The Radiation Chemistry of Benzyl Acetate at −196 and 20° in Polar Solvents[1]

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The γ-radiolysis of benzyl acetate at $\gtrsim 2$ mole % in ethanol gives $G(CH_3CO_2H)$ = 4.6 at 20° and 2.5 at −196°. In methyltetrahydrofuran the corresponding yields were 2.9 and 1.9. Yields of benzyl radical at −196° were equivalent to acid. Comparable yields of acid were obtained at ~2% benzyl acetate in acetone and in acetonitrile at 20°. In all these solutions CO_2 was a minor product. In hydrocarbon solvents, CO_2 was a major product and no acid was produced. The results are consistent with dissociative electron attachment as a primary process to give benzyl radical and acetate ion. In polar media combination of acetate ion with the protonated solvent, via the molecular cation, accounts for acetic acid by proton transfer. In nonpolar media it appears that charge recombination proceeds by field emission from acetate ion, followed by prompt decomposition of the acetoxy radical.

Introduction

Indirect evidence from chemical effects in γ-irradiated organic systems is consistent with the assumption of ionic mechanisms.[2,3] Since the development of techniques for demonstrating trapped or solvated electrons, anions, and cations in various γ-irradiated organic glassy solids,[4-6] greater weight can be attached to some of the proposed ionic mechanisms. Thus, dissociative electron attachment appears to be an efficient process and usually leads to simple, predictable

$$RX + e^- \longrightarrow R + X^-$$

chemical effects, e.g., formation of acid HX. A good correlation has been demonstrated between the yield of benzyl free radicals in γ-irradiated ethanol glass containing benzyl acetate and the yield of acetic acid from the thawed sample.[7]

Benzyl acetate is a particularly suitable test substance. The benzyl radical has a well-defined optical absorption band with large extinction coefficient (ϵ = 1.8 × 10^4 1. mole^{-1} cm.$^{-1}$ at λ_{max} 320 mμ)[7] and the electron affinity of the acetoxy radical, about 3.2 e.v.,[8] exceeds the bond-dissociation energy. The acetate ion can

form either acetic acid[7] or methane and carbon dioxide[2] following ion recombination, depending upon the environment. The acetoxy radical is extremely unstable, the lifetime under usual conditions being about 10^{-10} sec.,[9] and therefore $G(CO_2)$ provides a reliable measure of primary $G(CH_3CO_2^-)$. In protolytic media the chemistry of $CH_3CO_2^-$ is predictable.

This work extends the previous investigations of the radiolysis of benzyl acetate[2,7] by examining ionic, free-radical, and molecular products, both in polar and nonpolar solvents, in solutions at laboratory temperature, and also at −196° in the glassy state.

Experimental

Materials. Materials of the highest commercially available purity were used in all cases. Saturated hydrocarbons were passed through a 6-ft. silica gel column and tetrahydro-2-methylfuran (MTHF) was passed through a 3-ft. alumina column prior to use. All other materials were used as received. Purity was checked by vapor phase chromatography.

Cells. Square Pyrex cells were used for spectrophotometric analysis. Cylindrical Pyrex cells were used for chemical runs and cylindrical Vycor cells for photolysis.

Sample Preparation. Liquids were measured volumetrically; 5-ml. samples were used for runs at −196°. For all other runs 10-ml. samples were used at ambient temperature approximating 20°. Nitrous oxide was measured from *PVT*, but it was difficult to determine the amount actually in solution and results were not reproducible.

When gaseous product was to be recovered for analysis, the irradiated sample was refluxed on the vacuum line, and gas accumulated at the head of the column was removed intermittently.[2] The preliminary outgassing of the unirradiated sample was conducted similarly. For all other runs conventional freeze–pump–thaw evacuation was used.

γ-Irradiation, dosimetry, and photolysis followed methods already described.[2] Gaseous products were analysed by mass spectrometry and liquid products by v.p.c. with a flame ionization detector. Measurements of optical absorption, using a Cary Model 14R spectrophotometer, have been described.[6]

Results

The limiting 100-e.v. yield of acetic acid was 4.6 at $\gtrsim$ 1.5 mole% benzyl acetate in ethanol at 20°, nearly twice as great as the yield for a corresponding run at −196° and much larger than $G(CO_2)$ in benzene[2] and cyclohexane[10] at 20°. Most of the measurements

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(2) W. Van Dusen, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 3648 (1962).

