Ion–Molecule Reactions in the Radiolysis of Organic Liquids[1]

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Abstract: Conventional carbonium ion reaction mechanisms provide a basis for measuring yields of carbonium ions in suitable radiolytic systems, *e.g.*, hydrocarbon–alcohol liquid mixtures. Small yields of products expected from carbonium ions have been found: anisole from benzene–methanol; cyclohexyl ethyl ether from cyclohexane–ethanol; *t*-butyl ethyl ether from neopentane–ethanol; ethyl acetate from acetone–ethanol, all at *ca.* 20°. Complicating ion-molecular processes may include proton transfer from $c\text{-}C_6H_{11}^+$ and $t\text{-}C_4H_9^+$ to C_2H_5OH as well as competition between $RH^+ \rightarrow R^+ + H$ and $RH^+ + R'OH \rightarrow R\cdot + R'OH_2^+$. There is evidence for proton transfer from $c\text{-}C_6H_{12}^+$ to ethanol, but not from neo-$C_5H_{12}^+$. The structure of the parent molecule has a marked effect on yields with G(carbonium ion) ranging from ~0.03 for benzene to greater than 1.2 for neopentane.

Rather more than 100 ionic species have been identified, or partly characterized, and various ionic processes demonstrated in γ-irradiated organic solids using optical and epr spectroscopy.[3] Ionic processes have also been reliably inferred in liquids to a very limited extent by correlations between chemical analysis of such samples with physical measurements of corresponding solids.[4] Typically these measurements have been concerned with reactions of electrons and the resulting anionic species, *e.g.*, identification of a free radical, R, formed *via* dissociative electron capture

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

accompanied by determination of the yield of products arising from reactions of the resultant anion X^-. There has been little study of the reactions of the positive ions. The radiation chemistry of liquid hydrocarbons has been studied extensively with respect to formation of free radicals and their reactions, but there are few instances in which any attempt has been made to correlate the ultimate products with positive ion precursors.[5–7]

The total ion yields in condensed phases can be measured with some reliability from electron yields through dissociative electron attachment, and these have been found to approximate values for the gas phase.[3] The extent of positive ion fragmentation in condensed phases is not known but is presumably small because the process $RX^+ \rightarrow R^+ + X$ is, in practically all instances, endothermic for ground-state radical ions, and deactivation of excited states by the medium will compete with dissociation. Even when dissociation occurs, the geminate pair (R^+,X) will probably recombine efficiently except for $X = H$.[8]

On thermochemical grounds, recombination of a radical ion with an electron should lead to decomposition. Reactions of electrons with suitable reagents, such as RCl or RONO, can dissipate as much as 3-4 ev of this recombination energy, thereby enhancing the possibility that the radical ion may survive charge recombination. Even in a low dielectric medium, or prior to relaxation of high dielectrics, about 2 ev per ion pair is dispersed by polarization of the medium. Coulombic energy of the separated ion pair partially converts to kinetic energy during recombination and is expended to overcome viscous drag, dissipating an additional ~2 ev. If electron attachment occurs in a polar medium, this will still further moderate the charge-recombination process by slowing the rate of recombination and providing time for dipole relaxation.

The same device of electron attachment could be used to convert carbonium ions to the corresponding free radicals, and thereby measure yields, but there will usually be a large concomitant decrease in the yields of radicals from charge recombination for reasons just given. These two effects could not be reliably distinguished and carbonium ion yields cannot therefore be correlated simply with radical yields. A plausible, direct approach to the measurement of fragment ions is through established reactions of carbonium ions. Thus, in mixed cyclohexane–ethanol one expects $c\text{-}C_6H_{11}^+$ to form cyclohexyl ethyl ether. The yield of the latter measures the yield of the ion if the competing elimination process and other modes of forming the same products (*e.g.*, from $C_6H_{11}\cdot$ and $C_2H_5O\cdot$) can be excluded. It is the aim of this work to examine the feasibility of this procedure.

