Role of Ionic Processes in the Formation of Free Radicals in γ-Irradiated Glassy Toluene

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Spectrophotometric study has been made on the reaction intermediates generated by γ-irradiation in glassy toluene at 77 K. Benzyl and methylcyclohexadienyl radicals are generated roughly in equal amounts, and the total yield (G value) of the radicals is 0.19. The addition of biphenyl results in the formation of biphenyl anion and cation and depletes the radical yield by 40%. The results indicate that the excited-state toluene, the precursor of the radicals, is generated by recombination of ions as well as by the direct effect of the radiation on toluene.

Introduction

Aromatic hydrocarbons show notable stability against high-energy ionizing radiations.[1] There are efficient radiative processes for the degradation of the excited states of aromatic hydrocarbons.[2] The studies on the isomerization of added solutes[3,4] and on the intermediates in liquid benzene and its alkyl derivatives by means of pulse radiolysis technique[5-12] have revealed the nature of the excited states involved, the yields of the excited states, and the mechanism for the excitation. The excited states are generated either by the direct effect including geminate recombination or indirectly by the recombination of ions in liquid aromatic hydrocarbons. As to solid aromatic hydrocarbons, there have been ESR studies on the free radicals generated by the high-energy radiations.[13] However, optical studies on the radicals and other intermediates are still very scanty.[14-17] Freezing of aromatic hydrocarbons generally results in solidification into opaque polycrystals, which limit the use of the frozen samples for the optical spectroscopy of trapped radicals and ionic intermediates.[18] The mechanism for the generation of free radicals in irradiated solid aromatic hydrocarbons has not been fully elucidated.

In the present investigation, we have studied the ionic processes and the ionic contribution to the radical formation in γ-irradiated toluene at 77 K. The investigation has been performed by using transparent glassy toluene obtained by the rapid freezing of well-purified toluene at 77 K.

Experimental Section

Reagent grade toluene was washed with concentrated sulfuric acid several times, fractionally distilled, and treated with Na-K alloy under vacuum. Zone-refined biphenyl and reagent grade n-butyl chloride were used as received. Sample solutions were degassed and sealed in Spectrosil optical absorption cells (0.2-cm optical path) or ESR sample tubes. The quick freezing of toluene at 77 K gave clear glassy specimens.

The samples were irradiated with γ-rays from a ^{60}Co source at 77 K in the dark at a dose rate of 7.2×10^5 rd/h. Optical absorption spectra were recorded with a Shimadzu MPS-5000 spectrophotometer at 77 K. ESR and optical emission spectra were occasionally recorded with a Varian E-109 ESR spectrometer and a Hitachi MPS-2A fluorescence spectrophotometer, respectively. The photobleaching of the irradiated samples was carried out with light from a 500-W Xe lamp through appropriate glass filters.

Results and Discussion

Ionic Intermediates. On γ-irradiation of glassy neat toluene, the optical absorption spectrum with a few sharp peaks around 320 nm is observed (see the insert in Figure 1). This spectrum is due to the free radicals generated from toluene. No absorption is found in the visible and near-IR regions. The photoillumination of the irradiated toluene with light of λ >390 nm causes no change in the spectrum. Neither electrons nor positive holes are stably trapped in the toluene at 77 K. It contrasts with glassy saturated hydrocarbons and olefinic hydrocarbons (such as 2-methyl-1-pentene) from which the spectra due to trapped electrons and trapped positive holes are observed at 77 K. This difference may result from the fact that toluene acts as an electron scavenger in nonpolar media, while 2-methyl-1-pentene dose not.[18] The electron affinity of 2-methyl-1-pentene is of large negative value, whereas that of toluene is close to zero in the condensed phase. The difference is in accord with the observation that the excess electrons transport by the hopping between molecules in liquid benzene and toluene,[19] while they hop between physical traps in liquid olefinic hydrocarbons.[20]

Tochin and Buben[15,16] have observed the photoluminescence from the irradiated aromatic hydrocarbons at 77 K. In the present investigation also, faint thermoluminescence has been observed on melting the irradiated glassy toluene. These luminescence are probably due to the recombination of ions. The ions can be trapped in very small yield in the glassy toluene.