(3) J. R. Nash and W. H. Hamill, *J. Phys. Chem.*, **66**, 1097 (1962).

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

(5) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962); M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

(6) J. P. Guarino and W. H. Hamill, *ibid.*, **86**, 777 (1964).

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

(8) S. Tsuda and W. H. Hamill, "Advances in Mass Spectrometry," Pergamon Press, Inc., New York, N. Y., 1965.

(9) T. C. Vogt, Jr., and W. H. Hamill, *J. Phys. Chem.*, **67**, 292 (1963).

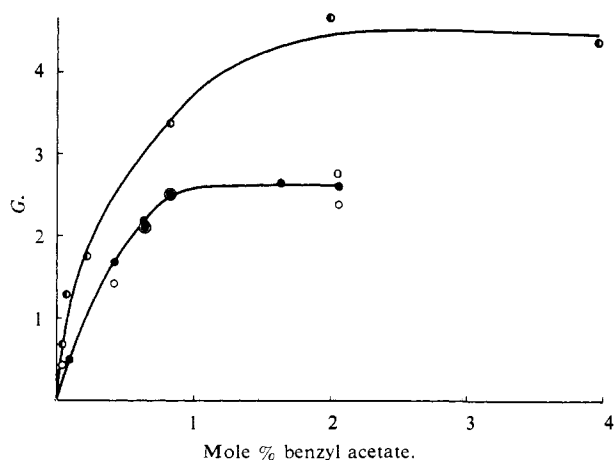(10) L. J. Forrestal and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 1535 (1961).

Figure 1. γ-Radiolysis of benzyl acetate in ethanol: ●, $G(C_6H_5-CH_2)$ at $-196°$; O, G(acid) for samples irradiated at $-196°$ and thawed; ◐, G(acid) for samples irradiated at $20°$.

Figure 2. γ-Radiolysis of benzyl acetate in methyltetrahydrofuran: ●, $G(C_6H_5CH_2)$ at $-196°$; O, G(acid) for samples irradiated at $-196°$ and thawed; ◐, G(acid) for samples irradiated at $20°$.

at $-196°$, included for comparison, were published recently.[7] The qualitative dependence of $G(CH_3-CO_2H)$ on solute concentration, shown in Figure 1, is approximately the same at these two temperatures.

Parallel experiments with benzyl acetate in MTHF at -196 and $20°$ gave results which resembled those in ethanol, as shown in Figure 2. All samples at $-196°$ were exposed to tungsten light for 15 min. prior to thawing in order to remove what we consider to be trapped electrons. In each system the values of $G(C_6H_5CH_2)$ at $-196°$ are based upon an extinction coefficient $\epsilon = 1.8 \times 10^4$ l. mole^{-1} cm.$^{-1}$ established using benzyl chloride in MTHF and assuming that the limiting yield of benzyl radical (by dissociative electron attachment) was equal to the corresponding limiting yield of naphthalenide ion when naphthalene was the only solute. This somewhat arbitrary assumption receives support from the correspondence between $G(C_6H_5CH_2)$ so determined and $G(CH_3CO_2H)$ from the thawed glasses in both series of measurements. If we accept instead the value $\epsilon = 1.1 \times 10^3$ l. mole^{-1} cm.$^{-1}$ from the work of Land and Porter,[11] our limiting values of $G(C_6H_5CH_2)$ would be unacceptably large in both systems.

The near-infrared band (λ_{max} 1300 mμ) in γ-irradiated MTHF has been attributed to trapped electrons.[4] They can be photodetached and, when small concentrations of naphthalene or biphenyl were present, the yield of naphthalenide or biphenylide ions was correspondingly increased. At sufficiently high solute concentration, no 1300-mμ band appeared.[5] Added benzyl acetate similarly decreased the 1300-mμ band and optical bleaching of the residual band enhanced the 320-mμ absorption of the benzyl radical.

It has been observed that the 540-mμ band in γ-irradiated alcohol, attributed to trapped electrons, was decreased by added biphenyl, but that optical bleaching of this band did not enhance the yield of biphenylide ion.[5] A completely parallel effect was found with added benzyl acetate, which depressed the 540-mμ band, with appearance of benzyl radical absorption, but bleaching the residual 540-mμ absorption did not enhance the yield of benzyl radicals.

(11) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963).

