reaction 11 were performed by Adams, Baxendale, and Boag for pulse radiolysis of benzophenone aqueous solution.[31] On the basis of these previous reports, the 554-mμ band observed in alcoholic glasses is assigned to the ketyl radical produced by reaction 3. This also explains the absence of the band at 554 mμ in nonalcoholic solvents.

Figure 13 shows the absorption spectra of aromatic diketones. The benzil anion in MTHF shows a double band which might be due to the interaction of α,β-carbonyl groups or to the fact that in MTHF glass both *cis*- and *trans*-benzil may exist. However, separation of the two carbonyl groups by an intervening CH_2 group caused an even more complicated structure of absorption band.

Acetophenone and propiophenone behaved similarly to benzophenone in various solvents. Figure 14 shows absorption bands assigned to the anions of these ketones. The λ_{max} values are much closer to those of aliphatic ketone anions than that of benzophenone anion. In addition to the blue shift, as in benzophenone solutions, the vibrational structure of acetophenone anion in nonhydroxylic solvents has been changed in alcoholic solutions, but apparently reaction 3 does not take place for acetophenone because the whole band could be easily photobleached.

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[31] G. E. Adams, J. H. Baxendale, and J. W. Boag, *Proc. Roy. Soc.* (London), **A277**, 549 (1963).

Molecular Ions in Radiation Chemistry. V. Intermediates in γ-Irradiated Glassy Solutions of Methanol

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Abstract: γ-Irradiated methanol glass at $-196°$ produces solvent-trapped electrons which are scavenged by solute aromatic hydrocarbons. Benzene and alkylated benzenes capture electrons to form molecular anions which, in turn, react rapidly with methanol by the reaction, $S^- + ROH \rightarrow SH + RO^-$. The cyclohexadienyl-type radicals thus formed have optical absorption bands in the near-ultraviolet. Aromatic vinyl compounds also undergo the same reaction, the net effect being H-atom addition to the terminal carbon of the vinyl group. The transformation of biphenyl anion to phenylcyclohexadienyl radical is measurably slow at $-196°$. The solvent-trapped electron can be photobleached giving an H atom by the reaction, $(e^-) + ROH + h\nu \rightarrow RO^- + H$. The H atom adds to the solute olefins, ethylene, propylene, butene-1, and isobutene, to yield the respective radicals, ethyl, isopropyl, *sec*-butyl, and *t*-butyl. The same radicals are produced also from the solutions of ethyl bromide, isopropyl chloride, *sec*-butyl chloride, and *t*-butyl chloride, respectively, by the dissociative electron attachment, $RX + e^- \rightarrow R + X^-$.

It is now well established that glassy organic solids can trap electrons ejected by ionization. The absorption band of trapped electrons appears in the near-infrared region (1–2 μ) in glassy alkanes, alkenes, ethers, and amines. It is easily photobleached and in the presence of negative ion formers, such as aromatic hydrocarbons, the solute anion is formed. Photobleaching of the trapped electron band normally enhances the solute anion band.

γ-Irradiated alcoholic glasses, however, were found to have several characteristic features. The electron-scavenging solute does not necessarily produce the molecular anion, but the ion may react further with alcohol to produce a neutral radical. The solvent-trapped electron band, which appears in the visible region, unlike the glasses mentioned above, is photobleached without significant increase of solute anions or radicals derived therefrom. In this work we studied the electron-scavenging effect of aromatic hydrocarbons in methanol and the mechanism of photobleaching of the solvent-trapped electron band. The spectral data of radicals derived from the solute hydrocarbons are presented.

Experimental Section

Pure methanol is polycrystalline at $-196°$, but addition of a small amount of 1-propanol gives a cracked but transparent glass. Since added propanol did not interfere with spectroscopic measurements, methanol with 4 vol % 1-propanol is simply designated "methanol" in the spectroscopic studies. Unless stated otherwise, samples were prepared in air, introduced into flat silica cells 1.6 mm thick, and plunged in liquid nitrogen. Throughout irradiation and optical measurement samples were kept at $-196°$. The optical density was measured against air before and after γ irradiation, and absorption spectra were obtained by difference.

For epr measurements samples were admitted to silica cells (Suprasil), 3 mm o.d. × 15 cm long, in which pure methanol formed a cracked glass; therefore, no propanol was added for epr studies. The sample was irradiated at $-196°$ to 1.1×10^{19} ev/ml. Measurements were made using a Varian V 4500-10A spectrometer with 100-kc modulation.

