

may be seen from the anharmonic k_{∞} values (Table X).

Consideration of cross-terms in the potential energy function, and of rotational interactions, would increase the anharmonicity correction relative to the above considerations. Despite this

fact, however, and the complementary one that much of the assumptions entering bending mode calculations merely represents crystallized ignorance, we believe that the estimates provided by Table XIII must fall in the region of physical significance.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Electron Attachment and Solvation in Gamma Irradiated Organic Glasses at -196° ¹

BY MICHAEL R. RONAYNE, JOHN P. GUARINO AND WILLIAM H. HAMILL

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Gamma irradiation at -196° of organic glasses containing small amounts of solutes whose anion absorption spectra are known results in the formation of optically identifiable anions by electron attachment. Using a tetrahydro-2-methylfuran glass the limiting value for $G(\text{anions})$ was 2.6 for naphthalene and 3.2 for biphenyl. With a hydrocarbon glass, the limiting yields were 1.1 and 1.7, respectively. For biphenyl in ethanol, $G(\text{anion}) = 2.94$. In all media, $G(\text{anion}) = 1$ for about 0.05 mole % additive. Anions of nitrobenzene, benzophenone and tetracyanoethylene have also been prepared by both methods and identified while spectra of styrene and carbon tetrachloride molecular anions, which cannot be prepared chemically, appear to form in gamma irradiated glasses. Irradiation of glassed tetrahydro-2-methylfuran alone produces a structureless absorption band in the visible and near infrared. With less than 0.5 mole % of naphthalene, the solute anion and solvent spectra both appear. The solvent spectrum can be selectively bleached, with a concomitant increase in the solute anion absorption bands. These facts indicate that the solvent absorption is due to solvated electrons. Similarly one observes solvated electrons in gamma irradiated ethanol but not in glassed alkanes or alkenes.

Introduction

The technique of isolating and stabilizing free radicals or other reactive entities for observation in rigid matrices at low temperature, although very useful in photochemistry, has received limited use in radiation chemistry.²⁻⁴ The method has not been successful hitherto for the identification of ionic species produced by high energy radiation, to our knowledge. It occurred to us that electron attachment by solutes in gamma irradiated organic glasses at -196° offered attractive possibilities since many organic compounds are readily reduced by alkali metals to produce anions of intense and distinctive optical absorption in convenient spectral regions, examples being naphthalene,⁵ benzophenone,⁶ etc. Comparison of the optical absorption spectra of chemically prepared and gamma-irradiated samples provides a basis for identification and, within limits, of quantitative measurement.⁷ Extensive measurements of e.s.r. spectra of such anions have been reported, although we are not now directly concerned with this technique.⁸ Other solutes, for which anionic spectra are unknown, can also be tested for electron attachment in turn by employing them competitively with naphthalene or biphenyl as a reference reagent.

Such methods have proven feasible and have considerable interest in their own right. We plan

to extend them further to investigate the role of ionic processes in radiation chemistry. For example, there is no *direct* evidence that electrons in gamma irradiated condensed phase chemical systems are involved in chemical changes, although such effects have been postulated on the basis of indirect evidence.⁹ It has been assumed by most investigators, at least implicitly, that charge recombination occurs so quickly that other ionic processes can be ignored. We find the argument from chronology misleading and hope to demonstrate that other processes can intervene and that the chemistry of ions is relevant to radiation chemistry. Aqueous systems provide a notable exception since there is now good evidence for a relatively long-lived negative entity.¹⁰ We also except from these generalizations the work on "ionic" polymerization, although the whereabouts of the electron or gegenion is altogether hypothetical, particularly in hydrocarbons,¹¹ and neither anion nor cation can be identified by e.s.r. spectra.¹²

Experimental

Solvents.—In general, solvents were chosen for their ability to form clear glasses, transparent from the near ultraviolet to the near infrared regions. Tetrahydro-2-methylfuran was chosen both for its ability to glass and also because chemical reductions of aromatic compounds could also be carried out in this solvent at room temperature. The drying and purification of tetrahydro-2-methylfuran was carried out by several vacuum distillations from clean sodium mirrors and finally the solvent was distilled into a storage bulb containing sodium-potassium alloy. This procedure removed water and prevented formation of peroxides. Phillips pure grade 3-methylpentane, methylcyclohexane and isopentane were stored in air over sodium. Phillips pure grade 2-methylpentene-1 was treated in the same way as tetrahydro-2-methylfuran to prevent peroxida-

(1) The Radiation Laboratory of the University of Notre Dame is operated under Atomic Energy Commission Contract AT(11-1)-38.