Experimental methods have been described.[4]

Results

Mixtures of benzene and methanol, alone and with added iodine and methyl iodide, were γ-irradiated at ~20°. Results appear in Tables I and II. Phenyl carbonium ions, if present, would form the corresponding methyl ether, anisole. The cross product of $C_6H_5\cdot$ and $CH_3O\cdot$ can yield the same product but this reaction should be suppressed by iodine.[9a] Conversion of e^- to I^- by addition of CH_3I, known to be an efficient reaction,[9b] delays recombination and may thereby increase formation of the adduct $(C_6H_5OCH_3)H^+$; it also moder-

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[3] T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 5376 (1966), and earlier publications in this series.

[4] J. A. Ward and W. H. Hamill, *ibid.*, **87**, 1853 (1965), and publications cited.

[5] S. Z. Toma and W. H. Hamill, *ibid.*, **86**, 4761 (1964).

[6] F. Williams, *Quart. Rev.* (London), **13**, 101 (1963).

[7] P. Ausloos, S. G. Lias, and A. A. Scala, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 264.

[8] J. R. Nash, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **82**, 5974 (1960).

[9] (a) This has been confirmed by J. P. Mittal for 2% C_6H_5Cl and 0.005 M I_2 in cyclohexane, C_6H_5 being formed efficiently by dissociative electron attachment. (b) D. W. Skelly, R. W. Hayes, and W. H. Hamill, *J. Chem. Phys.*, **43**, 2795 (1965).

Table I. Radiolysis of Benzene–Methanol at ~20° [a]

Mole % methanol	G(anisole) × 10^2	Mole % methanol	G(anisole) × 10^2
4.2	0.5	4.1[b]	0.3[b]
19.7	3.5	9.7	3.0
48.6	6.6	17.7	4.7
59.6	6.9	41.9	11.2
66.8	9.5	43.1	10.9
68.6	9.1	47.6	10.4
68.6	8.6	67.6	11.5
70.8	8.7	82.5	10.3
83.7	6.2	94.5	5.5
95.6	3.5		

[a] Dose = 20 × 10^{18} ev/ml. [b] Samples contained 0.3 M CH_3I.

Table II. Radiolysis of Benzene–Methanol–I_2 at ~20° [a,b]

Mole % methanol	G(anisole)	Mole % methanol	G(anisole)
1.10	0	83.7	0.29
4.24	0.31	95.6	0.10
9.97	0.57	4.13[c]	0.05[c]
18.1	0.64	9.72	0.23
19.7	0.57	17.7	0.50
48.6	0.48	47.6	0.44
66.8	0.43	67.9	0.38
68.6	0.40	82.5	0.28
70.8	0.39	94.5	0.17

[a] Dose = 20 × 10^{18} ev/ml. [b] All samples contained 5 × 10^{-3} M I_2. [c] The following results are for systems containing 0.3 M CH_3I.

ates the exothermicity of the charge recombination. In mixtures containing 31% C_6H_6 and 69% CH_3OH, G(anisole) was 0.09, 0.40, 0.59, 0.86, and 1.18 when the concentration of I_2 was 0, 0.005, 0.02, 0.1, and 1.00 M, respectively.

Cyclohexane–ethanol mixtures were analyzed for cyclohexyl ethyl ether, the product expected from $C_6H_{11}^+$ or, of course, from $C_6H_{11}\cdot$ and $C_2H_5O\cdot$. Results appear in Table III. Cyclohexene is an alternate product for both mechanisms, either by proton transfer or by disproportionation of radicals, but these reactions cannot be examined because C_6H_{10} is also a major product of the radiolysis of C_6H_{12}. If reaction 1 occurs

Table III. Radiolysis of Cyclohexane–Ethanol at ~20° [a]