The addition of an electron scavenger prevents the recombination of ions and facilitates the trapping of the positive holes in the glassy toluene. The spectrum shown in Figure 1 (solid curve) has been recorded from the toluene containing 1 mol dm^{-3} n-butyl chloride. In addition to the band due to the radicals around 320 nm, the absorption bands in the visible (~440 nm) and near-IR (~1100 nm) regions are observed. These bands are photobleached with light of λ >900 nm. The broad underlying absorption around 300 nm appears to be depleted by the photobleaching. The near-IR band is the charge resonance band of toluene dimer cation,[21,22] whose band maximum depends strongly on the solvent.[22] Two other bands in the visible and near-UV are tentatively assigned to the dimer cation, though the visible band may be attributed alternatively to a complexed cation.[22] All the cationic entities can be photobleached at the charge resonance band of the dimer cation. This shows that the excitation of the charge resonance band induces charge transfer to the solvent, as reported for glassy 3-methylpentane at 77 K.[23]

The intensity of the radical band is larger in the presence of n-butyl chloride than in its absence. The increase in the total radical yield can be attributed to n-butyl radicals

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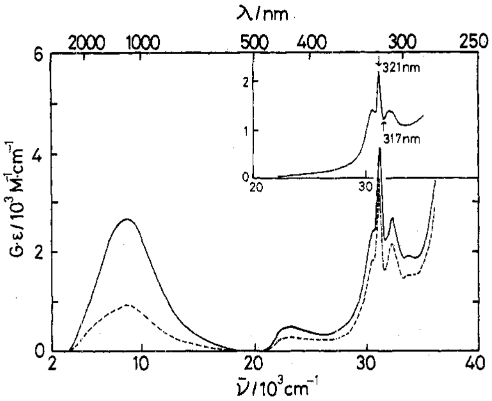

Figure 1. Optical absorption spectra of γ-irradiated toluene glass containing 1 mol dm^{-3} *n*-butyl chloride at 77 K before (full line) and after (dotted line) photobleaching with light of $\lambda > 900$ nm. The insert is the optical absorption spectrum of γ-irradiated neat toluene glass at 77 K (the scale of the drawing is the same as that in Figure 1).

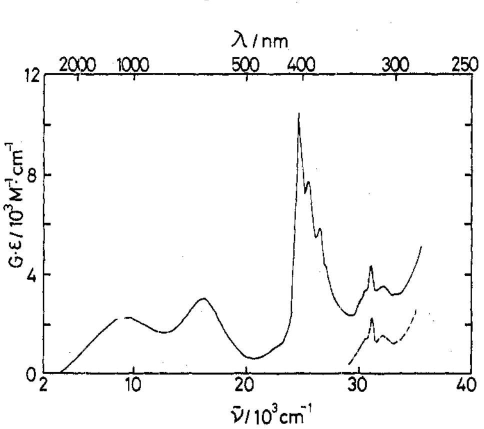

Figure 2. Optical absorption spectra of γ-irradiated toluene glass containing 0.08 mol dm^{-3} biphenyl at 77 K before (full line) and after (dotted line) photobleaching with light of $\lambda > 700$ nm.

which are generated by dissociative electron attachment to *n*-butyl chloride and which add to toluene to form cyclohexadienyl-type radicals.

The spectrum shown in Figure 2 has been recorded from the toluene containing biphenyl. In addition to the radical band around 320 nm and the bands due to toluene dimer cation in the visible and near-IR regions, the bands due to biphenyl ions (anion and cation) are observed in the visible region. Photobleaching with light of $\lambda >700$ nm eliminates the bands due to the toluene dimer cation and the biphenyl ions. The band due to the biphenyl anion is superimposed to a large extent on the band due to the biphenyl cation. However, the slight red shift of the anion band happens to give an absorption peak at 406 nm which is largely due to the anion and which can be used as a measure of the intensity of the anion band.

With increasing biphenyl concentration, the band due to toluene dimer cation decreases in intensity. The bands due to the biphenyl ions increase in intensity and change the relative peak heights at about 400 nm, indicating a change in the cation/anion yield ratio. Figure 3 shows the intensity of the bands of three ionic intermediates—the biphenyl anion (406 nm), the biphenyl cation (390 nm), and the toluene dimer cation (1100 nm)—as a function of the concentration of added biphenyl. The biphenyl cation band was separated from the recorded spectral shape by substracting the standard band shape for the biphenyl anion whose intensity was equaled by the recorded spectral shape at the 406-nm peak. The comparison of the initial slopes of the band intensity–biphenyl concentration curves, after being normalized at the plateau value, shows that the biphenyl anion is generated much more efficiently than the biphenyl cation.

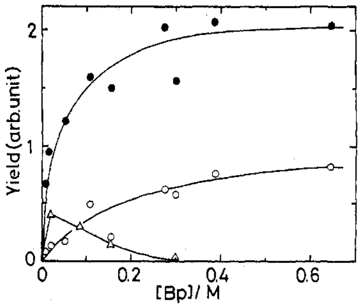

Figure 3. Relative yields of ionic intermediates vs. biphenyl concentration in γ-irradiated toluene glasses at 77 K: (●) biphenyl anion; (○) biphenyl cation; (△) toluene dimer cation.

