a typical ionic nature. That is, the visible band is not influenced by the addition of O_2, but is not observed following addition of ethanol, and has a short lifetime of 1.5 μs. So, the visible band in neat benzyl chloride is also due to the benzyl cation.

In order to further reinforce our finding, a weak base, pyrrole, was used as another positive ion interceptor. The results are shown in Figs. 1 and 2. It is noted that essentially the same UV spectrum was observed using pyrrole in place of ethanol. With pyrrole, the visible spectrum of the benzyl cation was obscured, because the reactions of pyrrole with cations give intermediates that absorb weakly in the visible

region. The enhanced $G\varepsilon$ values in Fig. 2 observed by using pyrrole may indicate that the amine, pyrrole, is a much more efficient cation scavenger than the alcohol.

The benzyl cation has been reported to have the absorption maximum at 290 nm in the gas phase.[6] Our λ_{max} at 303 nm is in line with this gas phase value. The λ_{max} may shift from 290 to 303 nm in going from the gas to liquid phase owing to the solvation of the cation in the liquid phase. The λ_{max} values predicted by theory[2] are 290 and 412 nm and their oscillator strengths are 0.46 and 0.08, respectively. Our spectrum is in accord with the predicted one with respect to transition energies and intensities.

In order to identify the cationic species that react with added ethanol, the analyses of end products were carried out using gas chromatography. If added ethanol really reacts with the benzyl cation, benzyl ethyl ether should be formed via reactions (5) and (6). The samples were γ-irradiated at room temp. (^{60}Co source) to a total dose of 38 kGy (1 Gy = 1 J kg^{-1}). In the radiolysis of benzyl chloride in the presence of O_2, benzaldehyde, dibenzyl, and toluene are formed with the G value of 3.2, 0.27 and 0.06, respectively. The benzaldehyde should stem from certain consecutive reactions of benzyl peroxyl radicals produced in reaction (4). In the presence of both O_2 and 0.6 mol dm^{-3} ethanol, benzaldehyde, benzyl ethyl ether, dibenzyl and toluene are formed, and their G values are 4.0, 0.70, 0.26 and 0.05, respectively. The formation of benzyl ethyl ether is good evidence that added ethanol reacts with benzyl cation. In the presence of radical scavenger, O_2, benzyl ethyl ether is probably not formed by recombination of benzyl radicals with eventual ethoxyl radicals. Thus, the G value for the benzyl cation is estimated as 0.70 in the radiolysis of liquid benzyl chloride.

The hydride-ion transfer from benzyl chloride to benzyl cation was reported to take place in a high pressure mass spectrometer;[11] see eqn. (7).

$$PhCH_2{}^+ + PhCH_2Cl \rightarrow PhMe + PhCHCl^+ \qquad (7)$$
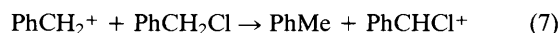
Since the G value of toluene formed in the benzyl chloride–O_2 mixture is only 0.06 as given above, the ion/molecule reaction such as (7) is not important under our experimental conditions.

Although the parent ion of benzyl chloride has been reported[12] to have an absorption peak at 590 nm, we were unable to observe an absorption band in this wavelength region.
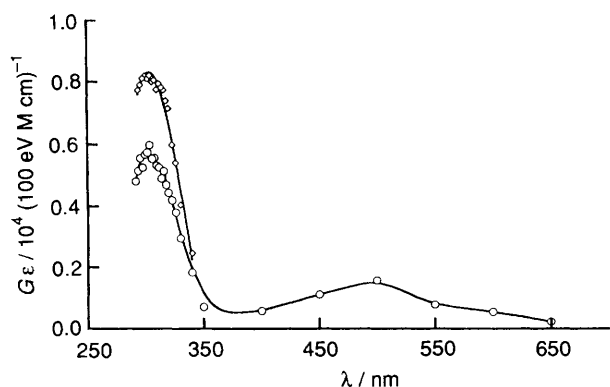
Fig. 2 The spectra obtained by subtracting the $G\varepsilon$ values for the 0.5 mol dm^{-3} solutions of ethanol (○), or for the 0.05 mol dm^{-3} solutions of pyrrole (◇) in benzyl chloride saturated with O_2 from those for benzyl chloride saturated with O_2.

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