Mole % ethanol	G(cyclohexyl ethyl ether)	Mole % ethanol[b]	G(cyclohexyl ethyl ether)[b]
0.91	0.04	0.84	0.02
3.3	0.10	3.2	0.04
8.4	0.13	7.8	0.15
15.5	0.11	14.4	0.17
26.9	0.12	25.3	0.15
64.8	0.04	86.5	0.03
90.2	0.04		
97.3	0.00		

[a] Dose = 20 × 10^{18} ev/ml. [b] The following systems contained 0.8 M CH_3I.

$$c\text{-}C_6H_{12}^+ + C_2H_5OH \longrightarrow c\text{-}C_6H_{11}\cdot + C_2H_5OH_2^+ \quad (1)$$

efficiently in this system, then products arising from c-$C_6H_{12}^+$ and e^- will be suppressed accordingly. The results in Table IV show that yields of c-C_6H_{10} and $(c\text{-}C_6H_{11})_2$ behave in this way. The corresponding proton transfer to methyltetrahydrofuran is to be expected by analogy with effects observed in glasses, and results are consistent with this assumption, as shown in Table IV.

Table IV. Radiolysis of Cyclohexane–Ethanol and Cyclohexane–Methyltetrahydrofuran at ~20° [a]

Solute	Mole % solute	G(cyclohexene)	G(bicyclohexyl)
None	0	2.70	1.60
Ethanol	0.91	2.23	1.47
	8.43	1.37	1.38
	15.5	1.41	0.60
	26.9	0.69	0.33
	64.7	0.41	...[b]
	94.8	0.13	...[b]
Methyltetrahydrofuran	0.52	2.52	1.30
	2.26	2.09	0.87
	5.46	1.45	0.52
	10.3	0.97	0.32
	18.7	0.65	0.15
	53.6	0.37	0.08
	85.2	0.11	...

[a] Dose = 50 × 10^{18} ev/ml. [b] Too small to measure.

The t-butylcarbonium ion is of particular interest and, on the basis of mass spectral cracking patterns, neopentane is an excellent source. The yields of t-butyl ethyl ether from mixtures of neopentane and ethanol, which appear in Table V, are remarkably large and addition of CH_3I increases them considerably. The mass spectral abundance of $C_5H_{12}^+$ from neopentane is negligible; some indication of its stability in mixtures with ethanol, which should act as proton acceptor with $C_5H_{12}^+$, is given by yields of H_2 and CH_4 which appear in Table VI.

Table V. Radiolysis of Neopentane–Ethanol at ~20° [a]

Mole % ethanol	G(t-BuOEt)	(G × 10^2)/% C_5H_{12}	Mole % ethanol	G(t-BuOEt)[b]	(G × 10^2)[b]/% C_5H_{12}
1.03	0.34	0.34	0.25	0.09	0.09
1.18	0.30	0.30	1.11	0.90	0.91
10.7	0.39	0.42	5.26	1.16	1.23
18.0	0.35	0.43	9.56	1.18	1.46
22.2	0.42	0.54	18.9	0.82	1.02
30.2	0.50	0.72	34.9	0.60	0.92
61.4	0.33	0.86	62.4	0.46	1.22
71.9	0.27	0.96	91.4	0.08	0.9
81.4	0.20	1.1			
88.9	0.21	1.9			
95.6	0.07	1.6			

[a] Dose = 50 × 10^{18} ev/ml. [b] Systems contained 0.8 M CH_3I.

Table VI. Radiolysis of Neopentane–Ethanol at ~20° [a]

Mole % ethanol	$G(H_2)$	$G(CH_4)_{obsd}$	$G(CH_4)_{calcd}$[e]
0	1.87	3.76	
22.9	3.37	2.83	2.88
35.2	4.16	2.31	2.62
70.4	3.84	1.58	1.47
100	4.20	0.35	
0[c]	...[b]	3.8	
100[d]	4.85	0.61	

[a] Dose = 6 × 10^{18} ev/ml. [b] $G(H_2)$ is dose dependent. Initial $G(H_2)$ = 2.6. [c] R. A. Holroyd, *J. Phys. Chem.*, **65**, 1352 (1961). [d] G. E. Adams and R. D. Sedgwick, *Trans. Faraday Soc.*, **60**, 865 (1964). [e] From $G = 3.76X + 0.5(1 - X)$, where X is mole fraction of $(CH_3)_4C$.