The maximum yield of the biphenyl anion, $G(\mathrm{Bp}^-)$, has been determined to be 0.50 (for 100-eV energy absorbed) from the initial slope of the dose–yield curve (not shown) for 0.38 mol dm^{-3} biphenyl present in glassy toluene and from the reported absorption coefficient at 406 nm, ϵ_{406} of 4×10^4 mol^{-1} dm^3 cm^{-1}.[24] This G value is much smaller using alkyldisulfide as the electron scavenger, $G(\mathrm{RSSR}^-)$ in the same medium, 1.40.[24] The similar trend has been found for glassy 3-methylpentane,[23] 2-methyl-1-pentene,[23] and cumene:[14] $G(\mathrm{Bp}^-)/G(\mathrm{RSSR}^-)$ is 0.36, 0.47, 0.42, and 0.75 in toluene, cumene, 2-methyl-1-pentene, and 3-methylpentane, respectively. This suggests that in aromatic and olefinic glasses the charge neutralization is enhanced via charge transfer through biphenyl molecules.[25]

Cooper and Thomas[5] have found in their pulse radiolysis work that in liquid benzene and toluene the biphenyl anion yield, $G(\mathrm{Bp}^-)$, is about 0.1, which, they claimed, is much smaller than the value expected from the yield of the excited states generated by ion recombination.

Effects of Biphenyl on the Yield of Radicals. The 320-nm band observed in the glassy toluene is a composite of the spectra due to the benzyl radical and the methylcyclohexadienyl radical. The G value of the total radicals in the neat toluene glass has been determined to be 0.19 by means of the ESR method based on the G value of the trapped electrons in γ-irradiated 10 mol dm^{-3} NaOH glassy ice, 2.1,[26] as a standard. This agrees with the G value reported previously.[27] The benzyl radical is known to give a prominent fluorescence spectrum in the visible region,[28] whereas the cyclohexadienyl radical gives practically no emission.[29] The G value of the benzyl radical, $G(\mathrm{Bz}\cdot)$, has been roughly estimated to be 0.07 by comparing the fluorescence intensities between the benzyl radical in the neat toluene glass and that generated by γ-irradiation at 77 K of benzyl chloride (0.2 mol dm^{-3}) in 2-methyltetrahydrofuran glass in which the G value is known to be 2.6.[24] This $G(\mathrm{Bz}\cdot)$ will give a lower limit to the true value, because the absorption spectrum of the benzyl radical is superimposed on the spectrum of the methylcyclohexadienyl radical at 320 nm (excitation wavelength). It can be concluded that the benzyl radical and the methylcyclohexadienyl radical are generated roughly in equal amounts when glassy toluene is irradiated at 77 K.

The addition of biphenyl to the toluene glass results in the depletion of the radical bands, without altering the band structure, and in the generation of the biphenyl anion and cation as well. The relative yield of the total radicals is estimated from the absorbance difference between 321 and 317 nm (see the insert of Figure 1) and plotted in Figure 4 as a function of the biphenyl concentration. The growth of the yield of the biphenyl anion with the increasing concentration of biphenyl is also shown in Figure

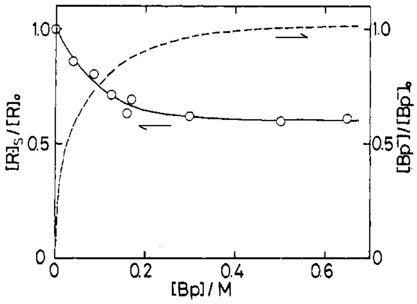

Figure 4. Relative yields of matrix radicals and of biphenyl anion (dotted line) vs. biphenyl concentration in γ-irradiated toluene glasses at 77 K.

4 for comparison. About 40% of the radical formation is depleted by the addition of sufficient concentration of biphenyl. The depletion of the radical formation is counterbalanced by the anion formation. This result shows that the presence of biphenyl suppresses electron–hole recombination followed by formaton of excited-state toluene and its dissociation into the radicals, though a minor contribution of the energy transfer from toluene to biphenyl cannot be excluded as a reason for the depletion of the radical yield by the added biphenyl. It is concluded that about 60% of the radicals from toluene (0.11 in total $G(R\cdot)$) comes from the dissociation of the excited toluene generated by the direct effect of the radiation including excitation by geminate recombination and the remaining 40% (0.08 in total $G(R\cdot)$) is generated via ion recombination.

Although the G value of ionization in the solid toluene at 77 K is as high as 1.40,[24] neither the toluene cation nor the electrons are trapped in the glassy toluene. Possibly the G value of the excited (singlet and triplet) toluene generated via the ion recombination is 1.40. An excited (singlet and triplet) toluene molecule dissociates into a benzyl radical and a hydrogen atom which adds to toluene to form methylcyclohexadienyl radical. However, the G value for the radical formation due to the ion recombination, 0.08, determined in this study shows that only 3% of excited toluene from ion recombination contributes to the radical formation.

