Pulse Radiolysis of Benzyl Chloride and -Bromide; The UV-Visible Absorption Spectrum of the Benzyl Cation

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Pulse radiolysis study of liquid benzyl chloride has been carried out at room temperature. In order to identify transient species that absorb in the UV-vis region, various scavengers were used including oxygen, ethanol, pyrrole, biphenyl, and mesitylene (1,3,5-trimethylbenzene). The spectrum of the benzyl cation was obtained by subtracting the transient spectrum for the 0.6 M solutions of ethanol in O_2 -saturated benzyl chloride from that for O_2 -saturated benzyl chloride. The difference spectrum obtained has a strong absorption band at 303 ± 2 nm and a weak broad band near 500 nm. The analyses of end products formed in the γ radiolysis of benzyl chloride were done in the presence and absence of scavengers. The formation of benzyl ethyl ether with a G value of 0.9 from a 0.6 M solution of ethanol in O_2 -saturated benzyl chloride were done just to give benzyl ethyl ether. Some pulse radiolysis experiments were performed with benzyl bromide. Transient spectra observed in benzyl bromide are similar to those observed in benzyl chloride. It is, however, inferred from the product analysis that the radiolytic mechanisms of benzyl bromide appreciably differ from those of benzyl chloride.

Introduction

The pulse radiolysis of halogenated compounds in the liquid phase has been investigated in many laboratories [1-11]. They indicate that dissociative electron attachment takes place in various organic halides. The occurrence of dissociative attachment of electron entails the replacement of the rapid geminate recombination of positive-ion electron pairs by a slower neutralization of the positive ions with the low mobility halide anions. Thus, the lifetime of transient ionic species is considered to be much longer in halogenated compounds than in compounds such as alkanes with no electron affinity. In fact, transient spectra of labile carbocations in chlorinated solvents have been observed at room temperature by means of submicrosecond pulse radiolysis [7, 8].

Benzyl chloride and -bromide possess a weak benzylic C-Cl (C-Br) bond, so if fragmentation of the parent ion occurs even in the liquid phase, it should lead principally to the formation of the benzyl cation. Furthermore, the benzyl halides are moderately polar molecules with a dielectric constant of 7.0 so that the stabilization of ions by solvation can take place. The solvation makes the ion mobility lower and assists in the lengthening of the lifetime of ionic species.

With this in mind, the submicrosecond pulse radiolysis of benzyl chloride and -bromide, a known electron scavenger [12], has been made with the hope of being able to observe the transient spectra of carbocations.

Experimental Section

Materials. Benzyl chloride and -bromide were obtained from Fluka and purified by a preparative gas chromatograph (Pye, Model 104) provided with a 1.4 m Apiezon L column. The benzyl halides have a tendency to undergo thermal decomposition upon contact with metallic or glass surface. Therefore, the temperature of preparative GC system including the injection port and the column was kept during purification as low as possible, i.e. $60 \,^{\circ}$ C. The purified benzyl halides were dried over freshly activated molecular sieve 3A under vacuum. The purified benzyl halides undergo autoxidation at room temperature on standing in the air to give benzaldehyde. Hence they were stored under vacuum in a refrigerator at $-30 \,^{\circ}$ C. Spectrophotometric and gas chromatographic purities of the benzyl halide used are given in the Appendix.

Pure ethanol as obtained was refluxed with $NaBH_4$ and dried over freshly activated molecular sieve 3A. Pyrrole, biphenyl, and mesitylene were purified by gas chromatography using either Apiezon L or Igepal CO 880 columns. Benzyl ethyl ether was synthesized from benzyl bromide and sodium ethoxide. Water for the dosimetry was obtained from Millipore Milli-Q units. Other chemicals were used as received.