The possible carbonium ion products from mixtures of 3-methylpentane and ethanol were not measured, but gaseous products were examined for evidence of diminished yields of products which might arise from interference with recombination of $C_6H_{14}^+$ and e^-. The results appear in Table VII.

Table VII. Radiolysis of 3-Methylpentane–Ethanol Mixtures at ~20° [a]

Mole % ethanol	$G(H_2)$	$G(CH_4)$	$G(C_2H_4)$	$G(C_2H_6)$
0	3.87	0.35	1.01	1.08
0.22	3.97	0.36	...	...
1.07	4.35	0.47	0.47	1.21
4.16	4.76	0.38	0.58	1.26
9.80	4.76	0.46	0.54	0.97
100[b]	5.53	0.80	0.27	0.30

[a] Dose = 6 × 10^{18} ev/ml. [b] R. H. Johnsen, *J. Phys. Chem.*, **65**, 2144 (1961).

The expected product of CH_3CO^+ from acetone in ethanol is ethyl acetate, which was found in small yields (see Table VIII). This system provides a second example of a fragment ion with CH_3 as the neutral product.

Table VIII. Radiolysis of Acetone–Ethanol at *ca.* 20° [a]

Mole % ethanol	G(ethyl acetate)	$(G \times 10^2)$/ % $(CH_3)_2CO$
0.62	0.11	0.11
2.44	0.28	0.28
5.88	0.27	0.29
11.1	0.22	0.25
19.9	0.17	0.21
55.5	0.13	0.30

[a] Dose = 50 × 10^{18} ev/ml.

Very limited, but significant, evidence of a quite different approach to the measurement of carbonium ions is provided by irradiation of 3.7 and 7.1 mole % benzyl acetate in cyclohexane for which G(cyclohexyl acetate) was 0.12 and 0.13, respectively.

Discussion

The energy released by recombination of electrons with protonated adducts arising from carbonium ion addition to alcohols, ROR′H+, can be estimated. Removal of the proton requires 7 to 8 ev, *i.e.*, the proton affinity of ROR′, while the recombination energy of H^+ is −13.6 ev, both *in vacuo*. In polar liquids probably more than 4 ev of the remaining 6 ev is dissipated to polarization and coulombic effects, and the net exothermicity may be *ca.* 2 ev or less. In fact, unless the proton affinity of the ether product exceeds that of alcohol (~8 ev), the proton will transfer to the solvent. The product of interest should therefore survive, even when e^- rather than I^- is involved, and the effect of adding CH_3I serves as a partial test of this assumption.

In benzene–methanol systems, Tables I and II, anisole can be produced by three conventional mechanisms.

$$C_6H_5^+ + CH_3OH \xrightarrow{H^+} C_6H_5OCH_3 \qquad (2)$$

$$C_6H_5\cdot + CH_3O\cdot \longrightarrow C_6H_5OCH_3 \qquad (3)$$

$$C_6H_6 + CH_3O\cdot \longrightarrow C_6H_6OCH_3 \longrightarrow C_6H_5OCH_3 \qquad (4)$$

If reaction 2 is very efficient, as seems probable, G(anisole) should maximize at *ca.* $\lesssim$10% methanol, barring other ion–molecule reactions. It can be seen, however, that G(anisole) attains maximum yields at high concentrations of methanol. Mechanism 3 would be expected to give maximum yield at ~50%, but would be strongly suppressed by I_2 and also by CH_3I through the reaction

$$C_6H_5\cdot + CH_3I \longrightarrow C_6H_5I + CH_3\cdot \qquad (5)$$

The corresponding reaction between $c\text{-}C_6H_{11}\cdot$ and CH_3I is known to be efficient.(10) Moreover, the yield of phenyl radicals is small since $G(C_6H_5I)$ is only 0.27 for 0.05 *M* I_2 in benzene. Furthermore $C_6H_5\cdot$ and $CH_3O\cdot$ should react with CH_3OH to give $\dot{C}H_2OH$. Radical combination is very probably unimportant.

