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IRRADIATION STUDIES OF MONOBASIC SATURATED
CARBOXYLIC ACIDS IN NON-CRYSTALLINE HYDROCARBON MATRICES AT 77°K

MASTER

By

E. P. Bertin¹ and L. L. Burger

Battelle Pacific Northwest Laboratories
Richland, Washington

¹Supported in part by a grant from the Northwest College and University Association For Science, with funds from the Atomic Energy Commission. Present Address: Department of Chemistry, Seattle University, Seattle, Washington, 98122

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ABSTRACT

The hydrocarbons 3-methylpentane and 2-methylpentene-1 form glassy non-crystalline matrices at 77°K, which are highly suitable for studies in radiation chemistry. The monobasic carboxylic acids are investigated for their ability to attach electrons freed from the solvent, upon absorption of cobalt-60 gamma rays. Relative electron capture cross-sections are determined through competitive electron capture with biphenyl as a reference solute. Decrease in the concentration of solvated electrons, with increasing concentration of acid, is also reported.

INTRODUCTION

Certain solvents such as 3-methylpentane (3MP), 2-methylpentene-1 (2MP-1) and 2-methyltetrahydrofuran (MTHF) among others form rigid glassy non-crystalline matrices at liquid nitrogen temperature, 77°K.² Spectrophotometric evi-

²P.S. Rao, J.R. Nash, J.P. Guarino, M.R. Ronayne and W.H. Hamill, J. Am. Chem. Soc., **84**, 500 (1962).

dence is at hand to show that negative ions of naphthalene, biphenyl, and tetracyanoethylene are formed by the gamma irradiation of these species in the systems discussed. Absorption frequencies from the gamma irradiation species are nearly identical to those of the anions, formed chemically by reaction with a sodium-potassium alloy.³

³M.R. Ronayne, J.P. Guarino and W.H. Hamill J. Am. Chem. Soc., **84**, 4230 (1962).

When organic glassy solids are used for high-energy radiation, the energy is deposited primarily in the matrix. It becomes a source of electrons and positive holes and must be selected with reference to its capability of conducting or trapping the charged species. Normally it is preferred that the matrix trap one charge species and conduct the other.⁴

⁴T. Shida and W.H. Hamill J. Chem. Phys., **44**, No. 12, 4372 (1966).

In the irradiation of 3MP systems with λ_{max} equal to ~ 1600 nm, $\epsilon(e^-)$ is set equal

to $3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.⁵

⁵J.B. Gallivan and W.H. Hamill, J. Chem. Phys., 44, 1279 (1966).

When certain species absorb electrons, freed from the solvent upon irradiation by cobalt-60 gamma rays, some molecules will be expected to release small-particle negative ions, because of dissociative electron capture. Others may well absorb the electrons without undergoing dissociation. In either case a species with a distinctive color center may or may not be present in the region covered by the Cary spectrophotometer Model 14 from the near infrared to the ultraviolet, inclusive. In either case however, if a competition between a solute under consideration and some reference solute possessing a color center is present, we may assume that the number of anions formed is proportional to the product of capture cross-section and concentration of the solute. It can be shown that the slope of a plot of the concentration of the competitive solute versus the reciprocal of the G value, (number of negative species per 100 ev energy absorbed), of the reference solute will give a value from which the ratio of capture cross-sections of the reference solute and the competitive solute may be determined.^{6,7}

⁶E.P. Bertin and W.H. Hamill, J. Am. Chem. Soc., 86, 1301 (1964).

⁷J.P. Guarino, M.R. Ronayne and W.H. Hamill, Radiation Research, 17, 379 (1962).

Even in cases where the ability of a solute to attach electrons is very weak, or concentration limitations make the above comparison impossible, a study of the competition for electrons with reference to the solvated electrons of the solvent itself may also be made.