The identified products from irradiated solutions of benzyl acetate in ethanol at $20°$ which contained the benzyl moiety were ethylbenzene and benzyl ethyl ether (Table I). The failure of added iodine to diminish these yields shows that the products did not arise from combination of free radicals in the stationary state.

Table I. Radiolysis of Benzyl Acetate-Ethanol[a]

Mole % benzyl acetate	G(ethyl-benzene)	G(benzyl ethyl ether)
100	0.50	0.00
100[b]	0.55	0.00
95.3	0.45	0.10
89.2	0.39	0.25
89.2[c]	. . .	0.15
80.5	0.37	0.33
80.5[c]	. . .	0.39
80.5[d]	0.37	0.50
67.3	0.23	0.55
67.3[c]	. . .	0.45
67.3[e]	0.34	0.65
29.2	0.04	0.71
29.2[c]	. . .	0.68
24.7	0.00	0.68
19.1	0.00	0.68
7.64	0.00	0.53
3.97	0.00	0.44
3.9[f]	0.00	2.35

[a] Dose = 20 × 10^{18} e.v./ml. [b] 0.02 M I$_2$. [c] Air-saturated. [d] 0.003 M I$_2$. [e] 0.005 M I$_2$. [f] 0.03 M I$_2$.

Yields of CO_2, CH_4, and H_2 from benzyl acetate at $20°$ in various solvents appear in Table II. Difficulties in outgassing benzyl acetate, noted previously,[2] may be responsible for some of the scatter in $G(CO_2)$. It is clear, nevertheless, that $G(CO_2)$ was much smaller for dilute solutions of benzyl acetate in polar solvents than it was in solutions of benzene[2] or cyclohexane.[10] Moreover, the results in Table III show that in media where $G(CO_2)$ was large, G(acid) was small. Results from solutions containing benzene and olefin show that H-atom reduction of the ester was not responsible for acid formation.

When 2.1 mole % benzyl acetate in ethanol was photolyzed at $20°$ using the 2537-Å. mercury line, the quantum yields of products were: $\Phi(CO_2) = 0.09$,

Table II. Radiolysis of Benzyl Acetate in Polar Solvents at Room Temperature[a]

Solvent	Mole % benzyl acetate	$G(CO_2)$	$G(CH_4)$	$G(H_2)$
Acetone	0.00	0.00	2.62	0.88
	1.02	0.07	1.20	0.50
	2.52	0.67	1.20	0.54
	5.42	0.20	0.91	0.32
	34.0	0.62	0.79	0.13
	82.3	0.49	0.56	0.10
	99.1	1.79	1.21	0.09
	100.	3.21	1.71	...
Methanol	1.35	0.31	0.35	1.91
Ethanol[b]	2.05	0.05	0.15	1.92
	29.2	0.47	0.26	0.37
	80.5	1.32	0.67	0.11
MTHF	3.19	0.45	0.18	1.72
	6.19	0.28	0.25	1.34
	86.8	0.66	0.49	0.05
	90.5	1.37	0.85	0.07

[a] Dose approximately 6×10^{18} e.v./ml. [b] Photolysis of 2.05% benzyl acetate in ethanol gave the following quantum yields: CO_2, 0.09; CH_4, 0.06; $C_6H_5C_2H_5$, 0.025; $C_6H_5CH_2OC_2H_5$, 0.025; CH_3COOH, 0.026.

Table III. Miscellaneous Experiments with Benzyl Acetate

Solvent	Mole % benzyl acetate	$G(acid)$
Benzene	5.9	0.0
Acetone	2.5	1.50
Acetonitrile	1.8	2.26
Ethanol (13.6%) Benzene (86.8%)	5.6	3.50
2-Methylpentene-1 (2.72%) in ethanol	2.0	3.50

$\Phi(CH_4) = 0.06$; $\Phi(C_6H_5C_2H_5) = 0.025$; $\Phi(acid) = 0.026$; $\Phi(C_6H_5CH_2OC_2H_5) = 0.025$.

Additives which react effectively with electrons would be expected to reduce yields of benzyl radical and of acetic acid. Two series of runs at $-196°$ in ethanol, using either 1.6 or 0.8 mole % benzyl acetate and various concentrations of nitrous oxide, gave rather erratic results for $G(C_6H_5CH_2)$ and $G(acid)$. The irreproducibility is presumably caused by the failure to retain nitrous oxide in solution during glassing. Qualitatively it was clear that increasing concentrations of nitrous oxide decreased both products. At both concentrations of benzyl acetate, $G(C_6H_5CH_2)$ was decreased from *ca.* 2.6 to 1.5 by 0.9% N_2O. The results for $G(acid)$, measured only in the series with 0.8% benzyl acetate, were comparable.

