JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. *© Copyright, 1966, by the American Chemical Society*

VOLUME 88, NUMBER 16 AUGUST 19, 1966

Physical and Inorganic Chemistry

Molecular Ions in Radiation Chemistry. IV. Optical and Electron Paramagnetic Resonance Studies of Ions of Aliphatic and Aromatic Ketones

Tadamasa Shida[1] and William H. Hamill

Contribution from the Department of Chemistry and the Radiation Laboratory,[2] University of Notre Dame, Notre Dame, Indiana 46556. *Received April 29, 1966*

Abstract: A number of aliphatic and aromatic ketones have been γ-irradiated at $-196°$, either pure and polycrystalline or in various glass-forming solvents. Pure acetone exhibits broad absorption bands at 460 and 740 mμ after irradiation, the first attributable to $CH_3COCH_3^+$, the second to $CH_3COCH_3^-$. Each band was also observed in solvents where the positive charge and electron are available to solute acetone. In an alcohol matrix acetone anion reacts with the substrate according to $ROH + CH_3COCH_3^- \rightarrow RO^- + CH_3\dot{C}OHCH_3$, confirmed by epr. The septet of irradiated 2-propanol is unaffected by addition of acetone since both solvent and solute form the 2-propanol radical. In pure acetone the cation partially undergoes the reaction, $CH_3COCH_3^+ + CH_3COCH_3 \rightarrow CH_3\dot{C}OHCH_3^+ + CH_3CO\dot{C}H_2$, substantiated by mass spectrometry. The recombination luminescence of irradiated acetone consists of a band at 455 mμ, corresponding to the combined fluorescence–phosphorescence of acetone. λ_{max} of alkyl ketone cations depends upon the alkyl group, probably due to hyperconjugation. Benzophenone forms the molecular anion with λ_{max} ~800 mμ in olefin, ether, and amine matrices but λ_{max} ~600 mμ in alcohols, the blue shift being attributable to H bonding. On limited warming the latter is replaced by a new band at λ_{max} 554 mμ, known to be $(C_6H_5)_2\dot{C}OH$.

Metastable intermediates in γ-irradiated organic systems at $-196°$ include solvent-trapped electrons, positive and negative ions, and neutral radicals. These species can sometimes be characterized and identified by their optical absorption and emission as well as their epr spectra.[3] Glassy solids have been preferred because of transparency but polycrystalline samples can also be examined by optical absorption in thin cells.[4] The study of ketones is expected to be particularly interesting because ketones are expected to capture electrons forming ketyls, and also to capture positive charge, in appropriate matrices because of the comparatively low ionization potentials. Methyltetrahydrofuran (MTHF) has been shown to provide an appropriate matrix for solute anion formation, and alkyl chlorides for cations.[4] In this work we present the results of studies on molecular ions and related radicals of ketones observed in these matrices or in the pure polycrystalline solids.

Experimental Section

Reagent grade ketones from Aldrich Chemical Co. were used as received, except acetone which was purified on a spinning-band column. The other aliphatic ketones used were 2-butanone, 2-pentanone, 4-methyl-2-pentanone, diisopropyl ketone, and di-*t*-butyl ketone. The aromatic ketones examined include acetophenone, propiophenone, benzophenone, benzil, and 1,3-diphenyl-1,3-propanedione. For optical measurements, they were irradiated at $-196°$ in a $^1/_{16}$-in. thick Suprasil cell, either as pure substances or in various solvents. To measure epr the liquid sample in a thin Suprasil tube was frozen and irradiated. The solvents were chosen from common ethers, alcohols, amines, alkyl chlorides, and

---

(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-38-466.

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

(4) (a) T. Shida and W. H. Hamill, *ibid.*, **44**, 2369 (1966); (b) *ibid.*, **44**, 2375 (1966); (c) *ibid.*, in press.

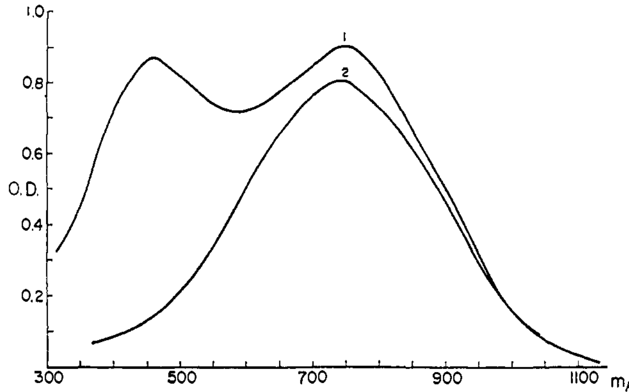

Figure 1. Absorption spectra of acetone γ-irradiated to 9×10^{19} ev/ml at −196°: (1) pure, (2) with 3 vol % isopropyl chloride.