The present report is intended to be part of an overall study of organic compounds related to Biochemistry. These include the carboxylic acids, the amines, the amino acids, the N-substituted amides, the dipeptides and the polypeptides. Specifically, the investigation centers around the ability of the acid group to attach electrons, (and whether a carboxylate ion is formed), the formation of a positive species by the amine group (and whether the resultant ion is $\text{H}_3\text{N}^+\text{R}$), and what happens to the peptide group, as distinguished from terminal groups in the peptides. These studies are all made at liquid nitrogen temperatures, with organic non-crystalline matrices, to study the more elementary species formed by the absorption of gamma irradiation. A later study will be

made at room temperature, with the collection, separation and identification of final chemical products. A correlation between the two studies will then be attempted.

EXPERIMENTAL

3-methylpentane, from Matheson, Coleman, and Bell, was treated with silica gel with the center fraction being saved. 2-methylpentene-1 from the same supplier was treated in a similar fashion. Biphenyl, ϕ_2 , practical grade from Eastman Organic Chemicals, was recrystallized from 95% ethanol. Water was removed from acetic acid by treatment of acetic anhydride with boric acid to form acetyl borate. This was then added to acetic acid and the mixture was distilled. Propionic acid, Eastman Kodak White Label, was dried over anhydrous sodium sulfate, distilled, then redistilled over potassium permanganate. Butyric acid was distilled over potassium permanganate. Isobutyric acid, Fisher, C.P., was treated in the same way. Heptafluorobutyric acid, Minnesota Mining and Manufacturing Company, research sample, was not repurified. Isovaleric acid, 3-methylbutanoic acid (3MBA), Eastman Kodak Company, was stored over sodium sulfate. n-Octanoic acid (NOA), Eastman Organic Chemicals, was tested for purity by treatment with a methyl acetate-ammonia solution, with paper chromatography, and developed with alcoholic methyl red. 4-methylhexanoic (4MHA), n-pentanoic acid (NPA), 4-methylpentanoic acid (4MPA), 6-methylheptanoic acid (6MHA), 2-methylbutanoic acid, (2MBA), and 4-methylhexanoic acid (4MHA), all from Analabs, Hamden, Conn., were used as received. Solvent and solute systems were degassed to 10^{-5} mm mercury by a freeze-pump-thaw cycle carried out three times.³ A specially designed dewar made with quartz windows was evacuated to 10^{-7} mm Hg and heated for 24 hours at 430°C before sealing. Radiation cells were formed from one by one centimeter Pyrex tubing, as well as Suprasil quartz. Gamma irradiation techniques and the measurements of absorption spectra have been previously reported.³ The solvent system used throughout was 75 volume percent 3MP and 25% 2MP1. Radiation doses were approximately 10^{19} ev gm^{-1} , as determined by Fricke dosimetry.

Very precise measurements of spectra and detailed computations on these data were made possible by a small computer (Raytheon 703) interfaced to the spectral instruments. Although it was possible to use input from cards, punched tape or magnetic tape, for the present work, data were read by the computer directly from the Cary Model 14 Spectrophotometer. Computations included arithmetic calculations, thinning of spectra, smoothing of data, baseline corrections, peak

analysis and resolution, subtraction of spectra, integration, differentiation and plotting. A Model 310 duPont Curve Resolver was employed to obtain preliminary parameters for curve resolution.

In an attempt to study any possible change in structure of the solvated electron absorption curve with time, the solvent system was irradiated and its spectrum was taken 1 min. 25 sec. after removal from the cobalt source. With the cell kept in the dark (except for the momentary addition of liquid nitrogen at the 1 hr. 10 min. point), the spectral measurements were repeated at approximately 10 min. intervals for a period of two hours. The spectrum before irradiation was then subtracted from each of these dark decay spectra to give the resultant difference spectra. The region covered was (800-2100) nm.

RESULTS

Figure 1 shows the spectra of the pure solvent system taken before irradiation, after irradiation, and the resultant difference between the two spectra. A broad absorption band appears, with a $\lambda_{\max}$ at approximately 1700 nm. This band has been previously attributed to the solvated electron. When optical densities at 1300 and 1550 nm, (convenient points for measurement), are plotted vs. dose, it is noted that a plateau is reached at about 10^{20} ev gm⁻¹, (fig. 2). Figure 3 shows the 410 nm anion band of biphenyl,⁶ together with peak resolution. (Table I). The presence of a competitive electron captor reduces the intensity of this peak.