There is evidence that methyl iodide is an effective reagent for electrons in γ-irradiated systems[5,10] and that two solutes compete for electrons in proportion to their respective concentrations.[12] The effect of methyl iodide on $G(C_6H_5CH_2)$ at $-196°$ in ethanol appears in Figure 3.

Discussion

The formation of benzyl radicals at $-196°$ and acetic acid at -196 and $20°$ as major products from

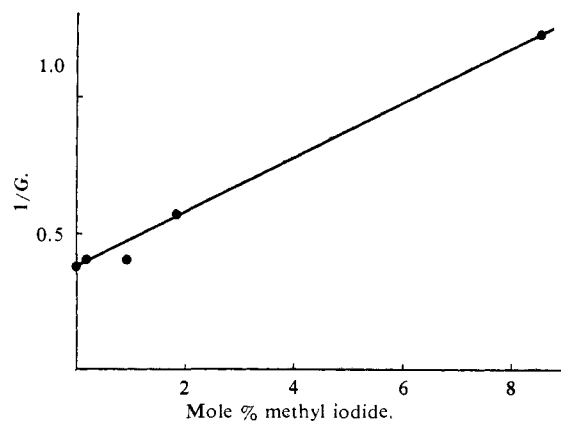(12) E. P. Bertin and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1301 (1964).

Figure 3. γ-Radiolysis of 1.6 mole % benzyl acetate in ethanol at $-196°$; $1/G(C_6H_5CH_2)$ *vs.* mole % methyl iodide.

the radiolysis of benzyl acetate in ethanol and in methyltetrahydrofuran is to be compared with the results in benzene[2] and cyclohexane[10] at $20°$ for which carbon dioxide and methane, but no acetic acid, were found. Benzyl radicals have also been observed when benzyl acetate was γ-irradiated in 3-methylpentane at $-196°$; carbon dioxide and methane, but no acetic acid, were recovered in good yield after thawing the sample.[13] A possible mechanism for the formation of acetic acid is

$$CH_3CO_2CH_2C_6H_5 + H \longrightarrow C_6H_5CH_2 + CH_3CO_2H \quad (1)$$
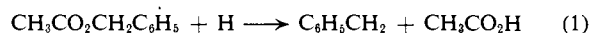
but it would require a larger yield of acetic acid in cyclohexane than in ethanol or methyltetrahydrofuran, both of which are rather reactive toward H atoms. This was not observed. Also, it is inconsistent with the large $G(acid)$ from benzyl acetate in ethanol with added olefin, and similarly in benzene–ethanol (Table III). Finally, in very dilute solutions of benzyl acetate in ethanol, one observes a solvated electron band which is removed by optical bleaching. Unlike optical bleaching of the electron band in other glasses, the electrons are not released.[5] Rather, it appears that H atoms are produced.[14] Under these conditions we found no enhanced benzyl radical absorption, which would be expected if reaction 1 occurred.

Another mechanism to be considered is homolytic dissociation of excited benzyl acetate

$$CH_3CO_2CH_2C_6H_5^* \longrightarrow C_6H_5CH_2 + CH_3CO_2 \quad (2a)$$

followed by H abstraction

$$CH_3CO_2 + RH \longrightarrow CH_3CO_2H + R \quad (2b)$$

This mechanism is completely inconsistent with the evidence that CH_3CO_2 is highly unstable.[9] Also, it does not account for the failure to find acid when hydrocarbon solvents were used.

The heterolytic mechanism

$$CH_3CO_2CH_2C_6H_5^* \longrightarrow C_6H_5CH_2^+ + CH_3CO_2^- \quad (3)$$
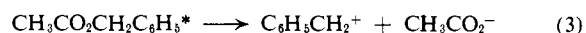
would account for effects of polar solvents, but it does not account for the large yields of benzyl radicals in both polar and nonpolar glasses. In fact, one cannot easily imagine the ion pair separating sufficiently to persist in the dense glassy state. Also, the yield of benzyl ethyl ether, which is the expected carbonium

(13) J. B. Gallivan and W. H. Hamill, unpublished results.
(14) J. A. Ward, Ph.D. Dissertation, University of Notre Dame, 1964.

ion product in ethanol, is only 10% as great as the yield of acetic acid in dilute solutions. The large enhancement of the ether yield with added iodine can be attributed to solvolysis of benzyl iodide.

