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Electronic Spectra and Related Ionic Effects in Gamma-Irradiated Organic Glassy Solids

By W. H. Hamill, J. P. Guarino, M. R. Ronayne and J. A. Ward

Dept. of Chemistry and Radiation Laboratory, University of Notre Dame,
Notre Dame, Indiana

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Gamma irradiation at 77°K of organic glassy solids which contain solutes RX or M provide evidence for the formation of R and X^- by dissociative electron attachment, M^- by simple electron attachment and M^+ by charge exchange with appropriate components of the matrix. Benzyl chloride and naphthalene illustrate the two types of solute. Detection in all cases was based upon electronic absorption spectra. Failure to observe M^+ in ethanol and other polar media indicates efficient formation of such protonated species as ROH_2^+. Benzyl radicals were observed in glassed ethanol containing benzyl acetate following gamma irradiation and equivalent yields of acetic acid were found in the subsequently thawed samples. It appears that ionic processes may play a major role in radiation chemistry.

Electron attachment and solvation in gamma-irradiated organic glasses at 77°K has been demonstrated in spectrophotometric observation of trapped intermediates.[1, 2] Irradiation ejects electrons from the solvent and these appear to become thermalized and diffuse through the matrix until they are attached by the solvent or by solutes, or else they recombine with positive holes after encountering some 10^3 molecules. When naphthalene, biphenyl, tetracyanoethylene or other appropriate solutes are present, the characteristic anion spectra appear in the irradiated glasses. In the absence of solute, or at low concentration, the irradiation of 2-methyltetrahydrofuran (MTHF) or other polar glass gives rise to solvent colour centres which are susceptible to optical bleaching. At low concentrations of naphthalene in MTHF, disappearance of solvent colour centres by illumination in the solvent band following gamma irradiation is accompanied by enhanced absorption in the naphthalenide ion spectrum. Similar effects were observed for other solutes capable of forming identifiable anions. The solvent colour centres appear to be trapped or solvated electrons. Their behaviour upon photodetachment produces effects closely resembling those arising directly from the gamma irradiation which suggests that low energy electrons are immediately responsible for anions so produced.

Halogen-containing molecules RX are expected to react with slow electrons via dissociative attachment, viz.,

$$RX + e^- \rightarrow R + X^-. \tag{1}$$

Such processes are well known in mass spectrometry. They have appearance potentials near zero whenever the electron affinity of X exceeds the bond dissociation energy of R—X and reaction cross-sections are very small at electron energies much above threshold.[3] In glasses, both R and X^- can be seen only in very favourable cases. When the spectrum of neither product of reaction (1) is known or accessible, suppression of $C_{10}H_8^-$ ion formation from solute naphthalene by addition of RX provides indirect evidence of electron attachment and serves to measure relative cross-sections of attachment.[2]

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EXPERIMENTAL

Methods of solvent purification, outgassing, gamma irradiation and the measurement of absorption spectra have been reported previously.[1] For observations in the ultra-violet region, ultra-pure 1 × 1 cm silica cells were used. A Cary model 14-R recording spectrophotometer was used for spectral measurements. Solutes of the purest available grades were used; purity was verified by gas chromatography whenever possbile. Solutions were prepared at laboratory temperature, plunged into liquid nitrogen prior to gamma irradiation and maintained continuously at 77°K until spectrophotometric measurements had been completed. All samples for which results are given consistently appeared to be homogeneous but no further verification of homogeneity was attempted.

RESULTS

Irradiations of triphenylmethyl (Tr) chloride or benzyl (Bz) chloride in MTHF at 77°K produce the well-known absorption spectra of trityl [4] or benzyl [5] radicals. Irradiation of MTHF alone to a dose of $1\cdot1 \times 10^{18}$ eV/g produces an optical density (O.D.) of 0·65 at the 1200 mμ absorption maximum of solvated electrons. Irradiation of 0·1 mole % TrCl in MTHF produced the trityl radical bands at 330, 341 and 510 mμ together with the solvent band at 1200 mμ for which the O.D. was 0·22. The O.D. of the trityl radical band at 341 mμ was 2·32 following irradiation and it increased to O.D. = 2·76 when the solvated electrons were released by illumination in the 1200 mμ band. Similarly, the addition of 0·18 mole % BzCl to MTHF resulted in the appearance of benzyl radical bands at 309 and 320 mμ following irradiation. The O.D. was 0·62 at 320 mμ and 0·16 at 1200 mμ for a dose of $1\cdot6 \times 10^{18}$ eV/g. Bleaching the latter band increased the former to 0·71.

