

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

Organic Ions in the Gas Phase. IX. Dissociation of Benzyl Alcohol by Electron Impact

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The mass spectra of deuterated benzyl alcohols reveal several ionic dissociation paths besides the previously studied formation of tropylium ion by loss of a hydroxyl radical. These competing paths seem generally directed by the oxygen atom. Metastable peaks and label retention in fragments allow the relative importance of a number of competing paths to be assessed. The most abundant ion in the spectra, $C_6H_7^+$, is formed by two different paths—loss of a formyl radical, and successive loss of a hydrogen atom and carbon monoxide. Although benzaldehyde (or an isomeric $C_7H_6O^+$) ion comprises only 0.5% of the total fragment-ion intensity, as much as 6.8% of the observed fragment ions seem best accounted for by a primary dissociation to form $C_7H_6O^+$.

When gaseous molecules are subjected to electron bombardment in a mass spectrometer, they react by unimolecular processes to yield a variety of ionized products. In a recent study,³ evidence was presented that benzyl chloride and benzyl alcohol, like 1-phenylalkanes, undergo ring-expansion and cleavage of a bond originally beta to the ring to form $C_7H_7^+$ with the tropylium structure. From benzyl chlorides, as from the lower 1-phenylalkanes, $C_7H_7^+$ is the most-abundant ion formed³; however, it was found to be only a minor decomposition product of benzyl alcohol. The most-abundant ion in the mass spectrum of this compound is instead $C_6H_7^+$, and oxygen-containing ions are prominent. The sharp contrast between the major mass-spectral features of benzyl alcohol and other benzyl compounds that have been examined suggested that the oxygen atom exerts an important influence on decomposition and prompted a more-extensive study of the alcohol.

The approach selected was isotope-labeling, which has contributed heavily to existing knowledge of the structures and reactions of gaseous ions. Label retention in many fragment ions can be simply calculated from the mass spectra of labeled compounds.⁴ Such retentions necessarily reflect, and can therefore help clarify, the structures of the precursors and the nature of the decomposition processes.⁴ Independent evidence on some reaction paths was provided by metastable peaks, which stem from decompositions that occur near the slit between the accelerating region and the analyzer of the mass spectrometer.⁵ The mass of a metastable peak nearly always determines a unique pair of values for the masses of the parent and daughter ion, and thus defines one step in a decomposition path.⁶

The mass spectra of benzyl alcohol unlabeled and deuterated in four different ways—*ortho-d*, *meta-d*, *alpha-d*₁ and *alpha-d*₂—were recorded in the earlier work.³ Table I⁷ shows the three mass regions

studied—105 to 110, corresponding to the composition $C_7H_nO^+$; 75 to 83, $C_6H_n^+$; and 29 to 33, CH_nO^+ . Table II lists metastable peaks corresponding to the formation of $C_7H_7O^+$, mass 107; $C_6H_5^+$, mass 77; $C_6H_7^+$, mass 79; and $C_6H_8^+$,

TABLE I
PARTIAL SPECTRA OF BENZYL ALCOHOLS

<i>m/e</i>	Relative intensities				
	<i>d</i> ₀	<i>o-d</i>	<i>m-d</i>	<i>α-d</i> ₁	<i>α-d</i> ₂
110	100.0
109	...	100.0	100.0	100.0	59.3
108	100.0	73.0	71.5	70.3	18.2
107	80.7	7.4	7.3	9.1	0.7
106	2.7	5.1	4.7	0.6	0.7
105	5.4	0.4	0.4	4.1	2.5
83	0.1	.1	.1	0.1	0.2
82	.1	.3	.4	.3	4.7
81	.4	5.1	5.0	4.8	65.9
80	4.4	111.9	111.3	94.4	57.3
79	117.4	21.4	20.1	32.0	17.2
78	11.0	54.1	53.5	35.2	33.2
77	65.5	16.9	15.8	36.5	21.4
76	2.3	1.9	1.7	2.0	2.5
75	2.7	3.6	3.3	2.8	2.6
33	0.0	0.0	0.0	0.1	11.0
32	0.2	0.6	0.6	10.4	1.2
31	9.8	10.8	11.6	2.0	1.3
30	1.2	2.2	1.7	8.7	12.8
29	14.1	14.2	14.3	7.3	4.1