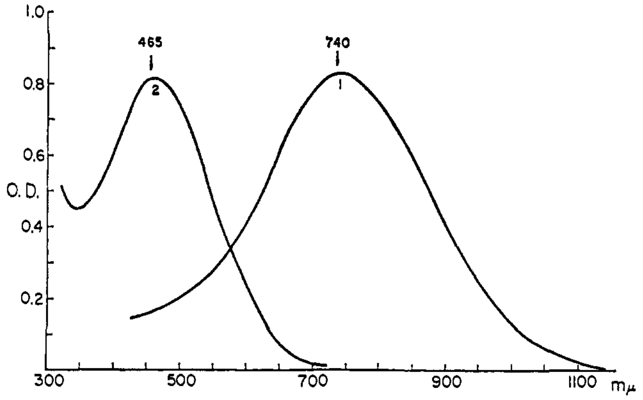

Figure 2. Absorption spectra of γ-irradiated solutions of acetone at −196°: (1) 10 vol % in *sec*-butyl chloride at 3×10^{19} ev/ml, (2) 10 vol % in methyltetrahydrofuran at 1.5×10^{19} ev/ml.

aliphatic hydrocarbons which form glasses at liquid nitrogen temperature.

The procedures for γ irradiation and optical measurements have been described.[4] Epr measurements were performed with a Varian V 4500-10A spectrometer at 100-kc modulation. Ion–molecule reactions were studied with a Nuclide 12-in., 60° mass spectrometer. An improvised rapid scanning spectrometer was used to measure the emission observed during warming of irradiated acetone. The instrument consisted of a prism, a mirror vibrating at 60 cps, a photomultiplier, and an oscilloscope. The range of wavelength was about 300 to 550 mμ. The irradiated acetone in a silica tube was removed from a dewar flask and warmed in air just in front of the entrance slit. A Jarrell-Ash (Model 82–000) spectrometer was employed to measure the phosphorescence of ultraviolet-excited acetone solution at −196°.

Results

Aliphatic ketones form semiopaque polycrystalline solids at −196°. Upon γ irradiation they exhibit two broad absorption bands in the visible and near-infrared regions. As a typical illustration, Figure 1 (curve 1) shows the absorption spectrum of irradiated acetone. Dissolved air seemed not to affect the spectrum. When a small amount of isopropyl chloride (or any other alkyl chloride) was added to acetone, the band at about 460 mμ disappeared and the sample became sky blue owing to the remaining 740-mμ band (curve 2).

In previous work it was found that irradiated pure BuCl glass or polycrystalline CCl_4 scavenged electrons and both conducted and trapped positive charge.[4] The positive charge trapped in a matrix of BuCl gives a characterisitic band at about 430 mμ. A small amount of acetone in BuCl prevents appearance of this band and gives rise to a band at about 740 mμ (curve 1 of Figure 2). Acetone in methyltetrahydrofuran gave the band shown by curve 2 of Figure 2.

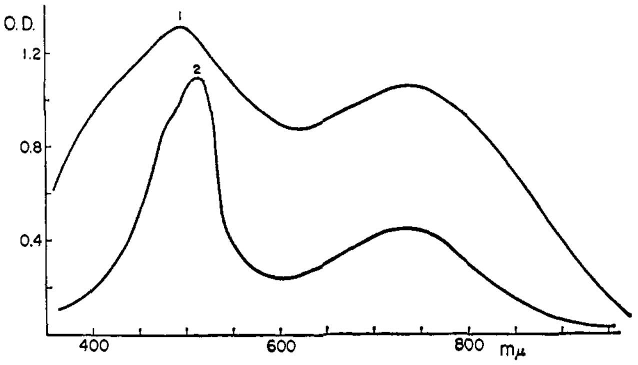

Figure 3. Absorption spectra of γ-irradiated *cis*-stilbene cation as solute in acetone at −196° and 9×10^{19} ev/ml: (1) 10 vol %, (2) 25 vol %.

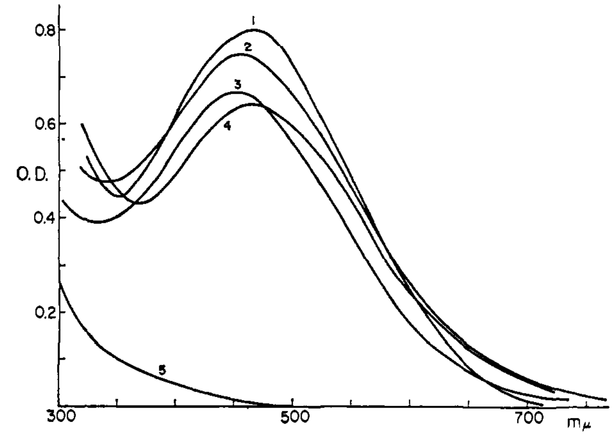

Figure 4. Absorption spectra of γ-irradiated acetone in various solvents at −196°: (1) 5 vol % in methyltetrahydrofuran at 2.4×10^{19} ev/ml, (2) 5 vol % in diethyl ether at 2.4×10^{19} ev/ml, (3) 5 vol % in *sec*-butylamine at 4.5×10^{19} ev/ml, (4) 5 vol % in triethylamine at 4.5×10^{19} ev/ml, (5) 10 vol % in ethanol at 4.5×10^{19} ev/ml.