Procedures. The pulse radiolysis technique has been described in our previous works [13 - 15], so only the salient features of the approach will be given here. 3 ml of the sample 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 0.5 µs pulses of 3-MeV electrons from a Van de Graaff accelerator (High Voltage, Model KS 3000). For recording the transient absorption, a pulsed xenon lamp and a Bausch & Lomb monochromator were used. The signals from the photodetector were recorded on a Tektronix 2430 oscilloscope. The dosimetry was carried out using O₂-saturated 5 mM KSCN solutions. The dose per pulse was determined to be 70 Gy (1 Gy = 1 J/kg). Appropriate corrections were made to allow for the relative electron densities of water and benzyl halides.

Product Analysis. In the steady-state radiolysis of benzyl halides, 0.3 ml of the samples were irradiated with a 60 Co γ -ray source at a dose rate of 2 kGy/h to a total dose of 30 kGy. The gas chromatographic analysis of the stable

products was done using a 1.4 m Apiezon L or Igepal CO 880 column. The column temperature was kept at $100 \,^{\circ}$ C for 140 min and then increased at a rate of $1 \,^{\circ}$ C/min to 150 $^{\circ}$ C and held at that temperature.

Results

Fig. 1a shows the transient absorption spectra observed in the pulse radiolysis of pure benzyl chloride and benzyl chloride saturated with one atmosphere of oxygen. In Fig. 1a, G and ε mean the number of molecules or reaction intermediates produced per 100 eV energy absorbed and the molar extinction coefficient in units of M^{-1} cm⁻¹, respectively. The product, $G\varepsilon$, is directly connected with the absorbance of transient species. Fig. 1a includes also the transitory spectrum recorded 1.5 µs after the end of electron pulse for the O₂-saturated benzyl chloride.



Fig. 1

(a) End of pulse transient spectra observed in the pulse radiolysis of pure benzyl chloride (\triangle), benzyl chloride bubbled with one atmosphere oxygen (\bigcirc), and the spectrum determined 1.5 µs after the end of pulse for the O₂-saturated benzyl chloride (\square). (b) The decay of absorption monitored at 304 nm in the pulse radiolysis of O₂-saturated benzyl chloride. Experimental conditions; dose per pulse, 70 Gy; electron pulse duration, 0.50 µs; irradiation temperature, 22 °C

The insert b in Fig. 1 displays the oscilloscope trace obtained in the pulse radiolysis of O_2 -saturated benzyl chloride.

Fig. 2 illustrates the transient spectra for benzyl chloride saturated with O_2 , 0.6 M solutions of ethanol and 0.05 M solutions of pyrrole in benzyl chloride saturated with O_2 .

Figs. 3 and 4 show, respectively, the transient spectra for 0.1 M solutions of biphenyl and 0.1 M solutions of mesitylene in benzyl chloride saturated with O_2 gas together with the spectrum for benzyl chloride- O_2 system. The increase or decrease in the absorbance of transient spectra has been studied as a function of the concentration of each additive. The concentrations chosen in this work are those at which the effects of the additives correspond to saturation.

Fig. 5 displays the spectra of transient species in neat benzyl bromide, benzyl bromide saturated with one atm. of O_2 , and 0.6 M solutions of ethanol in benzyl bromide



End of pulse transient spectra in the pulse radiolysis of O_2 -saturated benzyl chloride (\bigcirc), 0.6 M solutions of ethanol (\triangle) and 0.05 M solutions of pyrrole (\square) in benzyl chloride saturated with 1 atm. oxygen. Experimental conditions as in Fig. 1



Fig. 3

Transient spectra in the pulse radiolysis of O₂-saturated benzyl chloride (\bigcirc), and 0.1 M solutions of biphenyl in benzyl chloride bubbled with O₂ gas (\triangle). Experimental conditions as in Fig. 1





Transient spectra observed in O₂-saturated benzyl chloride (\bigcirc), and 0.1 M solutions of mesitylene (1,3,5-trimethylbenzene) in benzyl chloride saturated with O₂ gas (\triangle)

bubbled with O_2 gas. In this case, transient spectra were obtained only above 350 nm owing to the strong absorption by benzyl bromide below this wavelength.