TABLE II
SELECTED METASTABLE PEAKS IN THE SPECTRA OF BENZYL ALCOHOLS

Ap- parent <i>m/e</i>	Transition	Relative intensities				
		<i>d</i> ₀	<i>o-d</i>	<i>m-d</i>	<i>α-d</i> ₁	<i>α-d</i> ₂
108.0	(110 ⁺) → (109 ⁺) + 1	1.38
107.0	(109 ⁺) → (108 ⁺) + 1	..	1.59	1.77	1.86	..
106.0	(110 ⁺) → (108 ⁺) + 2	0.26
	(108 ⁺) → (107 ⁺) + 1	1.52
76.1	(80 ⁺) → (78 ⁺) + 2	..	2.05	2.35	2.34	1.08
75.1	(81 ⁺) → (78 ⁺) + 3	0.75
	(79 ⁺) → (77 ⁺) + 2	2.53	0.14	0.14	0.64	..
74.1	(80 ⁺) → (77 ⁺) + 3	..	.60	.65	.42	.46
60.5	(109 ⁺) → (81 ⁺) + 2832
59.6	(110 ⁺) → (81 ⁺) + 2958
	(108 ⁺) → (80 ⁺) + 28	..	.40	.51	.37	..
58.9	(109 ⁺) → (80 ⁺) + 29	..	.64	.69	.58	..
58.6	(107 ⁺) → (79 ⁺) + 28	0.35
58.2	(110 ⁺) → (80 ⁺) + 30	0.14
57.8	(108 ⁺) → (79 ⁺) + 29	..	.66
57.3	(109 ⁺) → (79 ⁺) + 30	..	0.05	0.04	0.06	..
56.7	(108 ⁺) → (78 ⁺) + 30	.03

(7) Spectra are corrected for isotopic impurities, for naturally occurring C^{13} , and, in the parent-mass region, for O^{17} and O^{18} .

(1) Research participant from Department of Chemistry, University of Notre Dame, summer, 1956.

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(3) S. Meyerson, P. N. Rylander, E. L. Eliel and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959); see also A. G. Harrison, L. R. Honnen, H. J. Dauben and F. P. Lossing, *ibid.*, **82**, 5593 (1960).

(4) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

(5) H. M. Rosenstock, A. L. Wahrhaftig and H. Eyring, "The Mass Spectra of Large Molecules. II. The Application of Absolute Rate Theory," University of Utah, Salt Lake City, Utah, 1952, pp. 95 ff.

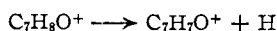
(6) P. N. Rylander and S. Meyerson, *J. Am. Chem. Soc.*, **78**, 5799 (1956).

mass 78, from the unlabeled alcohol and the analogous ions from the deuterated alcohols.

Ions in the $C_7H_nO^+$ Region

Two ions in the $C_7H_nO^+$ region were of particular interest: $C_7H_7O^+$ because of its high relative intensity, and $C_7H_5O^+$ because of its well-defined deuterium retention despite its low intensity.

The $C_7H_7O^+$ Ion.—The normal peaks at the parent mass (molecular weight) less one and the metastable peaks at 108.0, 107.0 and 106.0 establish the reaction



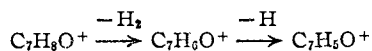
The observed deuterium retention in the $C_7H_7O^+$ ion corresponds closely to random loss of one out of the eight hydrogen atoms, or somewhat less closely to random loss of one out of the seven non-hydroxyl hydrogen atoms, with a slight preference for loss from the side chain rather than from the ring:

Deuterium retention, %	<i>o-d</i>	<i>m-d</i>	$\alpha-d_1$	$\alpha-d_2$
Calcd. for random loss:				
One out of eight	87.5	87.5	87.5	75.0
One out of seven	85.7	85.7	85.7	71.4
Observed	90.5	88.6	87.1	73.5

Whether hydrogen loss merely occurs in a random fashion among all the available atoms, or a randomizing rearrangement precedes the loss, cannot be determined conclusively from these data. Differences as large as 1 e.v. might be expected among the dissociation energies of the three types of bonds by which hydrogen atoms are held in the molecule. However, such differences evidently have little influence on the order of loss of hydrogen in forming the $C_7H_7O^+$ ion. Thus the data seem to favor a randomizing rearrangement, although details are not clear.