The photolysis in ethanol may involve both a homolytic and a heterolytic process. Ethylbenzene could result from combination of $C_6H_5CH_2$ and CH_3 following prompt decomposition of geminate CH_3CO_2.[15] This proposal is supported by the relative values $\Phi(CO_2)$ = 0.09 and $\Phi(C_6H_5C_2H_5)$ = 0.025. The efficiency of the cage recombination yielding ethylbenzene per event is given by 0.025/0.09 which is roughly the anticipated value, judging by several earlier studies of geminate combinations.[16] (Ethylbenzene cannot be detected at small concentrations of benzyl acetate from the radiolysis of ethanol, as shown in Table I.) Ethyl benzyl ether was found and it is the expected product of the carbonium ion in ethanol. Similar results from photolysis of homologous esters have been reported recently.[17] Since we find almost exclusively carbon dioxide (and methane) or acid as radiolytic products at small concentrations of benzyl acetate in different solvents, and no ethylbenzene, the first excited singlet state of benzyl acetate is not appreciably involved in the radiolysis.
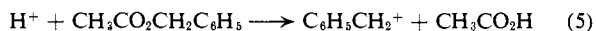
Acetic acid might be considered to arise from a protolytic process since molecular cations of polar molecules readily protonate[18]

$$H^+ + CH_3CO_2CH_2C_6H_5 \longrightarrow C_6H_5CH_2^- + CH_3CO_2H$$
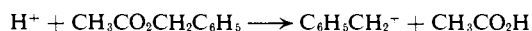
but again the mechanism does not provide a benzyl radical while it requires equivalent yields of acid and benzyl ethyl ether. Conversion of the primary molecular cation in a polar solvent to the protonated species, e.g.

$$C_2H_5OH^+ + C_2H_5OH \longrightarrow C_2H_5OH_2^+ + C_2H_4OH \quad (4)$$
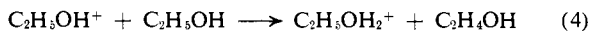
followed by protolysis of benzyl acetate

$$H^+ + CH_3CO_2CH_2C_6H_5 \longrightarrow C_6H_5CH_2^+ + CH_3CO_2H \quad (5)$$

is also to be considered for the formation of acetic acid. Aliphatic alcohols, nitriles, ethers, and ketones undergo protonation reactions in the mass spectrometer with remarkably large cross sections.[18] Reaction 4 probably occurs in condensed phases as well since small additions of polar solvents to hydrocarbons strongly inhibit positive charge migration to cation-forming solutes in rigid media.[6] On the other hand, reaction 5 cannot be an important mechanism for the production of acetic acid at $-196°$. It encounters the same objections as reaction 3 since it would provide no yield of benzyl radical and too great a yield of benzyl ethyl ether.

The efficiency of reaction between benzyl acetate and electrons in various rigid organic media has been demonstrated both by suppression of the optical absorption band of trapped electrons in polar and nonpolar rigid media and by suppression of naphthalenide and biphenylide ion formation.[4] It also exhibits dis-

(15) A completely analogous cage effect has been observed for the thermal decomposition of acetyl peroxide where formation of methyl acetate can be attributed to primary decomposition into two acetoxy radicals. One decomposes to CH_3 and CO_2; the other undergoes geminate reaction with CH_3 (cf. ref. 9).

(16) References to this work are given in ref. 9.

(17) H. E. Zimmerman and V. R. Sandel, J. Am. Chem. Soc., 85, 915 (1963).

(18) T. F. Moran and W. H. Hamill, J. Chem. Phys., 39, 1413 (1963).
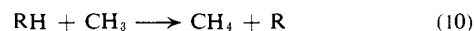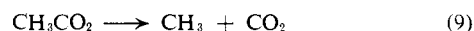
sociative electron attachment at ~0 e.v. in the mass spectrometer. The primary process leading to carbon dioxide and methane in hydrocarbon media and to acetic acid in polar media therefore is considered to be, properly speaking, an electrolysis