(2) H. T. J. Chilton and G. Porter, *J. Phys. Chem.*, **63**, 904 (1959).

(3) (a) R. S. Alger, T. H. Anderson and L. A. Webb, *J. Chem. Phys.*, **30**, 695 (1959); (b) H. Zeldes and R. Livingston, *ibid.*, **30**, 40 (1959).

(4) B. Smaller and M. S. Matheson, *ibid.*, **28**, 1169 (1958).

(5) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

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

(7) P. Balk, G. J. Hoijsink and J. W. H. Schreurs, *Rec. trav. chim.*, **76**, 813 (1957).

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(10) G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, **66**, 471 (1962).

(11) E. Collinson, F. S. Dainton and D. C. Walker, *Trans. Faraday Soc.*, **57**, 1737 (1961).

(12) P. B. Ayscough, A. P. McCann, C. Thomson and D. C. Walker, *ibid.*, **57**, 1487 (1961).

tion. Anhydrous ethanol from Commercial Solvents Corp. was used as received. Pure ethanol cracks at -196° but can be used with 5% methyl cyclohexane; this mixture is simply designated "ethanol" in the text.

Solutes.—The following materials were used as received: biphenyl, Monsanto (recrystallized from ethanol); benzophenone, nitrobenzene, styrene, tetracyanoethylene and naphthalene were all Eastman, white label grade. Styrene with *t*-butyl pyrocatechol inhibitor was stored in vacuum and distilled as needed.

Chemical Preparation of Anions.—The chemical preparations of various anions were carried out in tetrahydro-2-methylfuran using the methods of Weismann⁵ and Hoijtink.⁷

Sodium potassium alloy was generally used for preparations. Solutions for optical measurement were prepared free of excess alkali metal by pouring the solution through a glass wool filter into the absorption cell by rotating the preparation bulb about a ground glass joint on the vacuum line. The concentration of anion in the absorption cell could be controlled approximately by pouring over a small amount of concentrated solution and diluting it with distilled solvent. Extinction coefficients of naphthalene and biphenyl anions were determined both at room temperature and at -196° . Absorption bands are narrower at low temperature and optical densities at the absorption maxima increase much more than corresponds to the observed 20% volume contraction of solvent. Cells then were opened, CO₂-free water added and solutions titrated. The extinction coefficients found were 3.0×10^4 l./mole cm. for naphthalenide at 3250 Å. and 3.7×10^4 l./mole cm. at 4100 Å. for biphenylide, both at -196° . Extinction coefficients have been reported⁷ for naphthalenide, 1.55×10^4 l./mole cm. at 3250 Å. and for biphenylide 9.8×10^3 l./mole cm. at 4100 Å. We consider the latter to be in error.

Conventional vacuum techniques were used for degassing solutions. Small amounts of oxygen affected radiation yields of anions and degassing was generally necessary. In the preparation of tetrahydro-2-methylfuran solutions, solvent was distilled from the storage bulb into a small receiver, 5 ml. was pipetted into a clean dry bulb which was returned to the vacuum line and degassed at -120° . After trap-to-trap distillation with pumping, it was vacuum distilled into the absorption cell containing a weighed amount of solute and sealed.

When hydrocarbon solvents were used, the desired amount of alkane was pipetted into a cell containing the solute, and the cell was thoroughly outgassed on the vacuum line by trap-to-trap distillation. Alkene was stored *in vac.* over sodium-potassium alloy and was distilled as needed from the storage bulb, pipetted into the cell, then returned to the vacuum line and outgassed before sealing the cell. Ethanol solutions were outgassed by refluxing *in vacuo* 1 hr. at -70° .

Gamma Irradiations.—Samples were prepared, irradiated and examined in 1×1 cm. Pyrex cells, sealed in vacuum and immersed in liquid nitrogen prior to irradiation and during subsequent measurement. The Co⁶⁰ source has been described previously.^{13a} Dose rates, determined by Fricke dosimetry,^{13b} approximated 10^{17} ev./g. min. Doses usually approximated 10^{18} ev./g. except for a few samples tested for yield-dose linearity at up to 10^{19} ev./g. Radiation coloring of Pyrex cells was negligible.

Absorption Spectra.—A Cary Model 14 recording spectrophotometer was used for most measurements of absorption spectra. The cell was immersed in liquid nitrogen in a partially silvered dewar flask with silica windows. Most gamma irradiated samples bleached easily when scanned beyond 7,000 Å. because the light is not monochromatized before entering the cell compartment. Therefore, for measurements in the 7,000–13,000 Å. interval of samples which bleached readily, a Beckmann DU spectrophotometer was used.