The $C_7H_5O^+$ Ion.—The $C_7H_5O^+$ ion of mass 105 is a minor product in the spectrum of benzyl alcohol; it is formed only to the extent of 5% of the parent-ion yield. However, the 105–106 profile in the spectra of the labeled alcohols reveals a curious result. Intensities of the ring-*d* alcohols at 106 are nearly equal to that of the unlabeled alcohol at 105 and the ring-*d* species show almost no 105 peak. The $\alpha-d_1$ alcohol, on the other hand, shows little at 106 but gives a 105 peak of intensity approaching that of the unlabeled compound. Evidently the $C_7H_5O^+$ ion is produced by preferential loss of the α -hydrogens from the molecule-ion. The same preference for loss of alpha over ring hydrogen is found in the $\alpha-d_2$ alcohol, although the occurrence of an isotope effect makes interpretation here less clear.

No randomizing migration of hydrogens can have occurred in the formation of $C_7H_5O^+$, unlike $C_7H_7O^+$ and $C_6H_5^+$.³ Hence, formation of $C_7H_5O^+$ cannot involve a consecutive reaction *via* $C_7H_7O^+$ unless two different $C_7H_7O^+$ species occur, of which only one remains intact long enough to be detected and the other gives rise to $C_7H_5O^+$. A more probable sequence would seem to be



A likely structure for the $C_7H_5O^+$ ion is that of benzaldehyde; for $C_7H_7O^+$, the benzylium ion



The latter structure might be expected to have enhanced stability from the resonance forms shown and from conjugation of the carbonyl group with the ring. An ion with this probable structure is formed in high yield by electron impact from phenyl alkyl ketones⁸ and from benzaldehyde⁹; in the mass spectrum of benzaldehyde, loss of hydrogen is solely from the α -position.⁹

Ions in the $C_6H_n^+$ Region

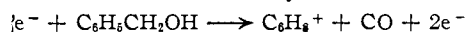
The $C_6H_n^+$ region contains two of the most abundant ions produced from benzyl alcohol by electron impact— $C_6H_7^+$ and $C_6H_5^+$ —and significant quantities of $C_6H_3^+$ and $C_6H_4^+$. Label retention in $C_6H_3^+$ and $C_6H_7^+$ is fairly well defined, but any calculation for $C_6H_5^+$ is subject to large cumulative errors.⁴ Yields of unlabeled $C_6H_5^+$ ions can be calculated if one neglects possible small contributions at mass 77 of deuterated $C_6H_4^+$ and $C_6H_3^+$ ions.

Total ion intensity in the mass range 77 to 83 is nearly constant for the five isotopic species:

<i>d_6</i>	<i>o-d</i>	<i>m-d</i>	$\alpha-d_1$	$\alpha-d_2$
198.9	209.8	206.2	203.3	199.9

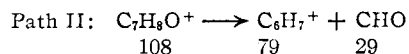
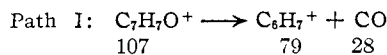
Thus, the over-all production of 6-carbon ions is attended by no more than (perhaps) a small isotope effect, in accord with the usual simplifying assumption⁴ that no appreciable isotope effect occurs in the formation of any one of the ions in the group.

The $C_6H_3^+$ Ion.—Relative intensities of the unlabeled, singly labeled and doubly labeled alcohols at masses 80, 81 and 82 are nearly enough equal to leave little doubt that the ion involved has retained all the original hydrogen atoms. The mass of this ion corresponds to the loss from the molecule of 28 units—evidently as CO rather than C_2H_4 , because some deuterium loss from the labeled species would surely be observed if ethylene were split out. The reaction may be summarized as



The $C_6H_3^+$ fragment must arise from some molecular rearrangement, although details of the reaction are not clear from the data thus far obtained. The evident loss of CO from the benzyl alcohol ion is in accord with the suggestion of Beynon¹⁰ that loss of CO is a favored reaction of gaseous ions even when it may entail extensive prior rearrangement.