Table 1 summarizes the G values of final products in the γ -radiolysis of benzyl chloride and -bromide. In the radioly-



Fig. 5

End of pulse transient spectra in the pulse radiolysis of neat benzyl bromide (\triangle) , benzyl bromide saturated with oxygen gas (\bigcirc) , and 0.6 M solutions of ethanol in benzyl bromide saturated with O_2 gas (\bigcirc) . Experimental conditions as in Fig. 1

sis of benzyl chloride in the presence of both oxygen and ethanol, benzyl ethyl ether is formed with the G value of 0.94. It is noted that benzyl ethyl ether is also formed on standing the 0.6 M solution of ethanol in benzyl chloride. The quantity of benzyl ethyl ether formed by solvolysis was, however, negligible compared to that formed by radiolysis. On the other hand, a nonnegligible quantity of benzyl ethyl ether is formed by solvolysis of benzyl bromide-ethanol mixtures. Thus, the G value of benzyl ethyl ether was not exactly determined for the solutions of ethanol in benzyl bromide.

Discussion

Transient Spectra in Benzyl Chloride. When a high energy incident electron beam interacts with benzyl chloride, ionization of the molecule takes place;

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

where Ph means the phenyl group. The electron ejected in reaction (1) undergoes dissociative electron attachment after thermalization.

$$PhCH_2Cl + e^- \rightarrow PhCH_2^+ + Cl^-$$
(2)

Fragmentation of benzyl chloride molecular ion also occurs to a limited extent as will be discussed later.

$$PhCH_2Cl^+ \rightarrow PhCH_2^+ + Cl \tag{3}$$

The transient spectrum in pure benzyl chloride shown in Fig. 1 a is similar to, but does not correspond exactly to the spectrum of the benzyl radical [12, 16]. The transient spectrum in neat benzyl chloride is supposed to be a superposition of the spectra of the benzyl radical produced in reaction (2) and other processes, and of the benzyl cation produced in reaction (3), as will be shown below.

In order to scavenge the benzyl radical, oxygen was added to benzyl chloride. The reaction between oxygen and the benzyl radical is described by

$$PhCH_{2}^{\cdot} + O_{2} \rightarrow PhCH_{2}O_{2}^{\cdot}$$
(4)

Reaction (4) is rapid, and proceeds with the rate constant [17] of $2.3 \times 10^9 \,\text{M}^{-1} \,\text{s}^{-1}$. As expected, the characteristic doublet absorption in the UV region of the benzyl radical disappeared to a large extent in the presence of dissolved oxygen as shown in Fig. 1a.

The residual UV absorption in the presence of O_2 is, however, still strong. The decay of the residual UV absorption consists of two portions as shown in Fig. 1b. A shortlived species decays with a halflife of less than 0.5 μ s. On the other hand, a long-lived species shows no significant decay over a few μ s. The UV-Vis spectrum recorded 1.5 μ s after the pulse is shown in Fig. 1a. It agrees well with the spectrum of the benzyl peroxyl radical [18]. Thus, the longlived species in O₂-saturated benzyl chloride is assigned to the benzyl peroxyl radical formed in reaction (4).

To elucidate the nature of the short-live species, ethanol was added to O_2 -saturated benzyl chloride. The addition of 0.6 M ethanol resulted in the appreciable decrease in the *G* ε values as shown in Fig. 2. 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

Table 1

G values of the products formed in the γ -ray radiolysis of liquid benzyl chloride and -bromide^a

System	G value ^b				
	toluene	benzaldehyde ^c	benzyl alcohol	benzyl ethyl ether	dibenzyl
PhCH ₂ Cl	0.14	0	0	0	1.27
PhCH ₂ Cl-O ₂ ^d	0.04	7.42	0.31	0	0.19
PhCH ₂ Cl-0.6 M C ₂ H ₅ OH	0.25	0	0	0.74	1.09
PhCH ₂ Cl-0.6 M $C_2H_5OH-O_2^d$	0.03	5.68	0.14	0.94	0.11
PhCH ₂ Br	1.94	0	0	0	0.16
PhCH ₂ Br-O ₂ ^d	0.91	7.38	_ e	0	0.06
PhCH ₂ Br-0.6 M C ₂ H ₅ OH	1.40	-	0	_	0.05
$PhCH_{2}Br-0.6 M C_{2}H_{5}OH-O_{2}^{d}$	0.21	5.40	_	-	0.04