Mechanism 4 is apparently involved since iodine dehydrogenates cyclohexadiene to benzene,(11) which accounts for increased G(anisole) with added I_2, and disproportionation of methoxycyclohexadienyl radical with any radical may very well contribute to the yields of anisole in Table I. As an approximate upper limit we suggest $G(C_6H_5^+) \cong 0.03$, based on the data of Table I.

Cyclohexane–ethanol (Table III) is expected to be a somewhat simpler system although reaction 6 may compete with reaction 7. The branching ratio of reactions 6 and 7 should be independent of composition. The yield of $c\text{-}C_6H_{11}OC_2H_5$ attains maximal values with 8% or less of ethanol which is much more nearly consistent with an ion–molecule reaction than with radical–radical combination. The efficiency of the carbonium reaction is also supported by the small effect of added CH_3I.

$$c\text{-}C_6H_{11}^+ + C_2H_5OH \longrightarrow c\text{-}C_6H_{10} + C_2H_5OH_2^+ \qquad (6)$$

$$c\text{-}C_6H_{11}^+ + C_2H_5OH \xrightarrow{H^+} c\text{-}C_6H_{11}OC_2H_5 \qquad (7)$$

There is, however, a complicating ion–molecule reaction, *i.e.*

$$c\text{-}C_6H_{12}^+ + C_2H_5OH \rightarrow c\text{-}C_6H_{11}\cdot + C_2H_5OH_2^+ \qquad (8)$$

which is to be expected *a priori* and is also indicated by the data of Table IV. Reaction 8, if it occurs and is efficient, would suppress products arising from recombination of $C_6H_{12}^+$ and e^- at rather small concentrations of ethanol. Excepting H_2, $c\text{-}C_6H_{10}$ and $(c\text{-}C_6H_{11})_2$ are the principal products, and both are suppressed efficiently (Table IV).(12) Methyltetrahydrofuran is also known to be an effective proton acceptor, and it shows an even greater effect than ethanol (Table IV).

It is impossible to say whether or not reaction 8 competes with carbonium ion formation

$$c\text{-}C_6H_{12}^+ \longrightarrow c\text{-}C_6H_{11}^+ + H\cdot \qquad (9)$$

which requires $c\text{-}C_6H_{12}^+$ to have energy of $\gtrsim$1.3 ev above the ground state. The results do not suggest such interference, and we conclude tentatively that $G(c\text{-}C_6H_{11}^+) \cong 0.1$.

The two runs with benzyl acetate in $c\text{-}C_6H_{12}$ which gave $G(CH_3CO_2C_6H_{11})$ = 0.12 and 0.13 suggest the

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(10) R. H. Schuler, *J. Phys. Chem.*, 61, 1472 (1957). More nearly direct evidence for reaction 5 is an observation of J. P. Mittal that 0.3 *M* C_6H_5Cl and 0.2 *M* CH_3I in benzene gives an appreciable yield of C_6H_5I.

(11) T. Gaumann, *Helv. Chim. Acta*, **44**, 1337 (1961).