The effect upon yield of solvated electrons in MTHF by each of several solutes of the type BzX appears in table 1 where the yields of benzyl radicals produced directly upon irradiation, and also after subsequent photodetachment of solvated electrons, are both presented. The relative reaction efficiencies of these additives toward electrons are reflected both by the O.D. at 320 mμ for benzyl radicals and by the extent to which the O.D. at 1200 mμ for solvated electrons is depressed.

TABLE 1.—BENZYL RADICALS IN MTHF *

solute	mole %	$\text{O.D.}_{320\ \text{m}\bar{\mu}}$	$\text{O.D.}_{120\ \text{m}\bar{\mu}}$
benzyl chloride	0·18	1·24 (1·42) †	0·32
	0·88	1·86 (1·86)	0·00
benzyl acetate	0·15	0·43 (0·71)	1·37
benzyl alcohol	0·21	0·05 (0·22)	1·65
	16·4	1·52 (1·51)	0·00
toluene	0·19	0·00 (0·00)	1·77 ‡
	2·0	0·07 (0·07)	0·40 ‡
none			1·94

* dose = $3\cdot2 \times 10^{18}$ eV/g.

† value of O.D._{320} after removing all solvated electrons by illumination in the 1200 mμ band.

‡ this decrease arises from an observable new anionic species, presumably the molecular anion.

Benzyl chloride is the most efficient of these solutes and it was therefore studied further in MTHF. The yield curve for Bz from BzCl appears in fig. 1 together with yields of solvated electrons and the effect of bleaching. Since solvated electrons

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do not appear at solute concentrations which give the plateau for radicals, $G(\mathrm{Bz})$ may be tentatively identified with the limiting value $G(C_{10}H_8^-) = 2{\cdot}6$ from naphthalene in MTHF.[1] Since O.D.(Bz) = 1·09 at 320 mμ and $1{\cdot}6 \times 10^{18}$ eV/g, the corresponding extinction coefficient (ε) is $1{\cdot}8 \times 10^4$ l./mole cm. The results of similar calculations for other radical bands appear in table 2. These values all refer to sodium naphthalenide in MTHF at 77°K for which $\varepsilon(C_{10}H_8^-) = 3{\cdot}03 \times 10^4$ l./mole cm at 325 mμ and is thought to be reliable to within about 10 %. In addition, when 1·05 mole % CCl_4 competes for electrons with 0·88 mole % BzCl in MTHF, O.D.(Bz) is depressed from 0·93 to 0·30.

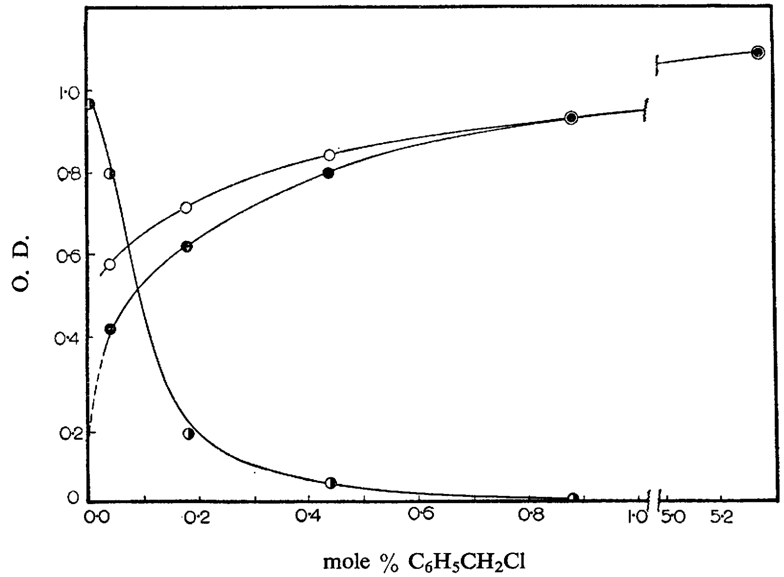

FIG. 1.—O.D. (benzyl) at 320 mμ against mole % benzyl chloride in MTHF at 77°K: ●, immediately after irradiation; and ○, after subsequent optical bleaching of solvated electrons; ◑, O.D. (solvated electrons) at 1200 mμ; the dose was $1{\cdot}6 \times 10^{18}$ eV/g.