Most bleaching experiments were performed in the spectrophotometer using the infrared light source with appropriate filters. The filters used most extensively were Corning no. 2600 which transmits light from 7,500 to 10,000 Å. and Corning no. 3961 which transmits between 3700–7400

Å., with a maximum at 5200 Å. When monochromatic light was required, a sodium vapor lamp was used. A narrow band pass filter (Jena) with λ_{\max} at 4760 Å. and a half width of 120 Å. was also used.

Results

Gamma Irradiation of Pure Solvents.—Irradiation of pure hydrocarbon solvents (alkane or alkane-alkene mixtures) produced no absorption in the interval 3,000–7,500 Å. Ethanol colored violet on irradiation and a wide band at 5400 Å. increased linearly with dose up to 10^{19} ev./g. The entire band bleached uniformly when illuminated with a 4760 Å. narrow band pass filter.

Tetrahydro-2-methylfuran became blue on irradiation and a structureless absorption increasing monotonically from 4,000 to 13,000 Å. (the limit of measurement) was found. Since the color bleached very easily, the spectrum was measured on a Beckmann DU spectrophotometer. The optical density at any wave length was linear with dose to about 10^{20} ev./g. The blue color bleached readily with sodium D light or with light transmitted by a Corning filter no. 2600. In either case the band bleached as a whole. Experiments using interrupted bleaching with filter no. 2600 tested the possibility that absorbed light was degraded to heat and bleached by softening the glass. When a sample was alternately illuminated for 5 sec. and kept dark for 15 sec., until the illumination time equaled that for a parallel run with continuous illumination, the extent of bleaching was the same. The quantum yield for bleaching with sodium D light was measured¹⁴ and found to approximate unity, assuming the 100 ev. yield of color centers to be 3.

Chemical Preparation of Solvated Electrons.—When sodium-potassium alloy and a mixture of 20% dimethoxyethane–80% tetrahydro-2-methylfuran was cooled to -196° , a blue solution resulted. The spectrum exhibited a symmetric absorption band with maximum at 6000 Å. and a half-width of about 1000 Å. at -196° . This color bleached with illumination at 6,000 Å. and was replaced by a structureless absorption extending from 4000 to 13,000 Å. These are essentially the same effects observed by Linschitz, *et al.*,¹⁵ in a similar experiment, which were interpreted in terms of solvated electrons. Our attempts to bleach the structureless absorption produced in this way were unsuccessful under experimental conditions which very quickly bleached gamma irradiated samples.

Solute-Solvent Competition for Electrons.—The addition to methyl tetrahydrofuran of a solute such as naphthalene which can attach electrons may be expected to reduce the absorption of the solvent band and to produce the absorption characteristic of the solute anion in gamma irradiated glasses. We find, in fact, that the solvent absorption band of gamma irradiated methyl tetrahydrofuran is diminished or prevented altogether by a few tenths % of naphthalene, biphenyl, benzophenone or tetracyanoethylene. The absorption spectra of chemically prepared anions, measured at -196° , correspond to the banded spectra of irradiated

(13) (a) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instr.* **473** (1951); (b) R. M. Lazo, H. A. Dewhurst and M. Burton, *J. Chem. Phys.*, **22**, 1370 (1954).

(14) R. G. Kaufman, this Laboratory.

(15) H. Linschitz, M. G. Berry and D. Schweitzer, *J. Am. Chem. Soc.*, **76**, 5833 (1954).

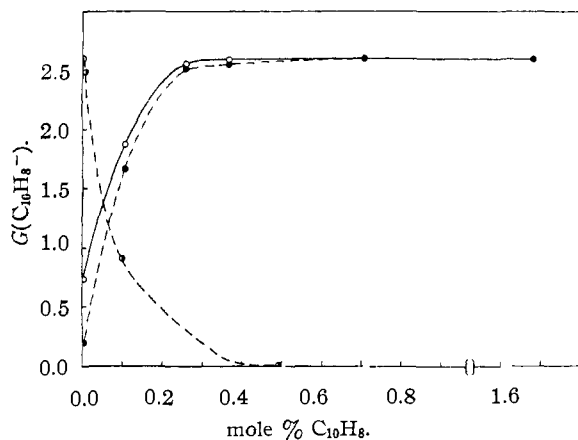


Fig. 1.—●, $G(\text{naphthalene anions})$ vs. mole % naphthalene in tetrahydro-2-methylfuran; ○, $G(\text{naphthalene anions})$ vs. mole % naphthalene in tetrahydro-2-methylfuran after bleaching solvated electrons; ●, $G(\text{solvated electrons})$ vs. mole % naphthalene in tetrahydro-2-methylfuran, all at -196° .

glassed solutions. These results appear in Table I.