One liter of methanol was purified by refluxing with 2,4-dinitrophenylhydrazine (5 g) and sulfuric acid (1 ml) in a spinning-band column for about a day and then distilled at 45 theoretical plates. Benzene was purified by shaking with concentrated sulfuric acid, washed with alkaline solution, dried over calcium chloride, and finally distilled. Vinyl compounds, such as styrene, were passed through an activated aluminum oxide column and used immediately without further purification. Isobutene gas, as received from Matheson, was dissolved in methanol by bubbling. The free base

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[1] On leave from the Institute of Physical and Chemical Research, Tokyo, Japan.

[2] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-467.

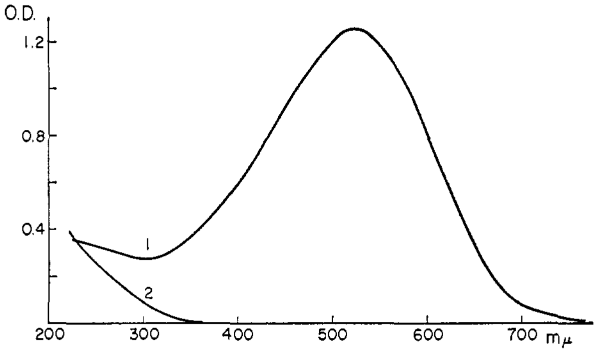

Figure 1. Absorption spectra of irradiated methanol containing 4 vol % 1-propanol: curve 1, after irradiation to the dose of 2.2×10^{19} ev/ml; curve 2, after 1 min of photobleaching with light of >530 mμ.

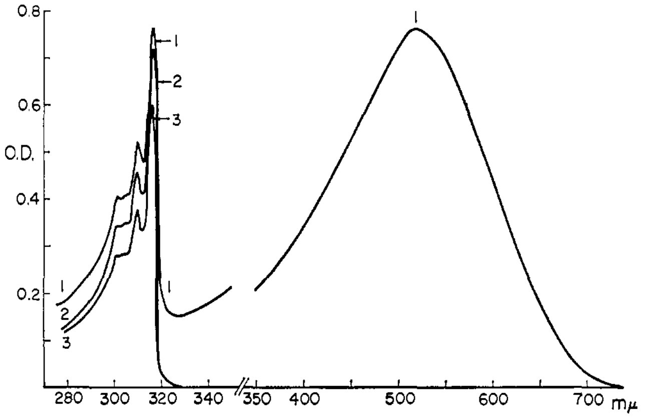

Figure 2. Absorption spectra of irradiated benzene solution in methanol (0.1 *M*): curve 1, after irradiation to the dose of 2.2×10^{19} ev/ml; curve 2, after 1 min of photobleaching with light of >530 mμ; curve 3, after an additional photobleaching for 3 min with full light of a tungsten lamp.

of tetramethyl-*p*-phenylenediamine (TMPD) was prepared from the dihydrochloride according to the method of Meyer and Albrecht.[3]

Results

Pure Methanol and Solutions of Aromatic Hydrocarbon. When methanol glass (with 4% 1-propanol) was γ-irradiated at −196°, it became red-purple, with the absorption spectrum shown in Figure 1. Tungsten light with Corning filter no. 3484, which transmits at λ >530 mμ, bleached the 520-mμ band, and the spectrum changed from curve 1 to 2. Thoroughly degassed methanol also gave an almost identical spectrum and the same spectral change upon photobleaching.

When benzene was added to methanol, the 520-mμ band decreased and new bands appeared in the near-ultraviolet region as Figure 2 shows. Photobleaching of the remaining 520-mμ band with light longer than 530 mμ eliminated the band while the ultraviolet bands remained almost unchanged. Because the contribution of the tail of the 520-mμ band underlies the 316-mμ peak, the absorption of the ultraviolet band (curve 2) is perhaps slightly higher than curve 1. The ultraviolet bands decreased when bleached with full light of a tungsten lamp (100 w, 25 cm distant from the sample), curve 3. Absorption spectra similar to Figure 2 were obtained for several aromatic hydrocarbons which are shown in Figures 3 and 4. The 520-mμ band was also always observed in dilute solutions of these hydrocarbons. In the absorption spectra of biphenyl solutions in methanol, ethanol, and propanols, shown in Figure 5, the bands at 404 and 650 mμ are unmistakably identified as biphenyl negative ion from observations of γ-irradiated biphenyl solutions in methyltetrahydrofuran (MTHF) glass.[4]