Radiolysis of Glassy Toluene. In conclusion, the radiation-induced dissociation of toluene in the glassy state is almost equally due to the formation of excited toluene by ion recombination and to the direct excitation. Although the yield of the total radicals is comparatively small for toluene, the ionic process cannot be ignored in radical formation.

There have been several investigations which show the importance of the ionic process in liquid aromatic hydrocarbons including toluene. Cundall and Tippett[3] have shown that the yield of the isomerization of 2-butene in toluene is reduced to 60% by the addition of 0.2 mol dm^{-3} N_2O, as an electron scavenger. Thomas and Mani[7] have found a decrease in the yield of triplet excited states to 70% caused by 0.1 mol dm^{-3} SF_6 added to naphthalene and anthracene. Similarly, Beck et al.[12] have reported the decrease in the yield of excited states by adding $CHCl_3$ or CCl_4 into toluene. Gangwer and Thomas[14] have shown that the yield of singlet excited state is suppressed to 50% in p-xylene by the addition of methanol, N_2O, or chlorobenzene. These show as a whole that the radiation-induced excitation of liquid aromatic hydrocarbons is due to the direct excitation as well as to ion recombination, the contribution of which can be inhibited by electron scavengers. Both of the processes contribute comparably. The present result for the glassy toluene is very similar to those for the liquid phase.

References and Notes

(1) Swallow, A. J. "Radiation Chemistry"; Longman: London, 1973; Chapter 8.
(2) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: London, 1970.
(3) Cundall, R. B.; Tippett, W. *Adv. Chem. Ser.* **1968**, *No. 82*, 387.
(4) Hentz, R. R.; Perkey, L. M. *J. Phys. Chem.* **1970**, *74*, 3047.
(5) Cooper, R.; Thomas, J. K. *J. Chem. Phys.* **1968**, *48*, 5097.
(6) Cundall, R. B.; Evans, G. B.; Griffiths, P. A.; Keene, J. P. *J. Phys. Chem.* **1968**, *72*, 3871.
(7) Thomas, J. K.; Mani, I. *J. Chem. Phys.* **1969**, *51*, 1834.
(8) Richards, J. T.; Thomas, J. K. *J. Chem. Phys.* **1971**, *55*, 3636.
(9) Salmon, G. A. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 13.
(10) Thomas, J. K. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 1.
(11) Beck, G.; Richards, J. T.; Thomas, J. K. *Chem. Phys. Lett.* **1976**, *40*, 300.
(12) Beck, G.; Ding, A.; Thomas, J. K. *J. Chem. Phys.* **1979**, *71*, 2611.
(13) Pshezhetskii, S. Ya.; Kotov, A. G.; Milinchuk, V. K.; Rodinskii, V. A.; Tupikov, V. I. "EPR of Free Radicals in Radiation Chemistry"; Halsted Press: New York, 1974.
(14) Gangwer, T. E.; Thomas, J. K. *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 305.
(15) Tochin, V. A.; Nikol'skii, V. G.; Buben, N. Ya. *High Energy Chem. (Engl. Transl.)* **1967**, *1*, 61.
(16) Tochin, V. A.; Buben, N. Ya. *High Energy Chem. (Engl. Transl.)* **1967**, *1*, 67.
(17) Masuhara, H.; Miyazaki, T.; Mataga, N.; Kuri, Z. *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 519.
(18) Hamill, W. H. "Radical Ions"; Kaiser, E. T.; Kevan, L., Eds.; Interscience: New York, 1968; Chapter 9.
(19) Shinsaka, K.; Freeman, G. R. *Can. J. Chem.* **1974**, *52*, 3495.
(20) Dodelet, J.-P.; Shinsaka, K.; Freeman, G. R. *Can. J. Chem.* **1976**, *54*, 744.
(21) Badger, B.; Brocklehurst, B. *Trans Faraday Soc.* **1969**, *65*, 2582.
(22) Bühler, R. E.; Funk, W. *J. Phys. Chem.* **1975**, *79*, 2098.
(23) Gallivan, J. B.; Hamill, W. H. *J. Chem. Phys.* **1966**, *44*, 2378.
(24) Shida, T. *J. Phys. Chem.* **1970**, *74*, 3055.
(25) Kieffer, F.; Klassen, N. V.; Lapersonne-Meyer, C. *J. Lumin.* **1979**, *20*, 17.
(26) Kevan, L. "Radiation Chemistry of Aqueous Systems"; Stein, G., Ed.; Interscience: New York, 1968.
(27) Buben, N. Ya; Tolkachev, V. A.; Chkheidze, I. I. *Kinet. Catal. (Engl. Transl.)* **1963**, *4*, 595.
(28) Irie, M.; Shimizu, M.; Yoshida, H. *J. Phys. Chem.* **1976**, *80*, 2008.
(29) Sheng, S. J. *J. Phys. Chem.* **1978**, *82*, 442.