In addition we found for sodium-benzophenone λ_{max} 6,650 Å., for potassium-benzophenone λ_{max} 7,150 Å. and for gamma irradiated solutions λ_{max} 8,250 Å. For sodium-nitrobenzene λ_{max} was 4,400 Å., for the gamma irradiated solution, λ_{max} 4,600 Å., all in methyltetrahydrofuran at -196° .

In each case, at small concentrations of solute in methyltetrahydrofuran, both anion and solvent

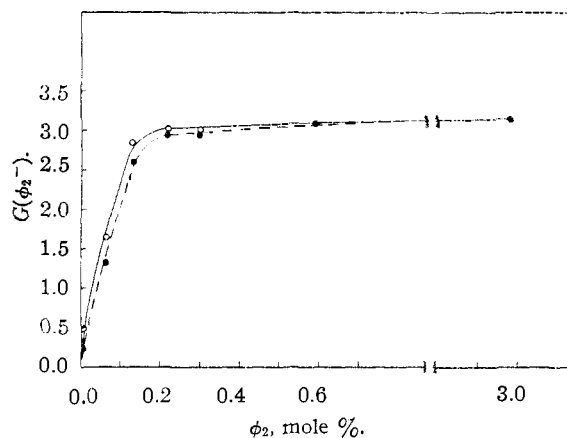


Fig. 2.—●, $G(\text{biphenyl anions})$ vs. mole % biphenyl in tetrahydro-2-methylfuran at -196° ; ○, $G(\text{biphenyl anions})$ vs. mole % biphenyl in tetrahydro-2-methylfuran at -196° after bleaching solvated electrons.

bands were present and bleaching the solvent bands increased the anion absorption bands. The anion yield vs. concentration curves for naphthalene and biphenyl appear in Figs. 1 and 2. Since the extinction coefficient for the solvent band is not known, the curve is arbitrarily normalized to the limiting yield of solute anions. Benzophenone was used to examine the effect of charge separation. At 0.01, 0.1 and 1 mole % benzophenone in methyl tetrahydrofuran the λ_{max} was 8,250 Å. for all cases. This is a very large shift relative to the chemically prepared ketyl.

Styrene in Tetrahydro-2-methylfuran.—The anion of styrene could not be prepared either directly with sodium or by rapid mixing with sodium naphthalenide. However on gamma irradiation of styrene in glassed solution two absorption bands with maxima at 4100 and 6000 Å. were observed. The bands were assigned to styrene anion by irradiating a 0.2 mole % solution, bleaching the solvated electrons and observing increases in solute bands. Using results for radiation produced naphthalene anions and assuming equal $G(\text{anions})$ for both solutes at sufficiently high solute concentrations, we estimate $\epsilon_{4100} = 2.3 \times 10^4$ l./mole cm. and $\epsilon_{6000} = 5 \times 10^3$ l./mole cm.

Gamma Irradiation of Solutes in Hydrocarbon Glasses.—Irradiation of naphthalene or biphenyl in alkane hydrocarbons gave both the spectra of the anions and also several extraneous bands. Proceeding on the supposition that these new bands were due to species formed by H-atom addition to the aromatic ring, olefins were added to the solvent. The unidentified bands disappeared with 5% or more 2-methylpentene-1. In addition, solute solubilities at -196° were larger in alkane-alkene mixture. Most hydrocarbon runs were performed in a 75 volume % 3-methyl pentane-25 volume % 2 methyl pentene-1 mixture which gave clear glasses with no cracking.

Figure 3 shows the anion yield vs. concentration curve for naphthalene and biphenyl in alkane-alkene. The yield of biphenyl anion was constant for doses as high as 5×10^{19} ev./g. Both naphthalene and biphenyl anions bleached easily

TABLE I
ABSORPTION SPECTRA AT -196° OF NAPHTHALENE, BIPHENYL AND TETRACYANOETHYLENE IN METHYL TETRAHYDROFURAN, ETHANOL AND HYDROCARBON SOLUTIONS FOLLOWING CHEMICAL REDUCTION OR GAMMA RADIATION;
 λ_{max} 1N Å.