^a Dose = 30 kGy. Irradiation temperature = $22 \,^{\circ}$ C. ^b Number of molecules formed per 100 eV energy absorbed. ^c The values of G for benzaldehyde are sensitive to O₂ concentration and not well reproducible. ^d Saturated with ca. 13 atm. O₂ gas. ^e (-), not determined. between ethanol and the benzyl cation may be written in terms of condensation and deprotonation;

$$PhCH_{2}^{+} + C_{2}H_{5}OH \rightarrow PhCH_{2}O(H)C_{2}H_{5}^{+}$$
(5)

As shown in Table 1, benzyl ethyl ether is formed in the radiolysis of benzyl chloride-0.6 M ethanol- O_2 mixture. The formation of benzyl ethyl ether is taken as evidence that added ethanol reacts with benzyl cation to give benzyl ethyl ether via reactions (5) and (6).

The decrement in the Ge values caused by the addition of ethanol to benzyl chloride- O_2 mixtures 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. 6. 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 disappeared by the addition of ethanol, and has a short halflife of 0.5 µs. Therefore, the visible band in neat benzyl chloride is also related to the benzyl cation.



(a) The oscillator strength, f, and electronic transition energies for the benzyl cation calculated theoretically by the LCAO SCF CI [25] (filled bars) and LCAO SCF [20] (empty bars) methods. (b) The spectrum obtained by subtracting the $G\varepsilon$ values for the 0.6 M solutions of ethanol ($^{\bigcirc}$) or for the 0.05 M solutions of pyrrole ($^{\triangle}$) in benzyl chloride saturated with O_2 from those for benzyl chloride saturated with O_2 (see Fig. 2). The difference spectrum obtained by subtracting the $G\varepsilon$ values for the 0.6 M solutions of ethanol in benzyl bromide saturated with O_2 from those for benzyl bromide saturated with O_2 (\Box)

Pyrrole was employed as another carbocation interceptor with the results shown in Figs. 2 and 6. With pyrrole, the visible spectrum was obscured, because the pulse radiolysis of benzyl chloride-pyrrole mixtures gives intermediates that absorb weakly in the visible region. It is to be noted that essentially the same UV spectrum of the benzyl cation was observed when using pyrrole in place of ethanol. In the near UV region, a low concentration (0.05 M) of pyrrole was more efficient than a high concentration (0.6 M) of ethanol in decreasing the G ε values for benzyl chloride-O₂ mixtures as shown in Fig. 2. Accordingly pyrrole, a kind of amine, should be more reactive than ethanol toward the benzyl cation. It has been noticed [8] that the amine has in general higher reactivity than the alcohol toward carbocations.

Many attempts have so far been made to observe the spectrum of the benzyl cation. The techniques employed include the use of strongly acidic media [19-21], pulse radiolysis [7, 15], photoionization in an argon matrix [22], photodissociation in a mass spectrometer [23] and laser flash photolysis [24]. There is, however, a large discrepancy between the reported UV spectra. One group [7, 22] reported with some experimental results that the benzyl cation has a strong absorption band at 360 nm. On the other hand, another group [23, 24] has shown that the benzyl cation has a strong absorption at near 300 nm, but not at 360 nm. The question of the spectrum of the benzyl cation seems not to have been settled. Our spectrum shown in Fig. 6 rather agrees with that observed by the latter group.

The spectrum of the benzyl cation has been predicted theoretically by many authors [20, 25-28]. Fig. 6a shows a few of theoretical spectra [20, 25]. Our spectrum agrees with that calculated by the LCAO SCF CI method [25] with respect to the electronic transition energy and absorption intensity.