It appears that the yield of available hydrogen atoms is very small in MTHF since it is an efficient reagent for them.[6] However, irradiations in an alkane matrix demonstrate effects attributed to hydrogen-atom reactions. In 3-methylpentane (3MP), yields of products due to reactions of hydrogen atoms with solute were determined by difference after adding 2-methylpentene-1 (2MP-1) as scavenger. The yields of trityl radicals from triphenylmethyl chloride in 3MP appear in table 3. Addition of 25 volume % 2MP-1 to 0·99 mole % TrCl decreased $G(\mathrm{Tr})$ from 1·04 to 0·90. If the difference is due only to hydrogen-atom reactions, then $G(\mathrm{H}) \simeq 0{\cdot}14$ in the alkane glass. Since this work is primarily concerned with electron mechanisms, most experiments in hydrocarbon media were performed in this alkane+alkene mixture. In order to supply additional evidence that trityl chloride and benzyl chloride were reacting predominantly with electrons even in hydrocarbons, each solute was used in competition with biphenyl in alkane+alkene glasses. The results appear in tables 4 and 5. Both $G(\mathrm{Tr})$ and $G(C_{12}H_{10}^-)$ can be measured and their sum is constant at *ca.* unity within experimental error. At 0·06 mole % BzCl in alkane+alkene glass (table 5), O.D.(Bz) = 0·15 at 320 mμ and 2×10^{18} eV/g when no biphenyl is present, corresponding to $G(\mathrm{Bz}) = 0{\cdot}36$. This band was too small

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for reliable measurement in glasses containing biphenyl and $G(C_{12}H_{10}^{-})$ alone was measured for runs with mixed solutes.

Irradiation of 2·0 % toluene in MTHF gave $G(Bz) = 0{\cdot}10$ through an apparently non-ionic mechanism, but it was not clear whether the reaction involved hydrogen

TABLE 2.—FREE RADICALS IN MTHF AT 77°K

radical	source	λ_{max}, mμ	$\varepsilon \times 10^{-3}$, l./mole cm
$(C_6H_5)_3C$	$(C_6H_5)_3CCl$	330	73
		341	41
		510	2·1
$C_6H_5CH_2$	$C_6H_5CH_2Cl$	307	5·7
		310	6·0
		320	18·0
		420	0·4
		438	0·3
		455	0·2
C_6H_5CHCl	$C_6H_5CHCl_2$	311	5·2
		314	5·0
		324	8·3
		420	0·3
		438	0·3
		455	0·4
$C_6H_5CCl_2$	$C_6H_5CCl_3$	299	9·5
		313	5·8
		325	5·0
		405	0·5
		423	0·5
		444	0·5
		458	1·0
$C_6H_5CHCH_3$	$C_6H_5CHBrCH_3$	313	2·4
		317	0·3
		323	12·0

TABLE 3.—YIELDS * OF TRIPHENYL METHYL RADICALS FROM $(C_6H_5)_3CCl$ IN 3MP AT 77°K

$(C_6H_5)_3CCl$, mole % × 10^2	O.D., 341 mμ	$G(Tr)$
1·5	0·25	0·22
2·9	0·57	0·51
3·6	0·63	0·57
6·4	1·22	1·10
9·9	1·16	1·04

* dose 1×10^{18} eV/g

TABLE 4.—COMPETITION FOR ELECTRONS BETWEEN $(C_6H_5)_3CCl$ AND $(C_6H_5)_2$ IN 75 % 3MP+25 % 2MP-1 *

$(C_6H_5)_3CCl$, mole % × 10^2	O.D., 341 mμ	$G(Tr)$	O.D., 410 mμ	$G(C_6H_5)^{-}$
0	0	0	0·76	1·02
0·8	0·10	0·09	0·68	0·91
3·2	0·42	0·38	0·54	0·72
6·4	0·53	0·48	0·36	0·48
8·1	0·53	0·48	0·27	0·36

* 0·11 mole % biphenyl throughout; dose $1{\cdot}08 \times 10^{18}$ eV/g

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TABLE 5.—COMPETITION FOR ELECTRONS BETWEEN $C_6H_5CH_2Cl$ AND $(C_6H_5)_2$ IN 75 % 3MP+25 % 2MP-1 *

$C_6H_5CH_2Cl$, mole % 10^2	O.D., 410 mμ	$G(C_6$
0	1·51	1·02
2·8	1·18	0·80
5·5	0·86	0·58
8·5	0·68	0·46
11	0·58	0·39