Figure 3 shows spectra of *cis*-stilbene mixtures with acetone at −196°. The band of stilbene cation[4b,c] can be seen only at very high concentrations of stilbene. Absorption spectra of acetone solutions in various solvents (Figure 4) show that in all instances the trapped electron band disappeared completely and a band appeared at about 450–470 mμ, except in alcohol. If we regard the shift in λ_{max} as a solvent effect, then the bands in these solvents are due to the same species produced in MTHF (curve 2, Figure 2).

Other aliphatic ketones behave similarly to acetone in BuCl and in MTHF glasses, producing bands which absorb at about 800–850 mμ in the former matrix, and at 460–470 mμ in the latter. Table I summarizes the results. All ketone anions bleached with tungsten light.

Figures 5 and 6 illustrate epr signals of pure methanol and acetone in methanol, respectively. Upon photobleaching with tungsten light the methanol signal changed to a 1:2:1 triplet, and the color changed from red-purple to colorless, while the sample containing acetone was colorless from the beginning and the epr signal was not changed significantly by illumination.

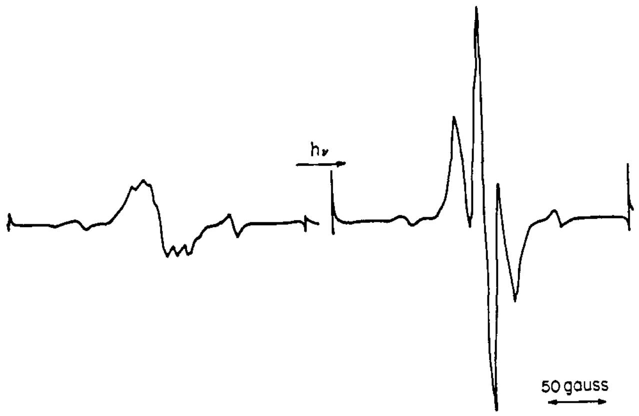

Figure 5. Epr spectrum of γ-irradiated glassy methanol at −196° and 1.1 × 10^{19} ev/ml.

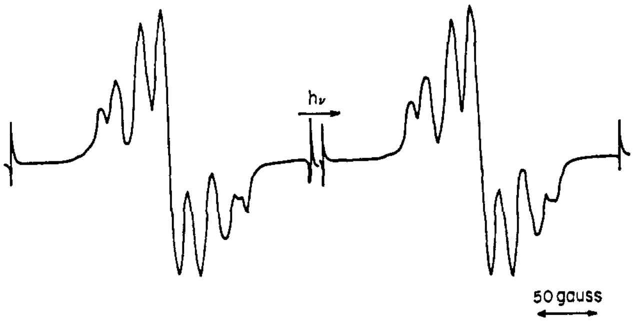

Figure 6. Epr spectrum of γ-irradiated acetone (10 vol %) in methanol at −196° and 1.1 × 10^{19} ev/ml.

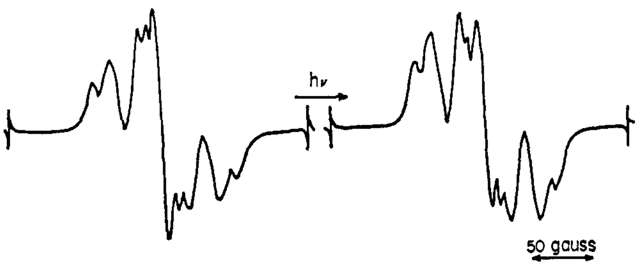

Figure 7. Epr spectrum of glassy 2-propanol, γ-irradiated at −196° and 1.1 × 10^{19} ev/ml.

Similarly, 2-propanol and acetone in 2-propanol gave the results shown in Figures 7 and 8. Except for the complexity in the central peak, the spectrum is quite similar to that of acetone in methanol.

Table I. Absorption B and Maxima (mμ) of Ketone Solutions in MTHF and in BuCl

	Acetone	2-Butanone	2-Pentanone	4-Methyl-2-pentanone
λ_{max} in MTHF	465	470	470	460
λ_{max} in *sec*-BuCl	740	808	840	855

When γ-irradiated pure acetone was removed from liquid nitrogen, it began to emit bluish light which lasted longer than a minute. The emission spectrum of such a sample during warming is given by the noisy curve in Figure 9 which is a reproduction of the oscillographic display obtained by using the rapid scanning spectrophotometer. The wavelength was calibrated against line spectra of mercury vapor as shown. The smooth curve in the same figure is the emission spectrum obtained by ultraviolet excitation of acetone in ethyl ether glass at −196°. In a thin silica cell the ether solution solidified to a glassy solid.