The G value of the benzyl cation has been estimated as 0.9 from the yield of benzyl ethyl ether (Table 1). The anticipated G value of total cationic species is much larger than 0.9. This suggests the existence of other cationic species than benzyl cation in our system. The benzyl chloride parent-ion, PhCH₂Cl⁺, produced in reaction (1), is a plausible candidate in this context. The parent ion of benzyl chloride has been reported [29] to have an absorption band at 590 nm. However, no descernible absorption peak was observed in this wavelength region under our experimental conditions. It appears that the extinction coefficient of PhCH₂Cl⁺ is small in the UV-Vis region.

In order to probe $PhCH_2Cl^+$, biphenyl was added to benzyl chloride-O₂ mixtures. The addition of 0.1 M biphenyl leads to the appearance of a new sharp absorption peak at 375 nm and a broad band in the visible region as shown in Fig. 3. The difference spectrum obtainable by subtracting the absorbances for $PhCH_2Cl-O_2$ mixtures from those for $PhCH_2Cl-0.1$ M biphenyl-O₂ mixtures corresponds well to the known spectrum of biphenyl radical cation [6, 9]. The appearance of biphenyl cation spectrum is ascribed to the occurrence of charge transfer reaction (7).

$$PhCH_2Cl^+ + Ph-Ph \rightarrow PhCH_2Cl + Ph-Ph^+$$
 (7)

The charge transfer reaction (7) can take place, because the ionization energy of benzyl chloride (9.19 eV) [30] is higher than that of biphenyl (8.27 eV) [30].

The occurrence of the similar charge transfer reaction was confirmed by using mesitylene (IE = 8.4 eV) [30] in-

stead of biphenyl. Although the spectrum of mesitylene radical cation has not been reported, the spectra of *p*-xylene [10] and hexamethylbenzene [31] radical cation are available. The spectral characteristic of *p*-xylene radical cation is similar to that of hexamethylbenzene radical cation. They have a medium absorption at 480 ± 10 nm and in the UV region. Consequently, mesitylene radical cation (Mes⁺) is surmised to have a medium absorption band at 480 nm and in the UV region. The addition of 0.1 M mesitylene to benzyl chloride-O₂ system enhanced the Ge values in the visible as well as in the UV region as shown in Fig. 4. The enhancement of the Ge values is associated with the occurrence of the charge transfer reaction (8),

$$PhCH_2Cl^+ + Mes \rightarrow PhCH_2Cl + Mes^+$$
(8)

where Mes stands for mesitylene.

Thus, the use of suitable charge scavengers enabled us to indirectly confirm the formation of benzyl chloride parention. The estimation of the G value for the benzyl chloride parentions scavengeable by 0.1 M biphenyl or mesitylene is hampered by the lack of reliable extinction coefficients for biphenyl and mesitylene radical cations.

Transient Spectra in Benzyl Bromide. The weak broad transient spectrum was observed in the wavelength 450-650 nm in the pulse radiolysis of neat benzyl bromide as shown in Fig. 5. The transitory spectrum in the visible region was not influenced by the addition of oxygen, but disappeared in the presence of ethanol, and has a halflife of less than $0.5 \,\mu$ s. These spectral features resemble those observed in benzyl chloride. The visible transient spectrum was assigned to benzyl cation in the case of benzyl chloride. The transient spectrum in benzyl bromide is, however, interpreted otherwise as described below.

Since the G value for toluene is negligible in the radiolysis of benzyl chloride- O_2 mixtures as presented in Table 1, neutralization reaction (9) should be faster than ion-molecule reaction (10),

 $PhCH_{2}^{+} + Cl^{-} \rightarrow PhCH_{2}Cl$ (9)

$$PhCH_{2}^{+} + PhCH_{2}Cl \rightarrow PhCH_{3} + PhCHCl^{+}$$
(10)

if one assumes that the benzyl cations disappear via neutralization (9) and ion-molecule reaction (10).