* 0·11 mole % biphenyl throughout; dose $2{\cdot}16 \times 10^{21}$ eV/g

atom abstraction or decomposition of toluene following electronic excitation. Toluene was therefore irradiated both in alkane and in alkane+alkene glasses. For 2 % toluene in 3MP, $G(\text{Bz}) = 0{\cdot}13$; for 8 % toluene in 3MP, $G(\text{Bz}) = 0{\cdot}19$. Irradiation of 2 % toluene in 80 % 3MP+20 % 2MP-1 gave $G(\text{Bz}) = 0{\cdot}00$. Irradiation of 1·1 mole % styrene in 3MP at $6{\cdot}48 \times 10^{18}$ eV/g gave O.D. = 0·05 at 323 mμ or $G(C_6H_5CHCH_2) = 0{\cdot}03$ (cf. table 2).

If energy transfer from solvent to solute contributes importantly to the yields of free radicals observed in this work it can be tested by using as solute an aromatic amine which photo-oxidizes by excitation to its first excited singlet state. N,N-dimethyl p-phenylene diamine (= NNDA) in MTHF at 77°K was illumined in a Pyrex cell using a high-pressure mercury lamp, producing the known bands of NNDA^+ at 576 and 515 mμ.[7] In a parallel gamma irradiation at 2×10^{18} eV/g no cation absorption was detected and $G(\text{NNDA}^+)$ must be less than 0·06. Similarly, efficient photo-oxidation occurs in ethanol, EPA and other polar glasses while no NNDA^+ can be detected following gamma irradiation in these media.

In hydrocarbon glasses, NNDA alone is not photo-oxidized. When a small concentration of alkyl halide or other electron acceptor is also present, an efficient photo-oxidation occurs. Parallel gamma irradiations do produce small yields of NNDA^+ in hydrocarbon glasses and yields are greatly enhanced when electro-acceptors are added.

Benzyl acetate had been demonstrated to be an efficient reagent for electrons.[2] Since the attachment process is now known to produce benzyl radicals, the other product of electron capture should be acetate ion by (2):

$$C_6H_5CH_2OAc + e^- \rightarrow C_6H_5CH_2 + OAc^-. \tag{2}$$

To test this hypothesis, benzyl acetate was chosen for supplementary chemical study. Solutions were irradiated in ethanol at 77°K, examined in the spectrophotometer, thawed and titrated for acetic acid.

Radiolysis of liquid solutions of benzyl acetate in benzene [8] gave carbon dioxide as a major product. This was assumed to result from prompt decomposition of the acetoxy radical following neutralization of acetate ion with benzene cation. In dilute ethanolic liquid or glassy solutions, however, no appreciable amount of carbon dioxide is produced ($G < 0{\cdot}05$) and the major product of decomposition is acetic acid. The results appear in fig. 2.

Attempts were made to observe the spectra of new radicals. Irradiation of 0·2 mole % chlorobenzene, bromobenzene, iodobenzene and 1-bromonaphthalene in MTHF to doses of 6×10^{18} eV/g showed, in each case, a greatly depressed yield of solvated electrons. No new absorption spectra were observed, however, above the absorption cut-offs of the parent compounds at *ca.* 300 mμ. Either the phenyl and 1-naphthyl radicals do not absorb in the accessible region or their extinction coefficients are not greater than *ca.* 100.

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Irradiation of 1·0 mole % allyl chloride in 3MP to a dose of $3{\cdot}2\times10^{18}$ eV/g gave a new structureless absorption band with a maximum at 228 mμ where its O.D. was 1·51, and its half-width ($\Delta\lambda_{\frac{1}{2}}$) was 18 m$\mu$. Since MTHF was not useful in this spectral region to test for reaction with electrons, another approach was used. Allyl bromide and allyl alcohol were also irradiated in 3MP and the 228 mμ band was observed in both cases. If this is the allyl radical and if its yield equals the limiting $G(C_{10}H_8^-) = 1{\cdot}1$ from earlier work in the same medium, then ε (allyl) = $3{\cdot}8\times10^4$ at 228 mμ. The irradiation of 3-chlorobutene-1 and 3-chlorocyclohexene in 3MP gave bands similar to that from allyl chloride. Thus for the 3-butene-1-yl radical, $\lambda_{\max} = 246$ mμ, $\Delta\lambda_{\frac{1}{2}} = 20$ mμ, and for the 3-cyclohexenyl radical, $\lambda_{\max} = 253$ mμ, $\Delta\lambda_{\frac{1}{2}} \simeq 20$ mμ.