$$CH_3CO_2CH_2C_6H_5 + e \longrightarrow CH_3CO_2^- + C_6H_5CH_2 \quad (6)$$
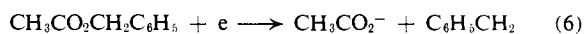
This reaction also accounts for equivalent yields at $-196°$ of benzyl radicals[19] and of acetic acid for polar solvents. If we also postulate that almost all cations are protonated, then the reaction products are well known to be given by

$$C_2H_5OH_2^+ + CH_3CO_2^- \longrightarrow C_2H_5OH + CH_3CO_2H \quad (7)$$
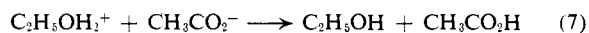
The mechanism for converting $CH_3CO_2^-$ to CH_3 and CO_2 in hydrocarbon solvents is less evident. Since the evidence for the formation of acetate ion is strong, it must be concluded that it undergoes simple electron transfer to the cation, followed by normal, rapid decomposition of the acetoxy radical

$$RH^+ + CH_3CO_2^- \longrightarrow RH^* + CH_3CO_2 \quad (8)$$

$$CH_3CO_2 \longrightarrow CH_3 + CO_2 \quad (9)$$

$$RH + CH_3 \longrightarrow CH_4 + R \quad (10)$$

The proton affinity of the acetate ion is certainly sufficient to abstract a proton from the high-potential ion RH^+ and it must therefore be supposed that the electron is lost by field emission to the cation in low dielectric media. For $C_6H_6^+$, reaction 8 is 6.0 e.v. exothermic in the attenuated gas. If the combined solvation energy and Franck–Condon effects dissipate >6 e.v., which is quite possible in polar solvents, electron transfer becomes impossible and only proton transfer can occur.

If reactions 5–10 are accepted we must next consider how to account for the effects of temperature and solvent upon $G(CO_2)$ or $G(acid)$. The large ratio of $G(acid, 20°)$ to $G(acid, -196°)$ of Figures 1 and 2 is qualitatively to be expected on the basis of a cage effect for electron attachment. That is

$$RX + e \underset{k''}{\overset{k'}{\rightleftarrows}} RX^{*-} \overset{k'''}{\longrightarrow} R + X^- \quad (11)$$
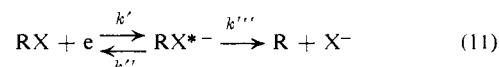
There is only one example of two-body electron attachment in mass spectrometry, viz., SF_6^-, and comparatively few molecular anions (e.g., NO_2^-) can be formed even indirectly. One concludes that many, and possibly most, molecular anions can exist only in repulsive states, or are inaccessible by vertical transitions. It is therefore very improbable that the nascent molecular anion RX^{*-} survives in the dense glass when it is constrained to a configuration approximating that of the neutral molecule. When the RX molecule is favorably situated in the medium with some accessible free volume, electron attachment can produce $R-X^-$ displacement, thereby lowering the energy of the anion and trapping the electron. This should be the dominant effect in nonpolar media. In a polar solvent the electrolytic process is promoted by the greater solvation energy of the small ion X^- relative to RX^-, but it requires relaxation of the solvent dipoles.

(19) At $-196°$ the optical absorption of the benzyl radical has been firmly established by comparison with a series of measurements in both polar and nonpolar media using ten solutes of the type $C_6H_5CH_2X$. In all instances $G(C_6H_5CH_2)$ was large when the electron affinity of X exceeded the bond-dissociation energy of $C_6H_5CH_2$-X (see ref. 13).

Both the cage effect and relaxation would be more unfavorable at $-196°$ than at $20°$, with correspondingly lower yields. Also, these considerations are consistent with larger yields of electrolytic products in polar than in nonpolar media. For benzyl acetate at $20°$ in hydrocarbons, the plateau value of $G(CO_2)$ was ca.

2 in contrast to $G(acid)$ between 3 and 4 in polar solvents. The limiting yields in hydrocarbons were only attained at concentrations of benzyl acetate five- to tenfold greater than were required in polar solvents. This suggests that k''/k''' is greater in nonpolar than in polar media, provided k' is the same for both.