The $C_6H_7^+$ Ion.—The most abundant ion in the mass spectrum of benzyl alcohol is $C_6H_7^+$, formed through loss of the elements of CHO. Metastable peaks at 58.6 and 57.8 in the spectrum of the unlabeled species indicate at least two paths for formation of this ion, one from the $C_7H_7O^+$ ion and the other from the parent ion



(8) S. Meyerson and P. N. Rylander, *J. Am. Chem. Soc.*, **79**, 1058 (1957).

(9) J. D. McCollum and S. Meyerson, in preparation.

Corresponding metastable peaks occur in the spectra of the labeled species.

Deuterium retention in $C_6H_7^+$ —95%, 95% and 80% from the *o-d*, *m-d* and $\alpha-d_1$ alcohols and 56% (both atoms) from the $\alpha-d_2$ alcohol—indicates a marked preference for loss of α -hydrogen in forming the $C_6H_7^+$ ion. Inasmuch as formation of the $C_7H_7O^+$ ion was shown to involve nearly random loss of hydrogen, $C_6H_7^+$ formed from it by path I should reflect the same random loss and show no preference for retention of ring over α -deuterium atoms in the spectra of the labeled species. Discrimination in formation of the $C_6H_7^+$ ion must then be attributed to path II, loss of CHO from the parent molecule-ion.

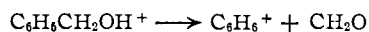
If all the hydrogen lost by path II came, with equal probability, from the two α -positions and the hydroxyl group, one would expect 100% retention of deuterium in the $C_6H_7^+$ fragment from the ring-*d* species, 67% retention from the $\alpha-d_1$ species, and 33% retention of both deuterium atoms from the $\alpha-d_2$. On this basis one may approximate the contribution of each of the two identified paths to formation of the $C_6H_7^+$ ion. The values of deuterium retention so calculated are

Deuterium retention, %	<i>o-d</i>	<i>m-d</i>	$\alpha-d_1$	$\alpha-d_2$
Calculated:				
Path I alone	90.5	88.6	87.1	73.5
Path II alone	100	100	67	33
55% path I, 45% path II	95	94	78	55
Observed	95	95	80	56

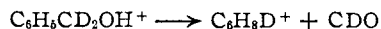
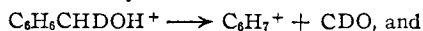
The 55:45 ratio of the contributions of the two paths is necessarily approximate. From metastable peaks, $C_6H_7^+$ ions are known to decompose further. The ratio was arrived at by assuming either that the $C_6H_7^+$ ions produced by the two paths have the *same structure* and energy content or that, in any case, the two groups decompose at about the same rate. Further, more than the two identified modes of formation of $C_6H_7^+$ may exist. Nonetheless, good agreement of calculated with observed values suggests that the two paths contribute about equally to $C_6H_7^+$ formation.

To account for the observed labeling of the $C_6H_7^+$ ions from labeled benzyl alcohols, some rearrangement must have occurred. Again, as in formation of the $C_7H_6O^+$ ion, the data preclude random commingling of the hydrogen atoms in all the parent ions decomposing to form $C_6H_7^+$ ions.

The $C_6H_6^+$ Ion.—Although label retention in the $C_6H_6^+$ ion cannot be deduced with any confidence, one path for its formation



is established by the metastable peaks at 56.7, 57.3 and 58.2 in the spectra of the unlabeled, singly labeled and doubly labeled alcohols.^{10,11}



The $C_6H_5^+$ Ion.—If possible slight interference from labeled $C_6H_5^+$ and, in the spectrum of the $\alpha-d_2$ alcohol, from doubly labeled $C_6H_3^+$ is neglected,