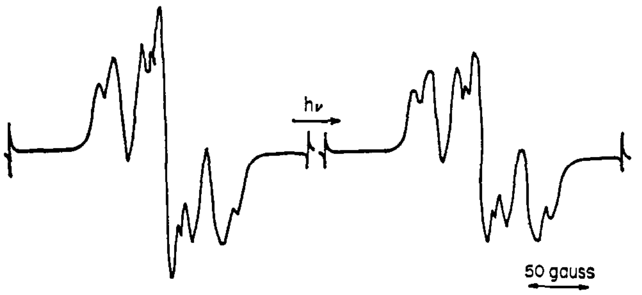

Figure 8. Epr spectrum of 10 vol % acetone in 2-propanol, γ-irradiated at −196° and 1.1 × 10^{19} ev/ml.

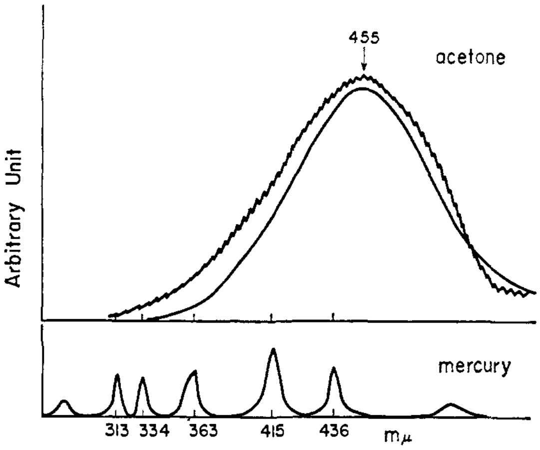

Figure 9. Emission spectra of acetone at −196°: upper curve, thermoluminescence after γ irradiation of pure acetone, 2.2 × 10^{19} ev/ml; lower curve, solution of acetone in diethyl ether under ultraviolet excitation. The Hg spectrum is for wavelength calibration.

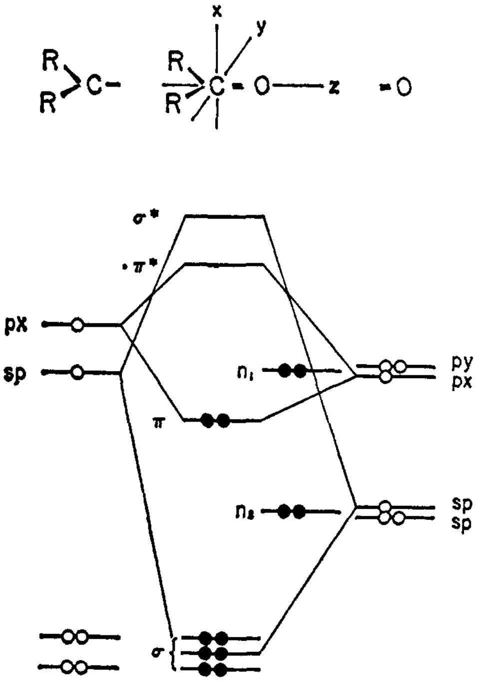

Figure 10. Energy diagram of ketone.

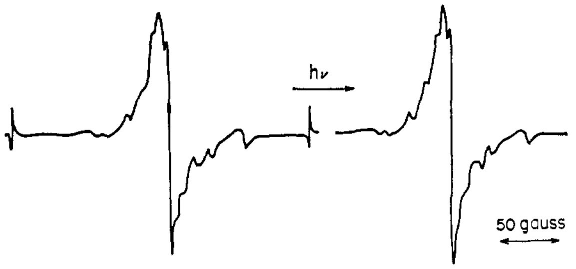

Figure 11. Epr spectrum of 20 vol % di-*t*-butyl ketone in methanol, γ-irradiated at −196°, 1.1 × 10^{19} ev/ml.