Methyl tetrahydrofuran, Na-K	Methyl tetrahydrofuran, γ	Hydrocarbon, γ	Ethanol, γ
Naphthalene			
3250	3250	3250	
3700	3700	3700	
4350	4350	4350	
4550	4550	4550	
4650	4650	4650	
7400	7800	7600	
8400	8650	..	
Biphenyl			
3800	3800	3800	3790
3950	3950	3950	3950
4100	4100	4100	4090
6500	6600	6600	6500
Tetracyanoethylene			
3995	4000		
4100	4100		
4190	4195		
4290	4295		
4395	4395		
4495	4495		
4615	4625		
4720	4730		

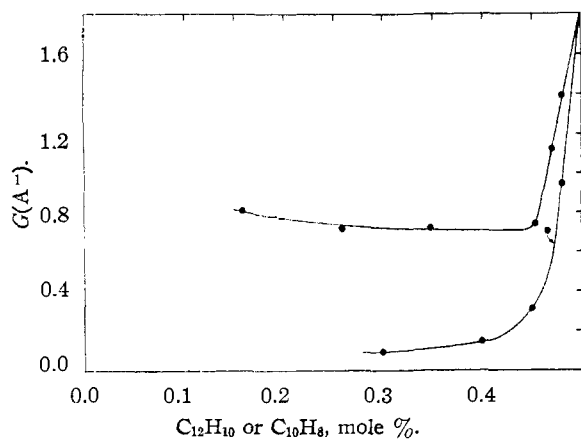


Fig. 3.—Yield of anion, $G(A^-)$, vs. mole % biphenyl (upper) or naphthalene (lower) in 25 vol. % 2-methyl pentene-1 and 75 vol. % 3-methyl pentane at -196° .

in this mixture with a Corning 3961 or 2600 filter. The effect of oxygen in these solutions, as a competitive solute for electron attachment, is indicated by the following results. In alkane-alkene glass with 0.05 mole % biphenyl, $G(\text{anion}) = 1.49$ *in vac.* and 0.39, air saturated. Bubbling nitrogen, prior to glassing, gave $G(\text{anion}) = 1.16$.

Irradiation of styrene in alkane-alkene mixture gave bands at 4100 Å., half width 450 Å. and at 5800 Å., half width 900 Å. Optical densities at 4100 Å. were 1.06, 1.65, 1.14 and 0.76 with 0.06, 0.27, 0.55 and 2.7 mole % styrene. Using our estimated extinction coefficient for styrene anion (see before), the 100 ev. yields were 1.25, 1.95, 1.35 and 0.89. The decrease in optical density with increasing styrene was also observed in alkane as solvent, in the presence of air. Both bands bleached uniformly with a Corning 3961 filter.

Gamma irradiation of carbon tetrachloride in 3-methylpentane or isopentane-methylcyclohexane produces a broad absorption band with $\lambda_{\text{max}} = 4880$ Å. and a half width of 1200 Å. The yield of color centers saturates at *ca.* 10 mole % carbon tetrachloride¹⁶ and the color is removed rapidly by illumination with a Corning 3961 filter. No 4880 Å. absorption appears in polar matrices, such as methyl tetrahydrofuran, ethanol etc.

Values of $G(\text{HCl})$ for thawed samples containing carbon tetrachloride in various matrices were 1.3 for hydrocarbons; 2.5 for 95% methylcyclohexane-isopentane, 5% diethyl ether; 7 for tetrahydro-2-methylfuran. Correspondingly, the optical density was 1.49 in 100% methylcyclohexane-isopentane and 1.16 in 95% methylcyclohexane-isopentane, 5% diethyl ether, both measured at 4800 Å.

Other halides in methyl cyclohexane-isopentane glasses gave the following results, where the first number is λ_{max} and the second is half width, both in Å: methyl iodide, 5350, 800; ethyl bromide, 6000, 1900; hexachloro ethane, 4200, 850; carbon tetrabromide 5100, 1700. All of these color centers bleached using unfiltered tungsten light.¹⁶

Gamma Irradiation of Solutes in Ethanol.—Figure 4 shows the anion yield vs. concentration for

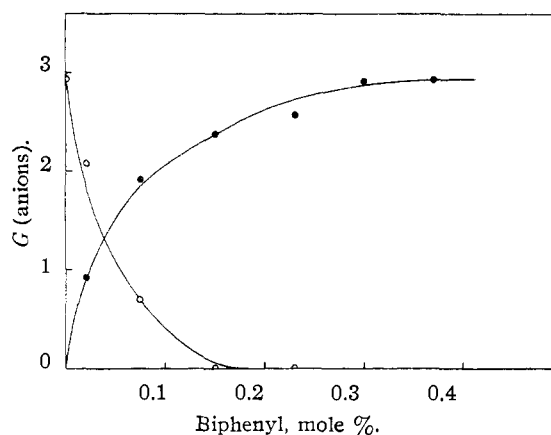


Fig. 4.—●, $G(\text{biphenyl anion})$ vs. mole % biphenyl in ethanol at -196° ; ○, normalized $G(\text{solvated electron})$ vs. mole % biphenyl in ethanol at -196° .

biphenyl in ethanol. In addition, the systematic decrease in the 5400 Å. ethanol band with increasing biphenyl concentration is presented. Carbon tetrachloride prevents formation of the 5400 Å. band.