On the other hand, the G value for toluene amounts to 0.9 in the radiolysis of benzyl bromide even in the presence of a radical scavenger, oxygen (Table 1). This may mean that the rate of hydride-ion transfer reaction (12) is faster than or comparable to that of neutralization reaction (11), and that the benzyl cation is partly converted to α -bromobenzyl cation, PhCHBr⁺,

$$PhCH_{2}^{+} + Br^{-} \rightarrow PhCH_{2}Br$$
(11)

$$PhCH_2^+ + PhCH_2Br \rightarrow PhCH_3 + PhCHBr^+$$
 (12)

Reaction (12) seems more exothermic than reaction (10), though the lack of the heat of formation for PhCHCl⁺ and PhCHBr⁺ prevents us to calculate the exothermicities for reactions (10) and (12). The occurrence of reaction (12) indicates that benzyl bromide is not a clean source of the benzyl cation.

Ethanol added to benzyl bromide- O_2 system intercepts benzyl cation that undergoes neutralization reaction (11) and ion-molecule reaction (12) and decreases the *G* value for toluene (Table 1).

Therefore, the difference spectrum obtained by subtracting the $G\varepsilon$ values for benzyl bromide-0.6 M ethanol-O₂ mixtures from those for benzyl bromide - O₂ mixtures corresponds to an overlap of the spectra for benzyl cation and α -bromobenzyl cation (Fig. 6b). The spectrum for benzyl cation can hardly be separated from that for α -bromobenzyl cation, as the visible transient spectra are broad and structureless, and no remarkable red-shift in λ_{max} may occur in going from benzyl to α -bromobenzyl cation.

Other possible complications in the interpretation of the transient spectra in benzyl chloride and -bromide are described below.

The chlorine atom has an optical absorption peak at 310 nm in aqueous solution [32]. The chlorine atom in some halogenated solvents forms temporarily the π -complex between a chlorine atom and an aromatic molecule. For example, the chlorine atom in carbon tetrachloride leads to the formation of the π -complex with an aromatic molecule such as biphenyl [2, 3]. The π -complexes between the chlorine atoms and various aromatic hydrocarbons have in general an absorption maximum near 320 nm and a weak band at about 500 nm [33]. These spectral features of the chlorine atom and the π -complex thereof resemble those observed in the pulse radiolysis of pure benzyl chloride. Since the chlorine atom is produced in reaction (3), it is likely that the transient spectrum in pure benzyl chloride is a superposition of the spectra of the benzyl radical, benzyl cation, free chlorine atom and/or chlorine atom complexed with benzvl chloride. The similar discussion holds for the transient spectrum observed in pure benzyl bromide. It is, however, difficult to predict whether or not the halogen atom in a given solvent forms a π -complex with a given aromatic hydrocarbon. The absorption spectra of the π -complex between chlorine atom and aromatic molecule have so far been observed only in certain inert solvents such as CHCl₃ [11], CCl₄ [2, 3, 10, 11, 33] and benzene [34]. No absorption spectrum of the π -complex between chlorine atom and aromatic molecule was observed in less inert solvents such as 1,2-dichloroethane [6] and *n*-hexane [18], simply because the chlorine atom in these solvents undergoes very fast hydrogen-atom abstraction from the solvents.

The free chlorine atom and/or the π -complex formed between chlorine atom and benzyl chloride should rapidly decay via addition to the benzene ring or hydrogen-atom abstraction from benzyl chloride. If the addition of the chlorine atom to benzyl chloride takes place, one expects the formation of the chlorocyclohexadienyl type radicals which give chlorinated benzyl chloride upon disproportionation. This seems to be the case, because chlorinated benzyl chlorides such as o-, m-, and p-chlorobenzyl chloride were produced in the radiolysis of pure benzyl chloride, although their G values are small (< 0.2) and not shown in Table 1. The chlorocyclohexadienyl type radicals have presumably an absorption band in the near-UV region. Thus, a further complication may occur in the interpretation of the transient spectra observed in pure benzyl chloride and -bromide. Since the G values for the chlorinated benzyl chloride are not influenced by the presence of oxygen, the chlorocyclohexadienyl type radicals seem to react with oxygen to give HO₂ and the chlorinated benzyl chloride. Thus, the transient spectra observed in the benzyl chloride-O₂ mixtures are considered to correspond to a superposition of the spectrum for the benzyl peroxyl radical and the benzyl cation as discussed before.