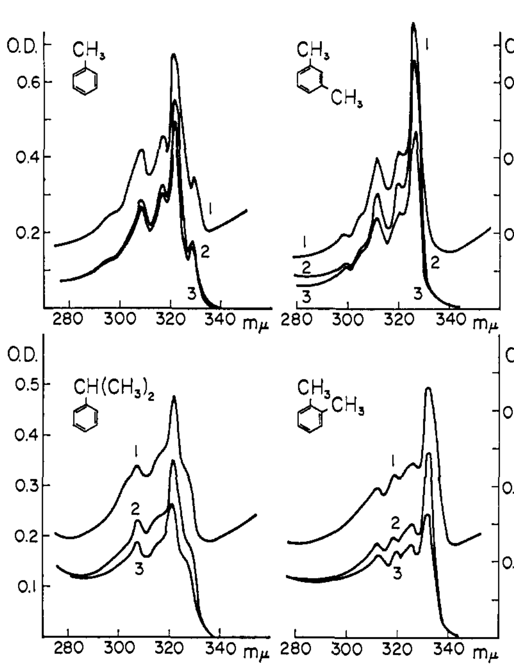

Figure 3. Absorption spectra of irradiated alkylated benzene solutions in methanol (0.1 *M*): curve 1, after irradiation to the dose of 2.2×10^{19} ev/ml; curve 2, after 1 min of photobleaching with light of >530 mμ; curve 3, after an additional photobleaching for 3 min with full light of a tungsten lamp.

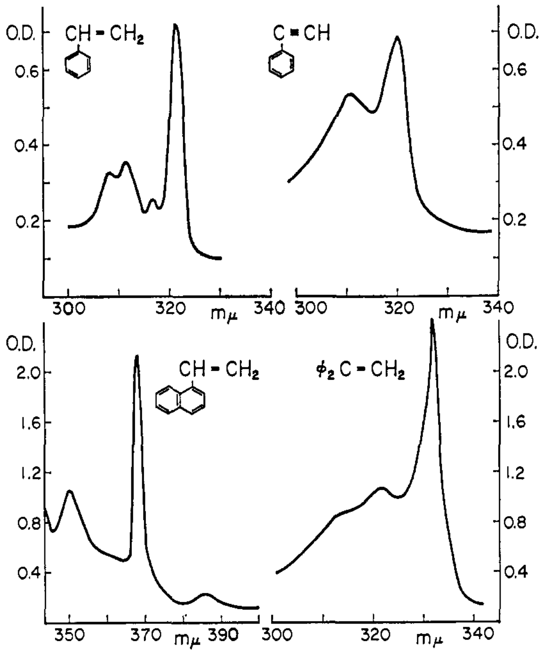

Figure 4. Absorption spectra of aromatic hydrocarbon solutions in methanol (0.5 *M*); dose = 1.1×10^{19} ev/ml.

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(3) W. C. Meyer and A. C. Albrecht, *J. Phys. Chem.*, **66**, 1168 (1962).

(4) T. Shida and W. H. Hamill, *J. Chem. Phys.*, in press.

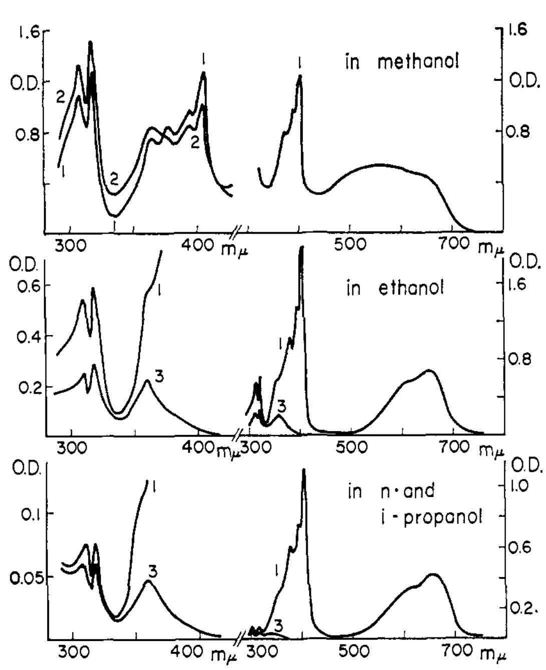

Figure 5. Absorption spectra of biphenyl solutions in alcohols (0.13 M): curve 1, after irradiation to the dose of 2.2×10^{19} ev/ml for methanol and ethanol solutions and 1.1×10^{19} ev/ml for propanol solutions; curve 2, after 45 min of standing of the irradiated sample in the dark; curve 3, after 3 min of photobleaching with tungsten light.

The bands appearing at <370 mμ behave differently toward photobleaching and resemble closely the corresponding bands in benzene solution of Figure 2. As shown in the upper part of Figure 5, the biphenyl anion peaks decreased gradually at −196° in the dark, and the ultraviolet bands increased correspondingly (curve 2).