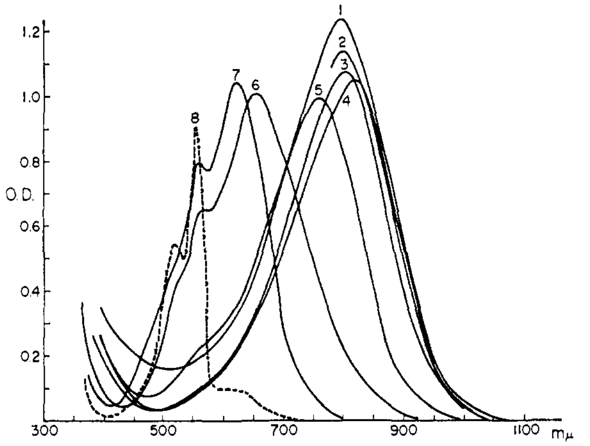

Figure 12. Absorption spectra of benzophenone in various solvents, γ-irradiated at −196°: (1) 20 m*M* in methyltetrahydrofuran, 1.5 × 10^{19} ev/ml; (2) 10 m*M* in 2-methylpentene-1, 7.5 × 10^{19} ev/ml; (3) 20 m*M* in diethyl ether, 2 × 10^{19} ev/ml; (4) 20 m*M* in triethylamine, 4.5 × 10^{19} ev/ml; (5) 20 m*M* in *sec*-butylamine, 4.5 × 10^{19} ev/ml; (6) ~0.1 *M* in propylene glycol, 4.5 × 10^{19} ev/ml; (7) ~ 0.1 *M* in ethanol, 1.5 × 10^{19} ev/ml; (8) after warming sample 6 to ~−100°.

Figure 11 shows epr signals for a methanolic solution of di-*t*-butyl ketone. The sample after irradiation was slightly purple, and photobleaching removed this color without much change in the epr signal. Similar results were obtained for diisopropyl ketone and 3-methyl-2-pentanone.

Optical absorption spectra for γ-irradiated benzophenone solutions in various solvents are shown in Figure 12. There was no trapped electron band in any instance. The samples in ethanol and propylene gycol solutions changed from purple-blue to pink when warmed slightly. The samples were plunged into liquid nitrogen again, and the absorption spectrum then consisted of a narrow band at about 554 mμ, shown by the dotted curve for propylene glycol. Because the glycol was much more viscous than ethanol, it was easier to obtain the pink transient in glycol than in ethanol. The spectra of benzil and of 1,3-diphenyl-1,3-propanedione γ-irradiated in MTHF appear in Figure 13, and those of acetophenone and propiophenone in various glasses in Figure 14.

Discussion

The band at λ_{max} ~740 mμ in γ-irradiated glassy solutions of acetone in MTHF (Figure 2) appears at the expense of the near-infrared, solvent-trapped electron band and is suppressed by electron scavengers. Acetone produces quite similar bands in various other matrices known to be suitable for producing solute anions (Figure 4). The 740-mμ band is therefore assigned tentatively to the acetone molecular anion. The band at 465 mμ in γ-irradiated glassy solutions of acetone in BuCl (Figure 2) appears at the expense of the solvent cation band, is suppressed by authentic positive charge scavengers such as ethanol (efficient proton-transfer reagent), and also occurs for acetone in CCl_4. It is accordingly attributed tentatively to the acetone molecular cation.

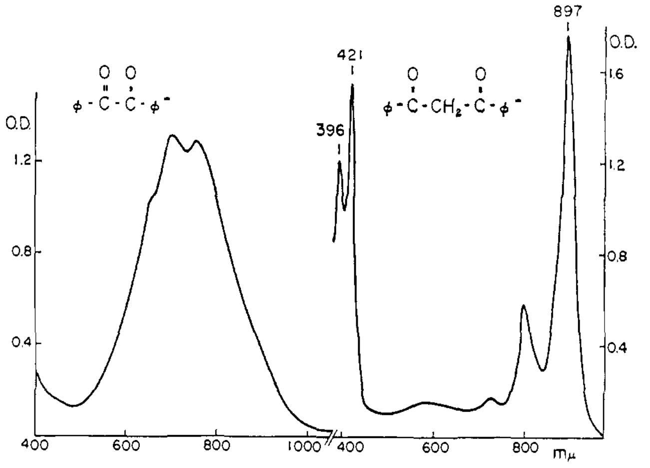

Figure 13. Absorption spectra of γ-irradiated benzil (4.4 × 10^{19} ev/ml) and 1,3-diphenyl-1,3-propanedione in methyltetrahydrofuran.

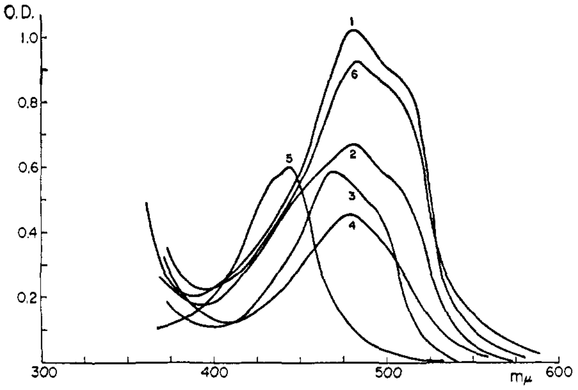

Figure 14. Absorption spectra of γ-irradiated acetophenone, 20 m*M*, at −196°: (1) in methyltetrahydrofuran, 3.3 × 10^{19} ev/ml; (2) in diethyl ether, 6.6 × 10^{19} ev/ml; (3) in *sec*-butylamine, 6.6 × 10^{19} ev/ml; (4) in triethylamine, 4.4 × 10^{19} ev/ml; (5) in ethanol, 6.6 × 10^{19} ev/ml; (6) propiophenone in methyltetrahydrofuran, 3.3 × 10^{19} ev/ml.