(10) J. H. Beynon, G. R. Lester and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(11) In the spectra of the $\alpha-d_1$ and $\alpha-d_2$ species, these metastable peaks may be due in part to the reactions

intensities at mass 77 measure the yields of unlabeled $C_6H_5^+$ ion. Furthermore, if the mass-77 intensity in the spectrum of the unlabeled alcohol is taken as a measure of total $C_6H_5^+$ yield, the percentage of unlabeled $C_6H_5^+$ formed from the labeled alcohols then can be computed: *o-d*, 26%; *m-d*, 24%; $\alpha-d_1$, 56%; $\alpha-d_2$, 33%. The only mode of formation for which metastable peaks were detected—at 76.1, 75.1 and 74.1—is loss of H_2 from $C_6H_7^+$.¹² This reaction alone—coupled with the assumption that hydrogen loss occurs in a random fashion—cannot account for the observed statistics. These can be accounted for by assuming that 78% of the $C_6H_5^+$ ions are so derived and that the other 22% consists of the elements of the original phenyl group:

Deuterium retention, %	<i>o-d</i>	<i>m-d</i>	$\alpha-d_1$	$\alpha-d_2$
Calculated:				
(a) Random loss of H_2 from $C_6H_7^+$	32	32	43	15
(b) Original phenyl group	0	0	100	100
78% (a), 22% (b)	25	25	55	34
Observed	26	24	56	33

A $C_6H_5^+$ ion derived from the original phenyl group might be formed either by direct dissociation of the $C_6H_5-CH_2OH^+$ bond in the molecule-ion or by a secondary reaction of a benzaldehyde-ion intermediate, as was suggested also for the $C_7H_6O^+$ ion. The lack of scrambling of hydrogens in these processes is consistent with the observed labeling of the complementary CH_3O^+ and CHO^+ ions discussed below. In the mass spectrum of benzaldehyde, $C_6H_5^+$ is the most abundant ion and it is derived almost solely from the original phenyl group.⁹

Ions in the CH_nO^+ Region

In the CH_nO^+ region, two ions, CH_3O^+ and CHO^+ , attract special attention both because they give rise to prominent peaks and because their intensities in the spectra of the variously deuterated alcohols are simply related numerically.

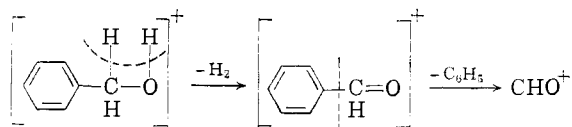
The CH_3O^+ Ion.—Intensities of the unlabeled and ring-*d* alcohols at mass 31, $\alpha-d_1$ at 32, and $\alpha-d_2$ at 33 are nearly enough equal to leave little doubt that they are due to CH_3O^+ ion containing the elements of the original side-chain. The carbon-carbon bond to the phenyl group is cleaved with no detectable exchange of hydrogen atoms between the fragments. Such behavior contrasts sharply with that of toluene, in which neither the $C_6H_5^+$ nor the CH_3^+ ion contains solely the elements of the corresponding group in the original molecule.¹³ The reaction of benzyl alcohol seems to reflect the influence of the hydroxyl group and is in keeping with the observed cleavage in aliphatic alcohols¹⁴ of the $C-CH_2OH$ bond—also with no accompanying hydrogen exchange.

(12) This reaction has been reported in the dissociation of several other benzene derivatives (see refs. 4 and 6). It seems to be characteristic of $C_6H_7^+$ ions regardless of the parent molecule.

(13) P. N. Rylander and S. Meyerson, *J. Chem. Phys.*, **27**, 1116 (1957).

(14) J. G. Burr, *J. Phys. Chem.*, **61**, 1477 (1957); L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957); W. H. McFadden, M. Lounsbury and A. L. Wahrhaftig, *Can. J. Chem.*, **36**, 990 (1958).

The CHO⁺ Ion.—Intensities at masses 29 and 30 are accounted for by CHO⁺ ions of which none is labeled in the ring-*d* alcohol, half are labeled in the α -*d*₁, and all are labeled in the α -*d*₂. These statistics suggest the reaction sequence



The second step of the path shown is known from study of the mass spectra of labeled benzaldehydes.⁹ An alternative possible route—loss of H₂ from CH₂OH⁺—cannot be ruled out, but such a reaction is not prominent in the spectra of aliphatic alcohols.¹⁴ Moreover, one would expect further dissociation of CH₂OH⁺ to be preceded or accompanied by extensive loss of identity of hydrogen atoms.