All the hydrocarbons of Figures 3 and 4 are liquid at room temperatures and moderately soluble in methanol glass at −196°. Aromatic hydrocarbons which are solid and have higher molecular weights are sparingly soluble in the glass. A test for *cis*-stilbene solution in methanol seems to indicate that larger hydrocarbons merely produce their molecular negative ions[4] which are not transformed into another species as observed for biphenyl.

The epr spectra of irradiated benzene solution in methanol consisted of a central triplet with three small peaks superposed on both sides of the triplet. When the concentration of benzene was small (0.5 vol %), the irradiated sample was still purple owing to the residual 520-mμ band. However, illumination at >530 mμ caused bleaching, and the central strong epr signal increased splitting more clearly into a triplet (Figure 6a) while the outer small peaks changed as the enlarged figure (6b) demonstrates. Repeated observations confirmed that the outermost pair decreased while the next two pairs increased very slightly. When the concentration of benzene was high (10 vol %), the irradiated sample was colorless, and exposure to full tungsten light did not change the central triplet nor the two intermediate pairs. Only the outermost pair decreased noticeably. The three small peaks did not appear in benzene solutions of ethyl ether or of 3-methylpentane (3-MP) glass. Figure 7 shows the epr signals obtained for ether solution.

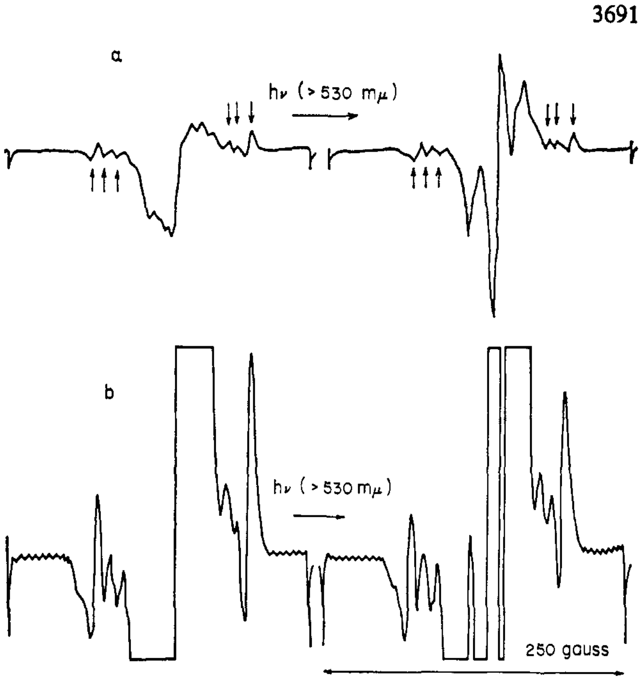

Figure 6. (a) Epr spectra of irradiated benzene solution in methanol, 0.5 vol %, dose = 1.1×10^{19} ev/ml; (b) 5× magnification.

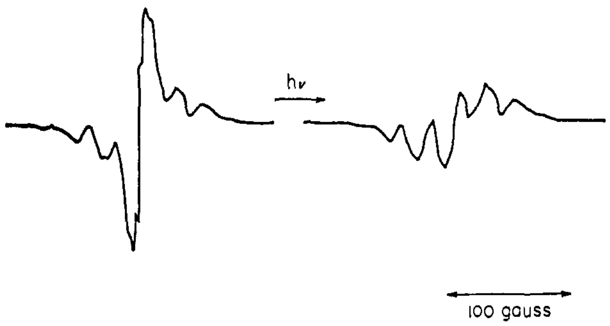

Figure 7. Epr spectra of irradiated benzene solution in ethyl ether: 5 vol %, dose = 1.1×10^{19} ev/ml.

Olefin Solutions. γ-Irradiation of methanol solutions of simple olefins produced the same optical spectrum as Figure 1. However, epr signals showed remarkable changes as Figure 8 (upper part) demonstrates for isobutene in methanol immediately after irradiation. The spectrum is almost identical with that of irradiated *t*-butyl chloride solution in methanol (middle, Figure 8). The lowest spectrum of Figure 8 was obtained for irradiated *t*-butyl chloride in 3-MP glass where electrons ejected from the paraffin molecule would be scavenged by the following reaction.

$$t\text{-BuCl} + e^- \longrightarrow t\text{-Bu}\cdot + Cl^-$$

The signals of both isobutene and *t*-butyl chloride in methanol glass increased appreciably when the purple sample was completely photobleached by yellow light (>530 mμ). Parallel experiments with ethylene, propylene, and butene-1 gave epr spectra similar to those for ethyl bromide, isopropyl chloride, and *sec*-butyl chloride in methanol, respectively. However, there was no measurable effect in solutions of pentene-1, 2-methylbutene-1, 3-methylpentene-2, or 2,3-dimethylbutene-2.