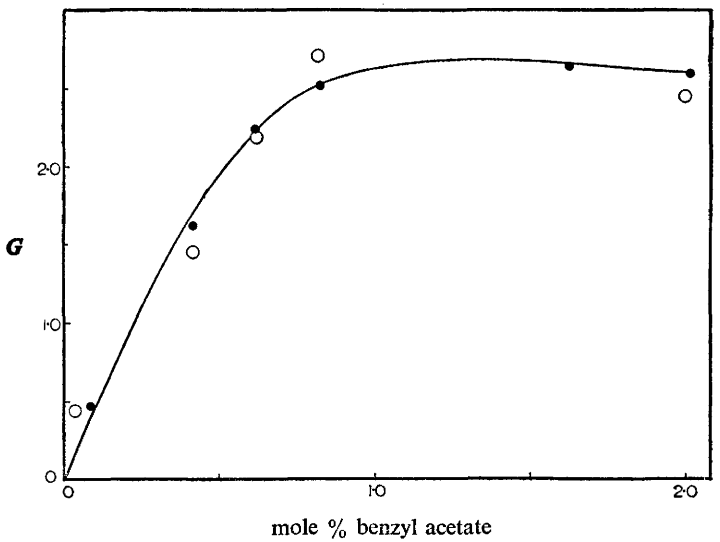

FIG. 2.—●, G(benzyl) against mole % benzyl acetate in ethanol at 77°K and $3{\cdot}2\times10^{18}$ eV/g; ○, G(acid) against mole % benzyl acetate in ethanol at 77°K and $0{\cdot}78\text{-}1{\cdot}30\times10^{20}$ eV/g after thawing.

In several other cases, radicals due to hydrogen-atom addition into aromatic rings could be assigned by verifying that yields were much smaller in MTHF than in 3MP and that addition of 2MP-1 to 3MP glasses prevented the appearance of these absorption bands. Such bands were observed for benzene, toluene, and biphenyl in 3MP, and these are listed in table 6. Half-widths given are approximate and were obtained, as were the optical densities, by reference to adjacent absorption minima.

DISCUSSION

The results presented here, supported by earlier work,[1, 2] provide evidence in support of the hypotheses that ionizing radiation expels electrons from molecules in condensed media, that these electrons are moderated to nearly thermal energy and migrate by diffusion, and that they produce chemical effects by dissociative attachment with significant yields.

The decreased O.D. of solvated electrons in MTHF caused by addition of various benzyl derivatives (table 1) suggests that these solutes react with electrons and the

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appearance of identifiable benzyl radical absorption indicates that dissociative attachment is involved. This conclusion is supported by the similarity of the yield against solute concentration curves in fig. 1 and 2 with earlier results involving formation of the identifiable naphthalenide and biphenylide ions.[1, 2] The previous identification of solvent colour centres as solvated or otherwise trapped electrons now serves to demonstrate by their photodetachment that these electrons can react with benzyl chloride (fig. 1) and other benzyl compounds (table 1) to generate benzyl radicals. The large depression in radical yield in glasses containing carbon tetrachloride, which is an efficient reagent for electrons,[2] supports the view that most radicals form by this process. One does not expect benzyl radicals from toluene by this mechanism, and they do not appear when H-abstraction is prevented. The suppression of the 1200 mμ band in MTHF by toluene relates to another phenomenon which is also produced by benzene, styrene and many olefins, viz., appearance of a new colour centre. The formation of molecular anions $C_6H_5CH_3^-$, etc., appears to be responsible.

TABLE 6.—ABSORPTION MAXIMA ATTRIBUTED TO HYDROGEN-ATOM ADDITION TO AROMATICS IN 3-MP *

radical	source	λ_{max}, mμ	$\Delta\lambda_{1/2}$†	O.D.
C_6H_7	2 % C_6H_6	311·0	3	0·09
		316·5	7	0·19
$C_6H_6CH_3$	8 % $C_6H_5CH_3$	323·5	5	0·14
		329·5	3	0·04
$C_6C_5C_6H_6$	0·07 % $(C_6H_5)_2$	365	5	0·53
		380	6	0·57
		390	10	0·68
		710	70	0·38
$C_{10}H_9$	0·19 % $C_{10}H_8$	375	60	0·46
		580	35	0·05
		640	30	0·16
		710	25	0·37

* dose $6{\cdot}5 \times 10^{18}$ eV/g † band half-width.