Discussion

The correspondence between absorption maxima of chemically prepared solute molecular anions¹⁷ and of the corresponding color centers in gamma irradiated glasses, as shown in Table I, adequately identifies these entities as molecular mononegative anions. The mode of their formation under radiation suggests that electrons are released from the matrix target and become attached by appropriate solute molecules after diffusing through the medium. The solvent absorption bands in pure methyl tetrahydrofuran can, in turn, be identified plausibly as solvated electrons since the yield of such solvent color centers is depressed by solutes capable of forming identifiable anions by simple electron attachment. Furthermore, the solvent absorption produced by gamma radiation resembles very much that of dissolved sodium-potassium after optical bleaching. Finally, selective light absorption in the solvent band of glasses containing small concentrations of solute anion formers, following gamma radiation, removes these color centers and simultaneously increases the identifiable anion absorption bands.

The gamma radiation induced absorption band in ethanol glass is considered to be due to solvated electrons principally because its formation is strongly suppressed by about 0.1 mole % of biphenyl or other electron attaching solutes. In particular, the systematic decrease in solvent absorption with increasing concentration of biphenyl (Fig. 4) accompanied by a complementary increase in biphenyl anion absorption closely resembles the corresponding experiments in methyl tetrahydrofuran and supports the proposed assignment.

One also might propose alternative mechanisms to account for the mechanism of formation of

(17) Extensive e.s.r. investigations of the anions of naphthalene, biphenyl, nitrobenzene, benzophenone and tetracyanoethylene as well as spectral measurements and m.o. calculations for several of these establish the mononegative character of these colored entities beyond reasonable doubt.

solvated and attached electrons. Thus, the solute molecule might serve as a nucleus for the collapse of collective excitation¹⁸ in the matrix or accept an electron from a neighboring electronically excited solvent molecule.¹⁹ Since photoelectric liberation of solvated electrons leads to qualitatively similar observed effects and since the relative efficiencies of attachment of these photoelectrons by solute approximates the concentration dependence for primary attachment, we conclude that primary attachment also involves low energy "free" electrons. We also find a close correlation of electron attachment efficiencies by many solutes with polarographic half wave potentials which would be difficult to reconcile with high energy processes.²⁰ Also solutes which have high anion appearance potentials by mass spectrometry are very inefficient solutes in radiated glasses and contrariwise.²⁰

Optical bleaching of ethanol color centers in glasses containing naphthalene or biphenyl does not enhance the solute anion bands and, granting the assignment, may be regarded as evidence for return of the electron to the positive hole, which is presumed to be $\text{CH}_3\text{CH}_2\text{OH}_2^+$. This fails to account for the absence of solute anion enhancement, as observed under similar conditions in methyl tetrahydrofuran. Alternatively, we may suppose that light produces $\text{C}_2\text{H}_5\text{O}^-$ and H. This proposal both accounts for an apparent failure to release photoelectrons and also corresponds to the difference in behavior of alcohols and ethers toward alkali metals. Either mechanism appears to be compatible with e.s.r. measurements.^{3b}

The uniform bleaching of the solvent band in gamma radiated methyl tetrahydrofuran by sodium light or 7,500–10,000 Å. light indicates that a single absorbing species is involved. The very wide absorption band may be accounted for qualitatively by electrons in very irregularly shaped boxes. Since both solvent and solute absorption bands can coexist, the electrons are not tunneling. There must be dissimilar boxes giving rise to somewhat different spectra, but even long term molecular agitation would tend to cause differences to average out.

Hydrocarbon matrices do not appear to be capable of solvating electrons, although this has been suggested for olefins undergoing radiation induced "ionic" polymerization in the pure liquid state.¹¹ Except for a few minor differences, the solute anion spectra are the same in all media and are presumably not subject to solvation effects. Insofar as chemical and radiation procedures lead to the same spectra, we conclude that the spectra are also uninfluenced by charge separation,⁶ as regards location of the band maxima.²¹

We cannot be sure that extinction coefficients are the same for chemical and radiation procedures;

(18) J. L. Magee in "Comparative Effects of Radiation," M. Burton, J. S. Kirby-Smith and J. L. Magee, Eds., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 130–146.