Figure 9 shows the epr spectra of TMPD solutions in methanol photolyzed with a GE AH6 high-pressure

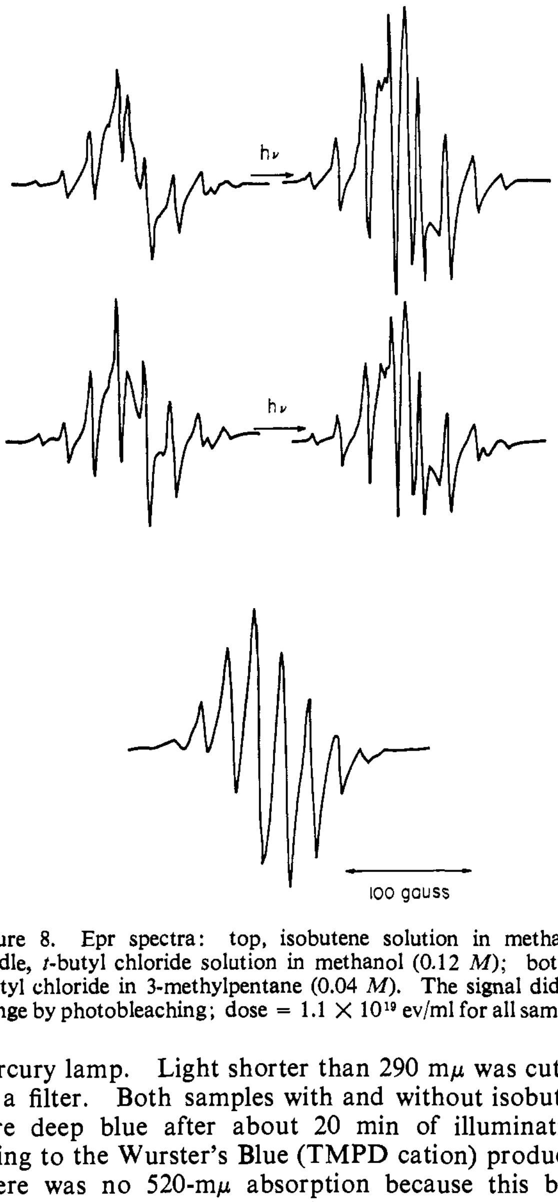

Figure 8. Epr spectra: top, isobutene solution in methanol; middle, *t*-butyl chloride solution in methanol (0.12 *M*); bottom, *t*-butyl chloride in 3-methylpentane (0.04 *M*). The signal did not change by photobleaching; dose = 1.1 × 10^{19} ev/ml for all samples.

mercury lamp. Light shorter than 290 mμ was cut off by a filter. Both samples with and without isobutene were deep blue after about 20 min of illumination, owing to the Wurster's Blue (TMPD cation) produced. There was no 520-mμ absorption because this band would bleach under the experimental conditions. The characteristic epr spectrum of the sample containing isobutene clearly indicates formation of the same paramagnetic species as that in Figure 8. Solutions of TMPD plus isobutene in 3-MP, MTHF, and triethylamine glasses were also photolyzed but showed no characteristic epr spectra (Figure 8 or 9 (upper)).

Discussion

The radiation chemistry of methanol, both in liquid and in solid, has been examined repeatedly. Among the primary processes commonly accepted are the ion–molecule reactions

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + CH_3O \qquad (1)$$

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + CH_2OH \qquad (2)$$

A mass spectrometric study indicates that reactions 1 and 2 take place approximately to the same extent.[5]

The electron pulse radiolyzed liquid methanol exhibits a broad absorption band at about 630 mμ which has been assigned to the solvated electron.[6–9]

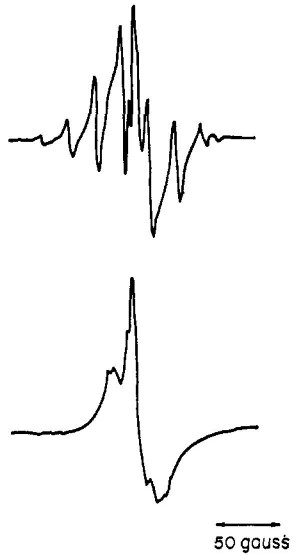

Figure 9. Epr spectra of photolyzed TMPD solution (10^{-2} *M*) in methanol: upper, with isobutene; lower, without isobutene.