(12) There is independent evidence for reaction 8 from unpublished results of J. P. Mittal in this laboratory. $G(c\text{-}C_6H_{11}I)$ from 0.01 *M* I_2 in $c\text{-}C_6H_{12}$ increases from 4.0 to 5.4 with addition of 2 mole % methanol.

reactions

$$CH_3CO_2C_6H_5 + e^- \longrightarrow C_6H_5CH_2\cdot + CH_3CO_2^- \qquad (10)$$

$$c\text{-}C_6H_{11}^+ + CH_3CO_2^- \longrightarrow CH_3CO_2C_6H_{11} \qquad (11)$$

The large electron affinity of 3.3 ev for CH_3CO_2[13] moderates the energy of recombination. The instability of $CH_3CO_2\cdot$ precludes the possibility of radical–radical combination. Yields are consistent with those of Table IV, and again $G(c\text{-}C_6H_{11}^+) \cong 0.1$.

The dominant ion in the mass spectrum of $(CH_3)_4C$ is $C_4H_9^+$, presumed to have the tertiary configuration, while the abundance of $C_5H_{12}^+$ is only *ca.* 0.1%.[14] It appears that electron impact can produce only excited $C_5H_{12}^+$ since the appearance potential of $C_5H_{12}^+$ from $(CH_3)_4C$ alone is 12.4 ev, whereas in mixtures with CS_2 it is 10.1 ev, and with added C_2H_4 it becomes 10.6 ev.[14] These lower values correspond to the ionization potentials of the additives, and the results show that $C_5H_{12}^+$ is produced by charge transfer with good cross section, but decreasing with increasing energy. Collisional charge transfer from ions of higher energy gave little or no $C_5H_{12}^+$.[14] The excess energy must appear as kinetic energy in the fragments, but only experiment can determine whether separation or geminate recombination will prevail in condensed phases. If excited $C_5H_{12}^+$ were collision stabilized, it would proton transfer to C_2H_5OH, thus suppressing the products of $C_5H_{12}^+$ and e^- recombination, one of which should be CH_3. In fact, the results of Table VI show that $G(CH_4)$ is substantially linear in concentration of ethanol over the entire range of composition, *i.e.*, simple dilution alone is involved, and there can be no extensive interaction involving $C_5H_{12}^+$. Methane apparently arises from decomposition to give $t\text{-}C_4H_9^+$ and $CH_3\cdot$, or from a nonionic process.

In $(CH_3)_4C$–C_2H_5OH mixtures (Table V), the yield of $t\text{-}C_4H_9OC_2H_5$ per unit concentration of $(CH_3)_4C$ increases with increasing concentration of ethanol to about $G = 1.2$ or higher. When CH_3I is also present, the same ratio tends to be constant at *ca.* $G = 1.2$. Since as little as 1% ethanol gives large yields of ether, combination of $(CH_3)_3C\cdot$ and $C_2H_5O\cdot$ is probably unimportant, and the effect of CH_3I is not attributable to delayed charge recombination. Dissipation of recombination energy by converting e^- to I^- and increasing ion dipolar solvation by increasing the concentration of ethanol can account for these effects.

Loss of $(CH_3)_3C^+$ by proton transfer to give $i\text{-}C_4H_8$ may be important. More significantly, for solvolysis of *t*-butyl halides in ethanol at 25°, 17% of the product is $i\text{-}C_4H_8$,[15] but at 65° the elimination reaction contributes 36%. Since we expect $(CH_3)_3C^+$ to be vibrationally excited, it may behave similarly. It appears that $G(t\text{-}Bu^+) \overline{>} 1.2$.

The results in Table VII are incidental to our main purpose but supply some further indication of the effects of proton transfer. Two products, CH_4 and C_2H_6, do not change notably. The increase in $G(H_2)$ at small concentrations of ethanol suggests proton transfer and, possibly, formation of H following neutralization of $C_2H_5OH_2^+$. The decrease in $G(C_2H_4)$ indicates that C_2H_4 has a positive ion precursor, but no attempt was made to identify it.