Cation and Solvent Effects on the Ultraviolet Spectra of Alkali Salts of Phenols and Enols

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Contribution from the Organic Chemistry Department, Research Division, Abbott Laboratories, North Chicago, Illinois. Received November 5, 1964

The long wave length maxima of the alkali metal salts of 26 phenols and enols have been measured in two aprotic solvents, 1,2-dimethoxyethane (DME) and dimethylformamide (DMF). Corresponding measurements in water and ethanol have been made or previously reported for salts of 15 of the compounds. Even at concentrations of 10^{-4} to 10^{-5} M, all of the salts in DME and many of them in DMF are associated. In the associated salts, observed bathochromic shifts are proportional to the inverse of the cationic radii, showing the absence of appreciable covalency interactions with the alkali metals. Bathochromic shifts resulting from increased polarity of the aprotic medium (DME to DMF) are produced mainly, if not entirely, by a lengthening or cleavage of the electrostatic bond of the ion pair, rather than by direct solvation of the anion. The "tightness" of ion pairs varies in an accountable manner with variation in the structure of the anion. Hypsochromic shifts observed in going from DMF to water for many of the salts are shown to be roughly proportional to the basicities of the respective anions. The only exceptions are salts of those β-dicarbonyl compounds capable of forming U-shaped anions, presumably with enhanced chelating abilities. It is concluded that most acyclic β-dicarbonyl compounds preferentially assume a U-shape on salt formation, and remain in some form of association with their counterions, even in aqueous solution.

Introduction

A previous report[1] described the marked acceleration by certain additives of the rate of alkylation of the sodium derivative of diethyl *n*-butylmalonate with *n*-butyl halides in benzene solution. Results indicated that this effect is produced by a specific solvation of the cation acting to dissociate the large ion-pair aggregate (mol. wt. $> 10,000$) of the sodio derivative known to exist in benzene solution. Extensive comparisons indicated this action to be directly related to the ability of the additive to localize electron density on both sides of a molecular plane, either by a π-orbital mechanism as in dimethylformamide (DMF) or by a lone-pair mechanism as in 1,2-dimethoxyethane (DME).

Further investigation,[2] however, revealed a quantitative distinction between the action of DME and of DMF. Therefore, these two media were chosen in the present work for an examination of the effect of solvent change on the ultraviolet spectra of alkali salts of a number of β-dicarbonyl compounds. Hopefully, further evidence could thus be brought to bear on (a) the existence of ion association suggested by the kinetic data and (b) the detailed nature of any ion association as probed by variation in the geometry of the anion.

The well-known[3] $\pi \to \pi^*$ transition energies of anions derived from β-dicarbonyl compounds are characterized by strong absorption ($\epsilon_{max} \sim 10^4$) in the ultraviolet. It has been the usual observation, however, that they are relatively insensitive to environmental influences. Nevertheless, in view of the high dilutions (10^{-4}–10^{-5} M) experimentally accessible to this approach, detection of even slight shifts in peak positions with variation of the cation would provide conspicuous indication of a strong tendency toward ion association.

Theoretically, anions derived from acyclic β-dicarbonyl compounds can exist in any one or all of three plane-parallel molecular orbital systems which can be termed U-shaped (I), W-shaped (II), and sickle-shaped (III).[4]

I   II   III
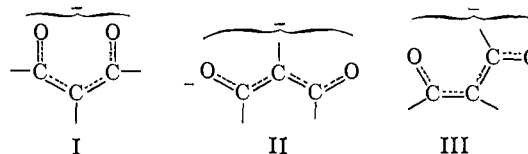
Representative examples possessing the unequivocal structure III are not known. Cyclic derivatives giving U-shaped and W-shaped anions, however, are avail-

(1) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Am. Chem. Soc.*, **82**, 2895, 2903 (1960).

(2) Part IV in the series, "Specific Solvent Effects": H. E. Zaugg, *ibid.*, **83**, 837 (1961). The present paper is part V.

(3) (a) E. R. Blout, V. W. Eager, and D. C. Silverman, *ibid.*, **68**, 566 (1946); (b) B. Eistert and F. Geiss, *Tetrahedron*, **7**, 1 (1959); (c) M. I. Kabachnik, S. T. Ioffe, E. M. Popov, and K. V. Vatsuro, *ibid.*, **12**, 76 (1961). In these and in many references cited therein, ultraviolet spectral determinations were conducted in hydroxylic solvents.

(4) This terminology has been applied to the analogous pentadienyl carbanion.[5a] The need for planarity in this system has been clearly demonstrated[5b] by the fact that bicyclo[2.2.2]octane-2,6,7-trione is neither enolic nor acidic.

(5) (a) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3031 (1963); (b) W. Theilacker and E. Wegner, *Ann.*, **664**, 125 (1963).