In the glassy solid at −196°, an absorption band appears at 520 mμ which presumably correlates with the 630-mμ band in the liquid. It is quite plausible that the solvent-trapped electron would be stable in methanol glass since no reaction is permitted unless a considerable activation energy is supplied. Compared to the trapped electron band in other matrices which appears in the near-infrared region, the band at 520 mμ is strongly blue shifted. There is no adequate theory which accounts for this effect, but corresponding bands in liquid alcohols subjected to pulse radiolysis show a systematic blue shift with increasing dielectric constant.[8] The band at 520 mμ in methanol glass, shown in Figure 1, is therefore attributed to the solvent-trapped electron.[10,11]

In methanolic solutions of benzene, alkylated benzenes, and aromatic vinyl compounds, the OD of the 520-mμ band decreased with the appearance of new bands in the near-ultraviolet region. This suggests that the bands are associated with formation of negative species involving the solute molecule. The new bands, however, cannot be assigned to the molecular anions because the anion spectra of benzene and alkylated benzenes should resemble those for the cations.[12] Anion spectra of the vinyl compounds in Figure 4 were obtained in the MTHF glass[4] and are definitely different from those in Figure 3. Considering that the spectra in Figures 2–4 were obtained only in alcoholic matrices, we assign them to the radical produced by the following type of reaction

$$S^- + ROH \longrightarrow SH + RO^- \qquad (3)$$

where S and ROH represent solute and alcohol, respectively. The same type of reaction has been postulated in the preceding paper.[13] In the case of benzene,

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(5) K. R. Ryan, L. W. Sieck, and J. H. Futrell, *J. Chem. Phys.*, **41**, 111 (1964).

(6) F. S. Dainton, J. P. Keene, T. J. Kemp, G. A. Salmon, and J. Teply, *Proc. Chem. Soc.*, 265 (1964).

(7) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

(8) M. C. Sauer, S. Arai, and L. M. Dorfman, *ibid.*, **42**, 708 (1965).

(9) I. A. Taub, M. C. Sauer, and L. M. Dorfman, *Discussions Faraday Soc.*, **36**, 206 (1963).

(10) F. S. Dainton, G. A. Salmon, and J. Teply, *Proc. Roy. Soc.* (London), **A286**, 27 (1965).

(11) C. Chachaty and E. Hayon, *J. Chim. Phys.*, **61**, 1115 (1964).

(12) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).

(13) T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 3683 (1966).

SH would be the cyclohexadienyl radical which has been observed on several occasions[14] and is characterized by absorption bands at 316.5 and 311 mμ in the intensity ratio of 2:1.[15]

For the vinyl compounds of Figure 4, H^+ adds to the vinyl group of the anion and not to the ring since the spectrum obtained for the styrene solution agreed quite well with that for the radical produced in MTHF glass by the reaction[15]

$$C_6H_5CHBrCH_3 + e^- \longrightarrow C_6H_5\dot{C}HCH_3 + Br^- \quad (4)$$

In these instances also, reaction 3 is invoked for the formation of radical. Reaction 3 seems to be fast even at −196° for the solutes listed in Figures 2–4, but the corresponding reaction is relatively slow for biphenyl. The absorption bands in Figure 5 at >380 mμ are due to biphenyl anion[4] (with some contribution from remaining trapped electrons in methanol), but the bands in the ultraviolet region are, by analogy with the cyclohexadienyl radical, assigned to the phenylcyclohexadienyl radical produced by reaction 3. As curves 1 and 2 in Figure 5 show, the anion bands decreased gradually when the irradiated sample stood at −196° in the dark. Correspondingly, the radical bands were enhanced. This shows that reaction 3 for biphenyl is slow at liquid nitrogen temperatures. In addition, it was found that the rate of reaction depends upon the matrix alcohol, because the radical yield at the same dose decreased in the order methanol > ethanol > propanol. The same tendency has been found by Arai and Dorfman in the pulse radiolysis of liquid solutions of biphenyl in alcohols.[7] Attempts to transform the biphenyl anion to the radical by photoexcitation with light longer than 380 mμ merely caused the disappearance of the anion band and no increase of the radical.

The formation of cyclohexadienyl radical in γ-irradiated benzene–methanol solution at −196° has been observed by Leone and Koski using epr, who showed that the H atom adding to the benzene ring originates from the hydroxylic group of methanol.[16] This conclusion supports the mechanism of reaction 3 where obviously the hydroxylic H atom transferred to the solute molecule.