(19) R. L. Platzman, *J. Phys. Rad.*, **21**, 853 (1960).

(20) J. P. Guarino, M. R. Ronayne and W. H. Hamill, *Radiation Research*, **17**, 379 (1962).

(21) We do find a marked difference in λ_{max} for benzophenone with mode of preparation. This appears to arise from an effect of charge separation according to recent theoretical consideration by B. J. McClelland, *Trans. Faraday Soc.*, **57**, 2073 (1961); see also ref. 6.

calculated values of $G(\text{anion})$ are necessarily based upon the assumption that extinction coefficients are equal. This uncertainty affects the comparison of $G(\text{anion})$ in polar and non-polar media. The dissimilarity of limiting apparent yields may be real, of course. Unlike $\text{Na}^+\text{C}_{10}\text{H}_8^-$, etc., which are thermodynamically stable as associated ion pairs, the corresponding solvent-solute cation-anion pair would be unstable since solvation energy cannot overcome the large positive energy resulting from ionization of the solvent molecule. Even in rigid media we must expect different minimal allowed charge separations of mechanically stabilized ions in polar and non-polar solvents. Plateaus for yield-concentration curves in Figs. 1–3 do not measure all electrons produced, then, but only all electrons trapped beyond a critical limiting radius which varies inversely with the static dielectric constant and also depends upon the rigidity of the matrix. The difference in ion stability between polar and non-polar media is also shown by the rate of bleaching solute anions, which is about ten times greater in the low dielectric glass.

The 4880 Å. band for carbon tetrachloride in hydrocarbon glasses we attribute to CCl_4^- . This accounts for fast optical bleaching and a small $G(\text{HCl})$ from the thawed sample. Any dissociative process would be expected to produce hydrogen chloride, and an expected $G(\text{H})$ of 1–2 should produce an additional corresponding $G(\text{HCl})$. This interpretation is supported by a large $G(\text{HCl})$ in methyltetrahydrofuran and the absence of 4880 Å. absorption; we account for both these facts by postulating solvolysis of CCl_4^- in polar media. If the absorption band of carbon tetrachloride in hydrocarbon arose from alkyl free radicals, it should have arisen also after attack by H-atoms or other reactive species; if it arose from CCl_3 , it also should have formed in a polar solvent. Finally carbon tetrachloride in small concentration prevents formation of solvated electrons.

The stabilization of anions and solvated electrons in rigid media requires corresponding immobilization of positive holes. In an environment of a single molecular species, charge exchange should occur readily between adjacent ion-molecule pairs unless they become differentiated by a chemical reaction which dissipates potential energy and traps the hole. In polar media we expect H or H^+ transfer to occur, producing protonated solvent molecules. Many such reactions are known from mass spectrometry of ethers, alcohols, etc.²² Corresponding reactions of alkanes do not appear under similar conditions, excepting CH_3^+ from CH_4 , and we expected low $G(\text{anion})$ in hydrocarbon glasses from hole migration. Small yields were observed during preliminary runs with alkane glasses. Subsequent runs with alkane-alkene glasses gave much larger $G(\text{anions})$, and the effect was attributed to trapping positive holes by olefin molecules.²³ It appears now that one-component alkane glasses are as efficient as alkane-alkene mixtures and that early measurements were vitiated by failure to exclude air. It appears also,

(22) Dr. T. F. Moran, unpublished results.

(23) P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 500 (1962).

from recent very high pressure mass spectrometry, that alkanes undergo many ion-molecule reactions²⁴; this provides the necessary mechanism for immobilizing positive holes.

If the concentration dependence in Figs. 1-3 be taken as exponential, then the mole fraction X of solute required for an anion yield of half the limiting value leads to $0.69/PX$ for the average number of molecular encounters, where P is an efficiency factor. This number approximates $1500P^{-1}$ for these systems and indicates that the electron describes a fairly extended track. Since many solutes have efficiencies equal within a factor of two,²⁰ it is plausible that $P \sim 1$ for efficient solutes. Samuel and Magee²⁵ arrived at a number 10^3 using a model which is probably as applicable to these systems as to water. Both the preceding considerations and the fairly large quantum yield for bleaching solvated electrons are inconsistent with the assumption that electrons escape from the

(24) S. Wexler, private communication.

(25) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

field of the cation. This is also indicated by the constancy of $G(\text{anion})$ for 0.01 M biphenyl in hydrocarbon at doses up to 6×10^{18} ev./l. The final concentration of holes was about $1.6 \times 10^{-4} M$. If electron capture cross sections by holes were 10 to 100 those for solute molecules, the ratio of hole to solute efficiencies for steady state kinetics would have been 0.16-1.6.