Previous results⁶ have shown that the yield of diphenyl anions plateaus at a concentration of about 0.15 mole % of diphenyl. Hence a constant value of 0.2 mole % diphenyl was chosen for competition studies.

Acetic acid, propionic acid and n-butyric acid failed to make suitable glassy solids. Even at low concentration they form polycrystalline systems which were unsuitable for spectrophotometric studies. Isobutyric acid could not be dissolved in sufficient concentration (or had too low an ability to absorb electrons) to be suitable for a competitive electron capture study with biphenyl. However, when the concentration of isobutyric acid was plotted versus the optical density of the solvated electron measured at 1550 nm, a straight line resulted. This is illustrated in Figure 4. In the same figure also is included the variation of O.D.₁₅₅₀ for heptafluorobutyric acid. When the concentration of the five-carbon monobasic carboxylic acids was plotted versus the reciprocal of the optical density of the biphenyl anion peak at 410 nm, the slopes of these

plots, and hence the relative capture cross-sections, were as follows: $\sigma_{3\text{MBA}}/\sigma_{2\text{MBA}}$ and $\sigma_{\text{NPA}} = 9.1/8.3/7.5$. These values are illustrated in Figure 5.

When two different doses are used to form solvated electrons, 7.6×10^{18} and 3.6×10^{18} ev gm^{-1} , the ratios of optical densities of the first spectrum to those of the second, at 50 nm intervals, are constant within experimental error. The mean value is 1.425, with a standard deviation of 0.135. The purpose of taking these data was to validate the assumption that the competition of isobutyric acid (and the corresponding fluoro-derivative) for solvated electrons could be measured at a wave-length different from that of maximum O.D. The reason for this procedure is that the absorbance of the solvents themselves in the region 1650-1800 nm was too great to record directly, since the optical density was greater than 2 in this region, even without irradiation. The slope for the plot of concentration of 4MHA versus $\frac{1}{\text{O.D.}_{410}}$ of ϕ_2 was 3.3.

Those of 4MPA and 6MHA were 1.5 and 1.8, respectively, although the scatter of points was greater than desirable. NOA proved to be extremely difficult to study. Its freezing point is 16°C ; its boiling point is 237.5°C ; and its vapor pressure at room temperature is lower than 0.01 mm of mercury. Hence it could not easily be added as a solid or as a vapor. Since it was extremely viscous, it was difficult to add small quantities of the substance as a liquid. The results with this sample were not considered trustworthy.

The "dark decay" spectra showed no noticeable change of structure of the solvated electron curve with time. Furthermore, no overall change in absorbance was noted at any of the following wave lengths: 1000, 1125, 1250, 1350, 1450, 1600, 1825, 1950, 2050 nm, with the possible exception of the longer wave lengths during the first run.

DISCUSSION

The lower molecular weight carboxylic acids failed to work as well in this particular type of study, most likely because of their high polarity. As the molecular weight increased, the fraction of the molecule bearing an organic characteristic also increased. Hence the acid was more compatible with the hydrocarbon solvent and would more easily form a glass. Branched-chain acids similarly seem to form organic glasses more easily than straight-chain isomers.

In the study of the behavior of isobutyric acid and heptafluorobutyric acid, linear relationships resulted between concentrations of solutes and the optical density of the solvated electron peak measured at 1550 nm. This is consistent with the assumption that the number of negative species formed by the acids is proportional to their electron capture cross-sections and their original concentrations. If electrons of only a restricted energy range are involved, it seems logical to conclude that the yield of negative species from the solutes and the yield of solvated electrons in the solvent system will add up to a constant value. This would result in a linear relationship of concentration of solute versus optical density at 1550 nm, with a negative slope.

After gamma irradiation at 77°K, the absorption spectrum of 3MP, 2-MP-1 is characterized by a maximum of ca. 1700 nm, due to the trapped electron, and a shoulder at 680 nm, which has been assigned to the radical cation (positive hole) of (2-MP-1)^{6,8}. Addition of solutes which yield anions by conventional chemical methods reduced the IR absorption of (e⁻) and the authentic anion spectra appeared. Optical bleaching led to a decrease in the solvated electron peak and an increase in anion absorption.