The central strong peak of Figure 6 is attributed to CH_2OH. Photobleaching of the residual trapped electrons in methanol is postulated to cause reactions 5 and 6 which will be explained later.

$$(e^-) + CH_3OH \xrightarrow{h\nu} H + CH_3O^- \quad (5)$$

$$H + CH_3OH \longrightarrow H_2 + CH_2OH \quad (6)$$

Thus, enhancement of the methanol radical signal by bleaching is expected only in dilute solutions retaining trapped electrons. This was observed for 0.5 vol % benzene. The small peaks flanking the central signal are further divided into two groups. The outermost pair have a splitting of 132 gauss, and they are therefore assigned to formyl radical which is invariably produced in small yield in irradiated methanol glass.[10,17,18] The other group of small peaks are regarded, in accordance with Leone and Koski,[16] as part of the complex spectrum of cyclohexadienyl radical. The very slight increase of the cyclohexadienyl radical caused by bleaching with yellow light agrees with the optical result shown in Figure 2. The increase may be due to a small fraction of trapped electrons reacting with benzene.

In radiation chemistry "hot" H atoms are known to react at −196° in many instances, but reactions involving thermal H atoms are not so common. Some olefins add H atoms generated at a heated tungsten ribbon.[19] To test reaction 6 directly we carried out a brief experiment as follows. Deaerated methanol was frozen on a cold surface at −196° and was exposed to H atoms produced at a hot tungsten filament.[19] The reaction products were analyzed by vpc with a 6-ft column of "Porapak." While formaldehyde was produced to an appreciable yield, ethylene glycol was not detected, which indicates the disproportionation of CH_2OH radicals formed by reaction 6. Reaction 6 may compete with H-atom combination to produce H_2, but the competition seems to be in favor of (6) because photobleaching increases the signal of CH_2OH efficiently.

The postulate that the cyclohexadienyl radical is produced by reaction 3 is further supported by the results of Figures 6 and 7. In contrast to the formation of the C_6H_7 radical in methanol, no signal of the radical was detected for ethyl ether or 3-MP glass as Figure 7 shows. In the ether matrix, benzene induced a central photobleachable singlet superposed on the spectrum of the solvent. In a separate experiment evidence was obtained that H atoms are produced abundantly during γ irradiation in all three solvents above, and migrate to solute isobutene producing the *t*-butyl radical.[20] Therefore, if H atoms reacted with benzene to form cyclohexadienyl radicals in methanol, we should equally expect the same reaction in the other two solvents, and it must be concluded that the reaction

$$C_6H_6 + H \longrightarrow \text{cyclohexadienyl} \quad (7)$$

does not occur noticeably at −196° in methanol.

Furthermore, in CO_2-saturated benzene–methanol solution, both solvent-trapped electron and cyclohexadienyl bands in Figure 2 (curve 1) decreased significantly, the former to 44% and the latter to 62% of the initial OD's. The competition for electrons between CO_2 and benzene is apparent. Evidence for CO_2^- formation was obtained in epr studies. The epr spectrum of the CO_2-saturated methanol solution consisted of a strong singlet with a splitting of 13 gauss which agrees with the reported value for CO_2^-.[21]

Photobleaching of the 520-mμ band in irradiated methanol, shown in Figure 1, has been repeatedly interpreted as photodetachment of trapped electrons followed by reaction 8. By this mechanism, appropriate solutes should capture some of the detached electrons during photobleaching. Figures 1 and 2 show that 0.1 *M* benzene reduced the electron band by about

$$CH_3OH_2^+ + e^- \longrightarrow CH_3OH + H \quad (8)$$

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(14) E. J. Land, *Progr. Reaction Kinetics*, **3**, 385 (1965).

(15) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963).

(16) J. A. Leone and W. S. Koski, *J. Am. Chem. Soc.*, **88**, 224 (1966).

(17) R. H. Johnsen, *J. Phys. Chem.*, **65**, 2144 (1961).

(18) R. S. Alger, T. H. Anderson, and L. A. Webb, *J. Chem. Phys.*, **30**, 695 (1959).

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(20) T. Shida and W. H. Hamill, to be published.

(21) P. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **44**, 1845 (1966).

30%, producing a significant amount of cyclohexadienyl radical. Photobleaching of the remaining 70% of the electrons, however, caused only very slight increase of the radical. If the trapped electron is photoreleased to be scavenged by reaction 3, one would expect more prominent increase of the radical, considering the comparatively high concentration of benzene.