The largest peak in the mass spectrum of acetone corresponds to CH_3CO^+. Also, it may be of interest that in a matrix of CH_3OH at −196°, $(CH_3)_2CO$ forms a negative ion which abstracts a proton from CH_3OH to give $CH_3\dot{C}(OH)CH_3$ and CH_3O^-.[16] Since $G(CH_3CO_2C_2H_5)/\%$ $(CH_3)_2CO$ is practically constant to rather small concentrations of ethanol, combination of $CH_3CO\cdot$ and $C_2H_5O\cdot$ is not important. A reaction first order in concentration of ketone and zero order in alcohol is consistent with the reaction

$$CH_3CO^+ + C_2H_5OH \longrightarrow CH_3C(OH)OC_2H_5^+ \qquad (12)$$

Reactions 13 and 14 also will give the ester product since

$$CH_3CO^+ + C_2H_5O^- \longrightarrow CH_3CO_2C_2H_5 \qquad (13)$$

$$CH_3CO^+ + C_2H_5OH \longrightarrow CH_2CO + C_2H_5OH_2^+ \qquad (14)$$

ketene will quickly convert to ethyl acetate (eq 15).[17,18]

$$CH_2CO + C_2H_5OH \longrightarrow CH_3CO_2H_5 \qquad (15)$$

The small yields of CH_3CO^+ from acetone implied by Table VIII, $G = 0.25$, suggest the probability of CH_3CO^+ involvement in geminate interactions.

In each of these systems, excepting C_6H_6–CH_3OH, there is the additional possibility of an exothermic disproportionation between the carbonium ion and the geminate neutral fragment to form the olefin radical ion and H_2 or CH_4 or, from acetone, to form CH_2CO^+ and CH_4. There is an indication of this effect in $(CH_3)_4C$ at 20° since addition of 0.03 *M* I_2 gave $G(CH_3I) = 2.3$ and $G(CH_4) = 1.66$[19] (*cf.* Table VI, $G(CH_4) = 3.8$). The nonscavengeable CH_4 can be attributed in part to

$$(CH_3)_3C^+ + CH_3 \longrightarrow i\text{-}C_4H_8^+ + CH_4 \qquad (16)$$

and is supported by $G(i\text{-}C_4H_8) = 1.2$. Although inherently quite plausible, such reactions are difficult to distinguish from the corresponding primary processes and will be formally treated as such here.

The possibility of positive-charge exchange between primary molecular ions and neighboring molecules has been invoked, but not demonstrated, for organic liquids.[20] It has been established for alkane, alkene, alkyl halide, and other glassy and polycrystalline solids. With suitable additives S, values of $G(S^+)$ from 2 to 3 have been measured. An extreme instance is the CCl_4 matrix at −196° where positive charge transfer is observed from a CCl_4 ion (presumably CCl_4^+) to olefins.[3]

$$CCl_4^+ + S \longrightarrow CCl_4 + S^+$$

Because the mass spectral abundance of CCl_4^+ is immeasurably small, it must therefore be even less stable than $(CH_3)_4C^+$ by vertical ionization *in vacuo.* However, we see no evidence for reactions of neopentane molecular ions.

In CCl_4 electron hopping must be rapid while in

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[13] S. Tsuda and W. H. Hamill, *Advan. Mass Spectry.*, 3, 249 (1965).

[14] N. Boelrijk and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 730 (1962).

[15] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 57.

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

[17] Kucera[18] has seen acetic acid in the radiolysis of acetone containing traces of water. The yields listed in this paper range from 0.3 to 0.9.

[18] S. Kucera, *Collection Czech. Chem. Commun.*, **31**, 355 (1966).

[19] R. Holroyd, *J. Phys. Chem.*, **65**, 1352 (1961).

[20] J. P. Keene, E. J. Land, and A. J. Shallow, *J. Am. Chem. Soc.*, **87**, 5284 (1965), observed ionic spectra for dilute solutions of biphenyl and other aromatic compounds in cyclohexane under pulse radiolysis at 20°, but they could not establish whether cations or anions, or both, were responsible.

neopentane the rate of positive ion migration is apparently quite slow. The effects in CCl_4 are explainable in terms of a series of fast, conservative, vertical transitions. The apparently different behavior of $(CH_3)_4C$ and CCl_4 may be due to the electron vacancies being well shielded in the C–C bonds, requiring large electron-hopping distances and, hence, a slow rate. The half-occupied lone pair of Cl_3–Cl^+ would overlap much more strongly with a neighboring chlorine, leading to very rapid charge migration.