The two bands observed in pure acetone (Figure 1) are therefore assigned to the molecular cation and anion. The effects of adding isopropyl chloride (curve 2, Figure 1) and *cis*-stilbene (Figure 3) can be understood as follows. Electrons ejected by ionization in pure acetone will migrate and eventually be trapped by an acetone molecule to give the anion absorbing at λ_{max} 460 mμ. In the presence of electron scavengers, such as isopropyl chloride, electrons will be competitively removed. In contrast to the sensitivity of the 460-mμ band of Figure 1 to isopropyl chloride, the 740-mμ band assigned to the cation was changed very little by the addition of 10% stilbene, a positive charge trapping solute.[4b,c] This suggests that the electron vacancy remains at the site of its origin in acetone and does not easily undergo positive charge transfer, unlike aliphatic chloride or hydrocarbon matrices.[4a,c] The necessity of using a high concentration of *cis*-stilbene to obtain an appreciable yield of its cation is understood if the reaction

$$CH_3COCH_3^+ + C_6H_5CHCHC_6H_5 \longrightarrow CH_3COCH_3 + C_6H_5CHCHC_6H_5^+ \qquad (1)$$

takes place only when a stilbene molecule is nearest neighbor to the acetone molecular ion.

Acetone cation has not been reported in condensed phase, but Lossing and Tanaka produced acetone molecular positive ion exclusively in the mass spectrometer by photoionization.[5] Although no stable molecular anion has been reported for acetone, an intermediate acetone anion is often assumed in the radiation chemistry of aqueous solutions.[6–9] In fact, acetone is used to discriminate between the solvated electron and hydrogen atom in the radiolysis of water.[9]

Although the anion band at 465 mμ was observed in several solvents (Figure 4), it failed to appear in any alcoholic solvents (methanol, propylene glycol, and ethylene glycol monomethyl ether were tested). Since solvent-trapped electrons do not appear in these media when acetone is present, it can be inferred that acetone anions form, but are reactive, and the following reaction is proposed.

$$CH_3COCH_3^- + ROH \longrightarrow (CH_3)_2\dot{C}OH + RO^- \qquad (2)$$

We have found that reaction 2 is an example of the following type of reaction, where S^- is a solute molecular anion.

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

Anions of butadiene, benzene, acetophenone, and *p*-quinones are among those which undergo this reaction.[10]

2-Propanol radical has been produced by reaction 2 in the pulse radiolysis of aqueous 2-propanol.[8] The radical absorbs only at 200–300 mμ, and this may account for the tailing absorption in ethanol solution, shown in Figure 4. Confirmative evidence for the reaction above was provided by epr measurements. Irradiated pure methanol glass yielded the epr spectrum shown in Figure 5 which has been explained in terms of paramagnetic species produced by reactions[11–13]

$$CH_3OH \rightsquigarrow CH_3OH^+ + e^- \qquad (4)$$

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + CH_2OH \text{ (or } CH_3O\text{)} \qquad (5)$$

Upon photobleaching the sample changed from red-purple to colorless, and the epr spectrum became a sharp triplet. The effect of illumination is explained by the following reactions.[10]

$$(e^-) + CH_3OH + h\nu \longrightarrow CH_3O^- + H \qquad (6)$$

$$H + CH_3OH \longrightarrow CH_2OH + H_2 \qquad (7)$$

In reaction 6, (e^-) denotes the solvent-trapped electron which is responsible for the red-purple coloration. When a small amount of acetone was added to methanol, the γ-irradiated, colorless sample gave a remarkably different epr signal, unchanged by illumination except for a slight decrease of the right outer peak (Figure 6). The result is understood if the alcohol has reacted with acetone anion to produce the 2-propanol radical by reaction 3, the epr spectrum being a composite of the septet of 2-propanol radical[14] and the triplet of methanol radical which is invariably produced from the positive ion of methanol *via* reaction 5. The slight decrease of the right outer peak may indicate loss of formyl radical which is produced in small amount.[1,11,15] Parallel runs for 2-propanol glasses gave similar results, shown in Figures 7 and 8. It is apparent from the simple spectrum that both solute acetone and solvent 2-propanol produce the same 2-propanol radical.