As shown in Figure 8, the epr spectrum of radicals from *t*-BuCl in methanol agrees well with that in 3-MP. In both solutions *t*-BuCl scavenges electrons by dissociative electron attachment

$$\mathrm{RX} + e^- \longrightarrow \mathrm{R} + \mathrm{X}^- \qquad (9)$$

giving the *t*-Bu radical, which has a well-defined epr spectrum.[22,23] The same spectrum was also obtained in the isobutene solution in methanol (Figure 8, middle). Since isobutene does not yield an anion nor depress the solvent-trapped electron band at 520 mμ, the formation of *t*-Bu radical in the isobutene solution must be attributed to the H-atom addition to the olefin. The radical is produced both during γ irradiation and subsequent bleaching of the 520-mμ band since the epr signal increases significantly by illumination. The latter effect might be accounted for by reaction 8. However, the following photolytic experiment with TMPD solutions indicates reaction 5 rather than 8 to be the effect of photobleaching. It is well known that ultraviolet excitation of TMPD gives TMPD cations and photoejected electrons which are trapped by the solvent in MTHF or 3-MP solutions.[24] In the methanol glass also, the electron would be trapped by the solvent as in the case of radiolysis, but then bleached almost immediately under the intense AH-6 lamp. The epr spectra of Figure 9 demonstrate that when both TMPD and isobutene were present in ultraviolet-excited methanol glass, *t*-Bu radicals form. Since in the photolyzed sample there is no $CH_3OH_2^+$, it must be concluded that the *t*-Bu radical is formed *via* reaction 5. Parallel photolytic runs with isobutene and TMPD in 3-MP, MTHF, and triethylamine yielded TMPD cation radical but no *t*-Bu radicals, indicating the specific effect of methanol.

Alger, Anderson, and Webb failed to detect photoconductivity in the irradiated alcohol.[18] This can be accounted for by reaction 5, but not easily by the neutralization reaction 8.

Reaction 5 may be exothermic from the following argument. In the mass spectrometer, the appearance potential (AP) of negative ions from dissociative electron attachment correlates with bond dissociation energy (D) and electron affinity (A) as follows.

$$\mathrm{AP} = D - A \qquad (10)$$

Methanol produces CH_3O^- ion by

$$\mathrm{CH_3OH} + e^- \longrightarrow \mathrm{CH_3O^-} + \mathrm{H} \qquad (11)$$

Direct observation of AP(CH_3O^-) gave 2.3 ev[25] while calculation based on $A(\mathrm{CH_3O}) = 2.6$ ev and $D(\mathrm{CH_3O{-}H}) = 4.3$ ev[26] gives 1.7 ev. The average of these two would be the optical threshold for reaction 5 *in vacuo*. It was found that light >700 mμ (1.8 ev) was ineffective in reaction 5. The proposed mechanism is exothermic provided that the solvation energy of CH_3O^- exceeds that of the electron.

It is rather surprising that butene-1 adds an H atom while pentene-1 does not, as described above, but similar differences among simple olefins have been observed by Klein and Scheer. For example, butene-1 produces *sec*-butyl radical at −196° whereas pentene-1 does not yield any radical.[27] They found that an H atom adds to the terminal carbon of olefin, producing *sec*- and not *n*-butyl radical from butene-1. This was confirmed by us since the epr signals from propylene, butene-1, and isobutene agreed with those from isopropyl-, *sec*-butyl-, and *t*-butyl chlorides in methanol, respectively.

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[24] J. B. Gallivan and W. H. Hamill, *ibid.*, **44**, 1279 (1966).

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Vapor Phase Photochemistry of 1,3-Butadiene-1,1,4,4-d_4

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Contribution from the IBM Watson Research Center,
Yorktown Heights, New York. *Received April 5, 1966*

Abstract: The mechanisms of the three primary processes in the vapor phase photolysis of 1,3-butadiene have been investigated by the use of deuterium labeling on the end carbon atoms. None of the processes proceeds by the obvious pathway exclusively. Thus ethylene and acetylene are formed not only by a 1,3 shift but also *via* an intermediate cyclobutene and a third path which gives $C_2H_2D_2$ and C_2D_2. Two mechanisms seem to be applicable to the other two primary processes which give 1,2-butadiene and $H_2 + C_4H_4$, respectively.

The primary processes in the mercury-photosensitized decomposition of 1,3-butadiene were first identified by Collin and Lossing.[1] The reactions which can be represented as

$$\mathrm{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow[\mathrm{Hg}]{h\nu} \mathrm{CH_3{-}CH{=}C{=}CH_2} \qquad (1)$$

$$\mathrm{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow[\mathrm{Hg}]{h\nu} \mathrm{C_4H_4} + \mathrm{H_2} \qquad (2)$$

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[1] J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).