⁸ J.P. Guarino and W.H. Hamill, J. Am. Chem. Soc., 86, 777 (1964)

The fact that the negative slope of concentration of heptafluorobutyric acid vs. O.D.₁₅₅₀ is far greater than the corresponding slope of isobutyric acid indicates that the former is a far more efficient electron captor than the latter. This is to be expected from the electronegative nature of the halogen substituents.

The plateau of solvated electron production, reached at a dose of about 10^{20} ev gm⁻¹, (fig 2), indicates that beyond that point recombination of positive and negative species occurs, and a steady state is reached.

Gallivan and Hamill⁵ in their study of gamma-irradiation induced electrons in 3MP show that their data are consistent with a rapid first-order decay of trapped electrons, followed by a slower second-order decay. They postulate a competitive reaction of electrons between solute biphenyl, positive holes h⁺, and some trapping center of the matrix itself. This center is called a vacancy, and the solvent trapped electron is given the symbol v⁻. "There is no evident mechanism for the initial step to form v⁻, but the relaxation

of the matrix will presumably stabilize v- and prevent migration of e- to another vacancy." The early part of the decay is attributed to associated ion-pair recombination; the second part of the decay, to interactions between randomized ion pairs. If this hypothesis is correct, one would expect a change in the structure of the spectrum of the solvated electron with time.

Failure to find such a change, under conditions of the "dark decay" experiments, may be due to the fact that such a change might take place extremely rapidly, so that conventional spectral measurement techniques are deficient. Similarly, the apparent discrepancy between the results and those of Gallivan and Hamill⁵ may be due to the presence of alkene in our study, whereas they used 3MP only.

If the negative species formed by the absorption of an electron by a carboxylic acid molecule involves the carboxylate anion, it would have a group structure identical with that of a salt or the zwitterion of an amino acid. It would perhaps absorb in the ultraviolet region.* Although there is absorption in this region, after the acid has been subjected to gamma irradiation, there is no $\lambda_{\max}$. In addition, the solvent system itself has an increased uv absorption background, with no peak, upon irradiation.

Acknowledgment- We are indebted to Dr. John R. Morrey, of Battelle-Northwest, for his extensive assistance in the use of his computer program for collecting spectral data and performing various calculations on them.

*(Aqueous sodium acetate absorbs strongly in the uv, but there is no $\lambda_{\max}$ in the 200 - 300 nm region).

Note to NORCUS and AEC: Considerable experimental work on primary and secondary aliphatic amines has been done by the authors and was continuing while the present report was being completed. It was considered preferable to continue gathering data while the NORCUS appointment was still in progress, and prepare a supplemental report on the amines at a later date. Preliminary studies were also made on some amino acids and peptides, but solubility limitations in hydrocarbon matrices indicate that a more polar solvent system, v.g., methyltetrahydrofuran, would be more suitable for studies at liquid nitrogen temperature.

A paper on the carboxylic acids has been accepted for presentation at the National Meeting of the American Chemical Society in Washington, D.C., September 12 - 17, 1971, by E.P. Bertin.

Ernest P. Bertin
NORCUS Participant

Leland L. Burger
Research Coordinator

SOLUATED ELECTRONS VS DOSE

PEAK ANALYSIS OF BIPHENYL ANION

PEAK POS. ANG. PROB XO	PARAM. ESTIM.				NO.
	GAUSSIAN		LORENTZIAN		
	YO	WO	YO	WO	
4295.884 + - 1.460 CERT	0.010	38.448	0.026	74.555	6
4262.961 + - 2.007 CERT	0.003	31.245	0.009	60.588	6
4091.899 + - 0.383 CERT	0.198	54.210	0.515	105.119	14
3971.828 + - 1.933 CERT	0.106	88.310	0.277	171.243	10
3798.236 + - 0.416 CERT	0.024	35.363	0.063	68.572	8
3686.978 + - 4.928 IMPR	0.002	28.332	0.005	54.939	4
3612.053 + - 1.212 CERT	0.011	35.778	0.028	69.377	6

BIPHENYL ANION

GAUSSIAN SPECTRUM FOR TESTING SYSTEM
N FIT: 0 STAND. DEV. OF FIT? 1.511287E-02