In solvents having no alcoholic group, the ketone anion remains unreacted as Figure 4 shows from optical evidence. However, no epr signal of the molecular anion of acetone was found for ethyl ether glass where its existence was indicated by the brown color. The acetone solution yielded essentially the same spectrum as that of pure ether, a symmetrical quintet.[8] Absence of the anion signal can be attributed to extreme dipolar broadening.[14]

The bright blue thermoluminescence of γ-irradiated acetone and other aliphatic ketones, which has already been reported,[3] can also be induced by illumination with tungsten light, although the induced emission is less intense for the conditions used. The thermoluminescent band at 455 mμ corresponds very well to the ultraviolet-induced phosphorescence[16,17] (Figure 9). The facts are consistent with the assumption that the band arises from ion recombination, the emitting species being the excited product of the neutralized cation.[18]

Nitta, *et al.*, studied the effect of illumination upon γ-irradiated solid acetone by epr spectroscopy.[19] The epr spectrum of irradiated acetone comprised a broad asymmetric singlet superposed on a weak triplet. Under illumination the singlet decayed slowly but the triplet remained. Studying CD_3COCD_3 also, they concluded that the stable triplet is due to the acetonyl radical, $CH_3CO\dot{C}H_2$. The decay of singlet may be related to the decrease of cation and anion bands observed by optical absorption. The small contribution of the acetonyl radical may be attributed to the concurrent ion–molecule reaction

$$CH_3COCH_3^+ + CH_3COCH_3 \longrightarrow CH_3\dot{C}OHCH_3^+ + CH_2CO\dot{C}H_2 \qquad (8)$$

As the triplet appeared before photobleaching and did not increase by illumination,[19] reaction 8 seems to take place during irradiation. A preliminary test in this laboratory indicated that the proton-transfer reaction

---

(5) F. P. Lossing and I. Tanaka, *J. Chem. Phys.*, **25**, 1031 (1956).

(6) M. Anbar, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, pp 65, 66.

(7) E. J. Hart and E. M. Fielden, ref 6, p 253.

(8) S. Gordon, E. J. Hart, and J. K. Thomas, *J. Phys. Chem.*, **68**, 1262 (1964).

(9) J. Rabani and G. Stein, *J. Chem. Phys.*, **37**, 1865 (1962).

(10) T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 3689 (1966).

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

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

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

(14) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths Scientific Publications, London, 1958, p 175.

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

(16) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **16**, 223 (1948).

(17) R. F. Borkman and D. R. Kearns, *ibid.*, **44**, 945 (1966).

(18) D. W. Skelly and W. H. Hamill, *ibid.*, **43**, 3497 (1965).

(19) I. Nitta, S. Ohnishi, S. Sugimoto, and K. Kuwata, Annual Report of the Japanese Association for Radiation Research on Polymers, Vol. 6, 1964–1965, p 283.

8 occurs to some extent in the mass spectrometer.[20] An acidic species is also present in γ-irradiated liquid acetone.[21]

A similar proton-transfer reaction involving acetone was found in 3-methylpentane (3MP) glass, in which acetone partly crystallized to form a cloudy solid which made it difficult to measure optical changes even in the thin cell. However, it was observed that acetone had eliminated the solvent-trapped electron band at about 1600 mμ and the sample was brown, suggesting that acetone anion was formed. Since it is known that in 3MP the positive charge on the solvent molecule can migrate to solute,[4] we would expect the formation of an acetone cation also. In fact, there was no absorption at 700–800 mμ where the acetone cation should appear, suggesting the following ion–molecular reactions

$$C_6H_{14}^+ + CH_3COCH_3 \longrightarrow C_6H_{13} + CH_3\dot{C}OHCH_3^+ \qquad (9)$$

or

$$C_6H_{14} + CH_3COCH_3^+ \longrightarrow C_6H_{13} + CH_3\dot{C}OHCH_3^+ \qquad (10)$$

Reaction 10 implies that the reaction takes place after the positive charge has been transferred from 3MP$^+$ to acetone. Mass spectrometric studies can provide some clues. The current due to the primary ions, 3MP$^+$ or (acetone)$^+$, should depend linearly upon the total pressure of the gaseous mixture at fixed composition, while that of the secondary ion, (acetone·H)$^+$, will depend upon the square of the total pressure. Therefore, the ratio of currents of secondary ion to primary should be proportional to the total pressure of the sample. Also, the appearance potential of secondary ion should be the same as that of the primary ion.

To improve mass resolution at high pressures and to distinguish clearly between reaction of acetone with itself and with hydrocarbon, acetone and cyclohexane-d_{12} mixtures were used.[20] The ratio of (acetone·D)$^+$ at *m/e* 60 to (acetone)$^+$ at *m/e* 59 (an isotopic peak of acetone) increased linearly with the total pressure confirming the proton-transfer reaction. The appearance potential of the *m/e* 60 peak agreed with that of acetone (*m/e* 58); therefore, reaction 10 may take place in the acetone plus 2MP system also.