The facts reported here provide qualitative support for the view that ionic processes are important in the radiation chemistry of liquids.⁹ Quantitatively, the $G(\text{anions})$ reported here rise much faster with concentration than do yields of chemical products in irradiated solutions at room temperature. We do find, however, that chemical yields from irradiated glassed solutions of ethyl iodide and phenyl acetyl chloride in methyl tetrahydrofuran, collected after thawing, increase about ten times more rapidly with solute concentration²⁶ than do the corresponding solutions in benzene.⁹

(26) J. R. Roberts, to be published.

[CONTRIBUTION NO. 1698 FROM THE DEPARTMENT OF BIOCHEMISTRY, DARTMOUTH MEDICAL SCHOOL, HANOVER, NEW HAMPSHIRE, AND DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

The Nature of the Slowly Exchanging Protons of Ribonuclease^{1a}

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The nuclear magnetic resonance spectra of ribonuclease in D_2O solutions between pD 2.8 and 4.5 showed exchange of NH protons with time. 24 ± 5 protons exchanged much more slowly than the others. Guanidinated ribonuclease was shown to contain 54 ± 7 hydrogens exchanging at a comparable rate. When both proteins were heated to 72° exchange of all the NH protons was noted. It has been suggested that these very slowly exchanging protons are attached to the guanidinium groups of both proteins.

The rate of deuterium exchange between proteins or polypeptides and an aqueous environment has been the subject of many investigations since Linderström-Lang proposed that those protons of the peptide backbone involved in the strongly hydrogen-bonded secondary structure might be distinguished from others by having a slower rate of exchange.^{1b} Slow exchange has indeed been observed in many proteins.^{2,3} Ribonuclease, typically, has been found to possess a distribution of NH and OH protons with widely differing exchange rates, both distributions and rates having a strong dependence on temperature, pH and other conditions.³⁻⁷

(1) (a) This work was supported in part by funds from National Science Foundation Grant C19973 and U. S. Public Health Service Grant RG8121. (b) A. Hvidt and K. Linderström-Lang, *Biochim. Biophys. Acta*, **14**, 574 (1954). The precise suggestion had been foreshadowed by H. Lenormant and E. R. Blout, *Nature*, **172**, 770 (1953).

(2) Multiple references to the technique and results of determining exchange by the density-gradient method of analyzing the solvent for deuterium content are given in (a) K. Linderström-Lang, in "Symposium on Protein Structure," ed. A. Neuberger, London, 1958, pp. 23-24. (b) H. A. Scheraga, in "Protein Structure and Function," Brookhaven Symposia in Biology, No. 13, 1960, pp. 71-88.

(3) References to infrared absorption studies are given in E. R. Blout, C. de Loze and A. Asadourian, *J. Am. Chem. Soc.*, **83**, 1895 (1961).

(4) A. Hvidt, *Biochim. Biophys. Acta.*, **18**, 307 (1955).

(5) M. Saunders and A. Wishnia, *Ann. N. Y. Acad. Sci.*, **70**, 870 (1958).

We were able to show⁵ that the exchange of protons between ribonuclease and D_2O could be observed directly by nuclear magnetic resonance spectroscopy (n.m.r.), since the n.m.r. spectra of deuterons and protons are widely separated. The area of the ribonuclease absorption peaks in the region corresponding to aromatic and NH protons decreased with time, presumably because of the exchange of the NH protons with the solvent. The data were not precise enough to justify kinetic analysis, but it was clear that in solutions of pD between 2.5 and 5, the NH-aromatic peaks still contained about 25 more protons than could be attributed to the aromatic hydrogens alone, even after several days. In isoionic solutions the exchange had been complete, leaving a single low-field peak of the proper area for aromatic hydrogens.⁸

Using the Linderström-Lang method, Linderström-Lang, Schildkraut, and Scheraga⁵ have observed that after 24 hours at pH 4.8 and 0, 38, or 60° , deuterated ribonuclease retained 49, 22, and 0 (± 5) deuterons, respectively. More recently, Hermans and Scheraga⁷ concluded that 20 refractory NH protons account for the residual absorp-

(6) C. L. Schildkraut and H. A. Scheraga, *J. Am. Chem. Soc.*, **82**, 58 (1960).

(7) J. Hermans, Jr., and H. A. Scheraga, *ibid.*, **82**, 5156 (1960).

(8) M. Saunders, A. Wishnia and J. G. Kirkwood, *ibid.*, **79**, 3289 (1957).