Temperature-Dependent Electron Spin Resonance Studies. I. Cyclooctatetraene Anion Radical

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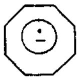
Abstract: Ion pairing affects the esr spectra of cyclooctatetraene (COT) anion radical (I), influencing the line widths of the individual hyperfine splitting, the activation energy of the line-broadening process, and the spin concentration. For this reason, the electron transfer (eq 5) and the disproportionation (eq 2) are replaced by their ion-pair counterparts, eq 6 and 7. When the concentration of dianion II is greater than 0.03 *M* for the system COT–DME–Na from −30 to +10°, the major source of line broadening is that due to electron transfer from dianion II to anion radical I. Other contributions to line broadening, such as that from the disproportionation and ion-pairing phenomena, are minor.

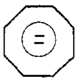
The importance of ion pairing in solution chemistry has long been recognized.[1] More recently, the study of ion pairing has received added impetus from esr,[2,3] conductance,[4] and optical[5] measurements. The various stages of solvation of the ion can be exemplified by

$$\mathrm{RM} = \underset{\mathrm{III}}{\mathrm{R}\cdot^-\mathrm{M}^+} = \underset{\mathrm{IV}}{\mathrm{R}\cdot^-||\mathrm{M}^+} = \underset{\mathrm{V}}{\mathrm{R}\cdot^- + \mathrm{M}^+} \qquad (1)$$

where III, IV, and V are contact, solvent-separated, and dissociated ion pairs.

Weissman and co-workers[2] were the first to recognize the importance of applying electron spin resonance (esr) to the study of ion pairing. Most of the esr work on ion-pairing phenomena has recently been reviewed.[6] Because of the unfavorable disproportionation equilibrium (eq 2) for the cyclooctatetraene (COT) anion radical (I),[7] the concentration of ions in solution is quite high (near 1 *M*) and ion pairing is expected to play a role. This study is concerned with the influence of ion pairing on the COT anion radical (I).


I


II

$$\mathrm{pi} + \mathrm{pi}^{2-} \rightleftharpoons 2\mathrm{pi}^- \qquad (2)$$

$$\mathrm{pi} = \mathrm{COT}$$

Experimental Section

The COT was purchased from Chemical Procurement Laboratories Inc. and was degassed and distilled under high vacuum before use.

The anion radicals were prepared by reduction of the COT with potassium or sodium metal mirrors or lithium metal in either dimethoxyethane (DME) or tetrahydrofuran (THF) using standard techniques.

Activation energies are determined from the slope of ln (line width) *vs.* $1/RT$ plots.[8] Line widths are measured between the extrema in the first-derivative spectrum. In the linear region of the ln (line width) *vs.* $1/RT$ plot, all hyperfine components of the same system give the same line width. Spectra of each system were run at several different metal and COT concentrations to verify that the energy of activation for the line broadening is independent of the concentration of the dianion. The concentration of the dianion was low enough that a visible amount of the dianion salt did not precipitate out of solution.

For the system COT–DME–Na kinetics for the line-broadening process was determined over the temperature range −30 to +10°. The dianion II concentration was maintained at 0.034 *M* for each run. Three different concentrations were prepared, with the concentration of COT equal to 1.30, 0.64, and 0.32 *M*, respectively. Details are given in Table I. The results are the average of three kinetic runs.

The spectra were recorded using the X band of a Varian V-4502-15 esr spectrometer with a 12-in. magnet. Temperature was controlled within ±1° by a Varian V-4557 variable-temperature controller.

Coupling constants and line widths were taken directly from the calibrated chart paper.

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