The energy diagram of a ketone molecule appears schematically in Figure 10. In the positive ion one electron will be removed, from orbital n, so that the 740-mμ band is considered to correspond to the $\pi \rightarrow n_1$ transition. On the other hand, in the negative ion one additional electron will be in the π^* orbital and the 465-mμ band should correspond to the $\pi^* \rightarrow \sigma^*$ transition. The most usual assignment of the absorption bands of acetone molecule is not incompatible with the above assignment of the two bands of ions.[22,23]

From Table I it is seen that the λ_{max} of anions do not differ noticeably among the four ketones, while those of cations change considerably. The shifts are much more drastic than those of the $n_1 \rightarrow \pi^*$ transition of neutral ketone molecules. This may be due to the fact that hyperconjugation effects should be more important in positive ions than in neutral molecules or anions.[24]

A number of molecular anions of aromatic ketones have been studied by epr,[25] but hexamethyl- and pentamethylacetone[26] and tetramethyl-1,3-cyclobutanedione,[27] reduced with alkali metal in ether solutions, are among the few aliphatic ketyls examined. Di-*t*-butyl ketone in γ-irradiated MTHF glass was brown, although the optical density was small compared to the 460–470-mμ bands in Table I. In epr studies results similar to those in Figures 6 and 8 were obtained; that is, the ketone in alcoholic glasses eliminated trapped electrons and produced an epr signal which was stable toward photobleaching (Figure 11). We regard the signal as due to the radical $((CH_3)_3C)_2\dot{C}OH$ formed by reaction 3.

In glassy solvents which trap electrons, benzophenone replaced the trapped electron band with a new absorption band at 600–800 mμ (Figure 12). The band behaved normally as a solute anion band; *e.g.*, in dilute solutions it was easily photobleached and it was suppressed by chlorides or other electron scavengers. Therefore, the band is assigned to the ketyl of benzophenone. It can be seen in Figure 12 that maxima of the anion bands in MTHF, ethyl ether, triethylamine, and 2-methylpentene-1 lie at about 800 mμ, but a remarkable blue shift occurs in alcoholic solvents. The alkali metal ketyls of benzophenone display systematic blue shifts of >60 mμ in λ_{max} from Cs$^+$ to Li$^+$, while the band shape remains unaltered.[28] This has been examined theoretically by McClelland[29] and attributed to a preferential lowering of the ground state of the ion pair by e^2/r, where r is the ionic radius. The calculated effects were very similar for benzophenone and fluorenone anions, the cation being localized near the oxygen atom, and affecting the ground state preferentially. It follows that H bonding of $(C_6H_5)_2CO^-$ would also lead to an electrostatic effect of the protonic charge at the oxygen atom, with a consequent blue shift.

Figure 12 also shows that the absorption bands of benzophenone anions in alcoholic solvents have a hump at about 560 mμ. Upon warming the γ-irradiated sample, the main band disappeared quickly but the component at 554 mμ increased and revealed the resolved band at 560 mμ shown by curve 8 for a propylene glycol matrix. Porter and Wilkinson, using flash photolysis of aqueous benzophenone solutions containing alcohol, established the reaction[30]

$$(C_6H_5)_2\dot{C}OH + OH^- \rightleftharpoons (C_6H_5)_2CO^- + H_2O \qquad (11)$$

That is, at high pH the neutral ketyl radical, which is produced transiently by the reaction between excited benzophenone and alcohol, dissociates into benzophenone anion. According to this work, the ketyl radical absorbs at about 550 mμ. Similar studies on

---

[20] W. P. Hauser and W. H. Hamill, to be published.

[21] J. A. Ward and W. H. Hamill, *J. Am. Chem. Soc.*, **87**, 1853 (1965).

[22] H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy, " John Wiley and Sons, Inc., New York, N. Y., 1962, p 108.

[23] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 160.

[24] C. H. Coulson in "Molecular Orbitals in Chemistry, Physics and Biology," Academic Press Inc., New York, N. Y., 1964, p 12.

[25] B. J. McClelland, *Chem. Rev.*, 301 (1964).

[26] N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

[27] R. L. Ward, *J. Chem. Phys.*, **36**, 2230 (1960).

[28] H. V. Carter, B. J. McClelland, and E. W. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960).

[29] B. J. McClelland, *ibid.*, **57**, 1458 (1961).

[30] G. Porter and F. Wilkinson, *ibid.*, **57**, 1686 (1961).

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.

---

[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

Tadamasa Shida[1] **and William H. Hamill**

Contribution from the Department of Chemistry and the Radiation Laboratory,[2] *University of Notre Dame, Notre Dame, Indiana 46556.* *Received April 29, 1966*

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

---

[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.