The fact that visible light from Ar laser (488 nm) induces photofragmentation of the benzyl cation to acetylene and $C_5H_5^+$ ion in a mass spectrometer [35, 36] is an additional proof that the benzyl cation has an absorption band in the visible region.

Product Analysis in the Radiolysis of Benzyl Chloride. Dibenzyl is the main product in the radiolysis of neat benzyl chloride as shown in Table 1. Recombination of the benzyl radicals produced by reaction (2) as well as unimolecular decomposition of excited benzyl chloride leads to the formation of dibenzyl. The transient spectrum in the pulse radiolysis of neat benzyl chloride is mainly composed of benzyl radicals (Fig. 1). So, the formation of dibenzyl in the radiolysis of neat benzyl chloride is in harmony with the transient spectrum. The G value of dibenzyl seems somewhat smaller than anticipated. This may mean that the benzyl radical recombines not only with benzyl radical but also with other radical species than benzyl. Addition of the benzyl radical to the benzene ring to give polymeric products is also conceivable.

Benzaldehyde becomes the principal product in the presence of oxygen. Benzaldehyde may be formed by certain consecutive reactions of benzyl peroxyl radicals produced in reaction (4). The G value of benzaldehyde seems too large in comparison with the G value of dibenzyl. It is, however, unknown whether one or two molecule(s) of benzaldehyde is formed from one benzyl peroxyl radical. Reaction mechanisms involving peroxyl radicals are in general complicated.

Benzyl ethyl ether is formed in the presence of ethanol. The formation of the ether is taken as evidence that benzyl cation is formed in the radiolysis of benzyl chloride as discussed before. Since the yield of ether is not influenced by the addition of oxygen, recombination of benzyl radicals with eventual ethoxyl radicals can be excluded from the mechanisms for the formation of ether.

The product distributions are as a whole in accord with the transient spectra in the pulse radiolysis of benzyl chloride.

Appendix

It may be impossible to observe the transient spectrum in the UV region by using benzyl chloride "as received", because nonpurified benzyl chloride is opaque in the UV region as shown in Fig. 7a. Accordingly, benzyl chloride was purified by gas chromatography and subsequently treated with molecular sieve 3A. The purified benzyl chloride became transparent down to 290 nm as shown in Fig. 7a.



Fig. 7

(a) UV absorption spectra measured with a quartz cell of 1 cm optical path; (i) Benzyl chloride as received. (ii) Benzyl chloride purified by gas chromatography. (iii) Benzyl chloride purified by gas chromatography and subsequently subjected to about 100 electron pulses ($\approx 7 \text{ kGy}$) in the absence of O₂. (b) Gas chromatograms; the temperature of the Apiezon L column was held at 60 °C for the first 7 h and was then increased at a rate of 1 °C/min to 150 °C. (i) Benzyl chloride a received. Peaks other than benzyl chloride are due to impurities. (ii) Benzyl chloride purified by gas chromatography. (iii) Benzyl chloride purified by gas chromatography and subjected to about 100 electron pulses ($\approx 7 \text{ kGy}$) in the absence of O₂

The gas chromatographic purity of nonpurified and purified benzyl chloride is shown in Fig. 7b. Some peaks of radiolytic products overlap with that of impurities in nonpurified benzyl chloride. Furthermore, the concentration of impurities is much higher than that of radiolytic products. So, the G value of radiolysis products could be determined only when purified benzyl chloride was used. The concentration of products formed by 100 electron pulse irradiation does not exceed 0.05% as displayed in Fig. 7b.

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