Conclusion

Any appreciable benzaldehyde impurities that might have escaped detection would compromise the data for C₇H₆O⁺, C₆H₅⁺ and CHO⁺. However, the evident consistency among the spectra of the five differently labeled benzyl alcohols seems to rule out such impurities. Moreover, even if benzaldehyde were solely responsible for the observed C₇H₆O⁺ intensities, it could account for no more than half the observed C₇H₆O⁺ intensities, 5% of the C₆H₅⁺ and 3% of the CHO⁺. Thus, the characteristic features of the spectrum resulting from these ions must be attributed to benzyl alcohol itself.

Intensity of the C₇H₆O⁺ ion—benzaldehyde or an isomeric structure—comprises only 0.5% of the total fragment-ion intensity in the mass spectrum of benzyl alcohol. However, if, as suggested, the entire observed yields of C₇H₆O⁺ and CHO⁺ and 22% that of C₆H₅⁺ result from further reactions of benzaldehyde ions, the fraction of the total fragment-ion yield resulting from a primary dissociation to form benzaldehyde ion rises to 6.8%. The intensities attributed to further decomposition products of the C₇H₆O⁺ ion, relative to the intensity of C₇H₆O⁺ itself, are much greater than are those of the corresponding ions in the spectrum of benzaldehyde. Thus, the C₇H₆O⁺ ion derived from benzyl alcohol appears to be formed in a different distribution of excitation states from those formed directly by electron impact on benzaldehyde.

The mass spectrum of benzyl alcohol presents a more complex network of competing and consecutive reactions than do those of toluene, ethylbenzene and higher alkylbenzenes.^{4,6,8,13,15} The added complexity evidently results from the presence in the molecule of a second functional group that can also serve as a center of reactivity. The factors that make interpretation of the spectra of such molecules more difficult can, at the same time, serve as probes to explore aspects of competition and interaction between functional groups within a molecule.

(15) S. Meyerson, *Appl. Spectry*, **9**, 120 (1955); P. N. Rylander, S. Meyerson and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957); J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **81**, 4116 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

Kinetic and Electron Spin Resonance Studies of the Radiation Decomposition of Crystalline Choline Chloride^{1,2}

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The free radicals that accompany the radiation decomposition of crystalline choline chloride were investigated by electron spin resonance spectroscopy. The e.s.r. spectrum obtained from the normal compound was compared to the spectra obtained from selectively deuterated choline chlorides. The differences observed in these spectra were used to assign a structure to the radical. The radical decay reaction was found to be of 3/2 order; this indicates that the observed radicals function as a chain-initiating reactant and not as an intermediate in the radiation decomposition reaction. A kinetic mechanism for this reaction is proposed. The study of the radiation damage was extended to cover a dose range from 0.002 to 200 megarads. An unusual damage-saturation phenomenon was observed at approximately 12% decomposition.

The anomalous radiation sensitivity of choline chloride, [(CH₃)₃NCH₂CH₂OH]⁺Cl⁻, was first recognized in 1953.^{3,4} It was observed that crystalline choline chloride labeled with C¹⁴ rapidly decomposed to trimethylamine hydrochloride and acetaldehyde. The *G*-value for the decomposition (molecules decomposed/100 e.v. of radiation absorbed) was 490. In contrast, *G*-values for the

radiation decomposition of organic compounds are almost invariably found in the range of 1–10. In the present study experimental conditions have been found that give *G*-values as high as 55,000. Cobalt-60 γ -rays (1.1 and 1.3 Mev.), 4.5 Mev. electrons and C¹⁴ betas (50 Mev. average energy) all appear equally effective in initiating this decomposition.

Ever since the earliest work, the large *G*-values have been attributed to a chain decomposition reaction. The radiation damage develops gradually over a number of hours and can be deferred indefinitely by storing the irradiated samples at -196°. The radicals produced by irradiation of crystalline choline chloride have been observed to disappear

(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

(2) Abstracted from a thesis submitted by Robert O. Lindblom in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of California.

(3) B. M. Tolbert, *et al.*, *J. Am. Chem. Soc.*, **75**, 1867 (1953).

(4) R. M. Lemmon, M. A. Parsons and D. M. Chin, *ibid.*, **77**, 4139 (1955).