For benzyl chloride and acetate the electron affinity (E.A.) exceeds the bond dissociation energy (*D*) and O.D.(Bz) is large at small concentrations of solute. Benzyl alcohol is much less efficient while *D* exceeds E.A. and dipolar solvation energy would be required to produce OH^-.

Yields of radicals are appreciably lower in hydrocarbon glasses than in polar glasses and this is also true for molecular anion yields in the two systems. It is not expected that $G(e^-)$ would differ by as great an amount for the two types of media. In part, the difference may be related to stabilization of the positive solvent ion in polar media ; this is demonstrated by failure to observe various solute cations in MTHF which do appear in 3MP, where the mechanism appears to be positive charge migration from solvent to solute (see below) ; this positive charge migration in turn must favour ion-pair recombination which may compete with electron attachment. In part, if RX^- molecular ions are unstable with respect to ionization, then the cage effect would hinder dissociation to R and X^- in low dielectric media and cause inefficient attachment. In polar media, however, solvation energy is greater the smaller the ion radius and solvolytic dissociation is favoured.

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When two solutes are present the results in tables 4 and 5 suggest that, when the small yield due to hydrogen-atom abstraction is eliminated, competition for electrons can account for radical yields. The suppression of benzyl radical formation from toluene by 2MP-1 demonstrates that when both ionic and hydrogen atom processes are eliminated, formation and decomposition of electronically-excited toluene by energy transfer in the glass is a very inefficient mechanism for producing radicals. Similarly, in alkane + alkene glasses, the yield of trityl radicals from triphenyl methane was too small to detect. As a further example, since efficient photo-ionization of NNDA was demonstrated in MTHF and other polar media, both positive charge exchange and energy transfer to NNDA might be expected to produce $NNDA^+$ by ionizing radiation. In fact, $NNDA^+$ is observed in hydrocarbon glasses following gamma irradiation but is not observed at all in rigid polar solvents which are required for photo-ionization and neither of the mechanisms mentioned is operative. Similar results have been obtained for cation formation from simple olefins and aromatic hydrocarbons upon gamma irradiation. It may be concluded that positive charge exchange from solvent to solute occurs in hydrocarbons, but not in several polar media.[9]

H_2O^+ is quickly converted to H_3O^+ in aqueous systems, and water, alcohols, ethers, amines and some other dipolar molecules undergo corresponding reactions in the mass spectrometer.[10] It is expected that these protolytic reactions will be of general occurrence in the corresponding irradiated liquids. Since the potential energy of a protonated MH^+ is always much less than that of M^+, positive charge exchange from solvent to solute in these polar media will be impossible for ordinary molecules M and N, even when the ionization potentials are in the sense $I(M) > I(N)$.

The correlation between $G(Bz)$ for benzyl acetate in glassed ethanol and $G(HOAc)$ in the corresponding thawed samples (fig. 2) demonstrates the relevance of ionic processes in rigid media to the nature and magnitude of the ultimate chemical effects. Other parallel runs at *ca.* 20°C, not reported here, give values of $G(HOAc)$ varying similarly with concentration of benzyl acetate but uniformly some 70 % higher at corresponding concentrations. In both series of runs, the formation of acetic acid and the absence of carbon dioxide strongly suggests dissociative electron attachment to give OAc^- and indicates the substantial absence of acetoxy radicals which decompose rapidly under normal conditions. The results are understandable in terms of ion recombination between $CH_3CH_2OH_2^+$ and OAc^-.

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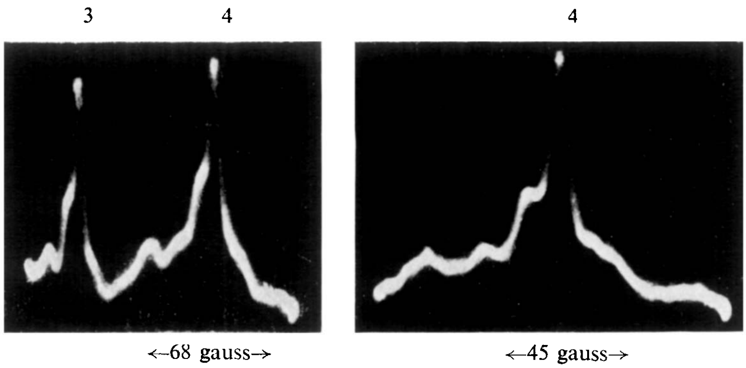

FIG. 1.—Section of paramagnetic resonance spectrum of 10^{-5} Mc in cubic ZnS.

[*To face page* 176.