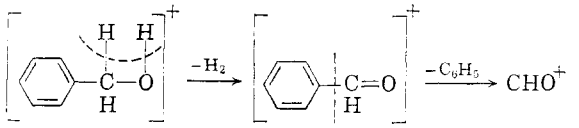
The CHO^+ Ion.—Intensities at masses 29 and 30 are accounted for by CHO^+ ions of which none is labeled in the ring-*d* alcohol, half are labeled in the α-d_1, and all are labeled in the α-d_2. These statistics suggest the reaction sequence



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 H_2 from CH_2OH^+—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 CH_2OH^+ 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 $C_7H_5O^+$, $C_6H_5^+$ 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 $C_7H_6O^+$ intensities, it could account for no more than half the observed $C_7H_5O^+$ intensities, 5% of the $C_6H_5^+$ 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 $C_7H_6O^+$ 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 $C_7H_5O^+$ and CHO^+ and 22% that of $C_6H_5^+$ 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 $C_7H_6O^+$ ion, relative to the intensity of $C_7H_6O^+$ itself, are much greater than are those of the corresponding ions in the spectrum of benzaldehyde. Thus, the $C_7H_6O^+$ 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. Spectr.*, **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]

BY ROBERT O. LINDBLOM, RICHARD M. LEMMON AND MELVIN CALVIN

RECEIVED JANUARY 28, 1961

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, $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$, was first recognized in 1953.[3,4] It was observed that crystalline choline chloride labeled with C^{14} 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 C^{14} 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).

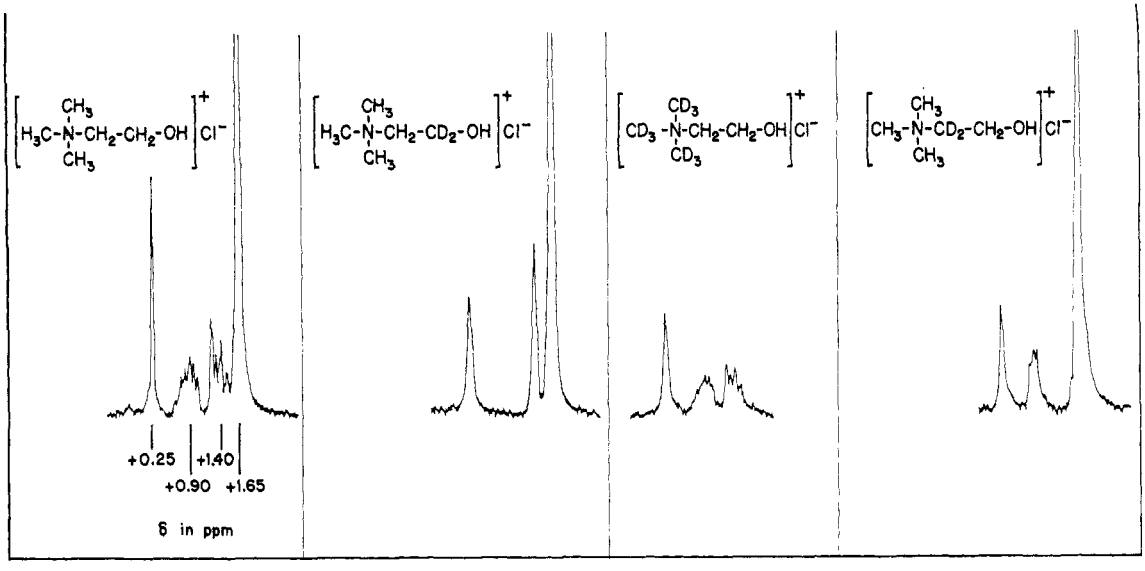


Fig. 1.—N.m.r. spectra of deuterated choline chlorides.

over about the same time required to show the large radiation sensitivity.[5] This observation led to the previously held belief that the radicals, observed by spin resonance (e.s.r.) spectroscopy, were the chain-propagating species. This belief has been abandoned as a result of the present work, in which the dependence of radical concentrations in irradiated crystalline choline chloride on both initial irradiation dose and the post-irradiation chain propagation time have been studied.

We have also used e.s.r. spectroscopy to shed light on the character of the radicals that appear in the irradiated compound. Selective deuteration of choline chloride was employed to establish the localization of the unpaired electron in the radical. The character of the e.s.r. spectrum of irradiated choline chloride, together with those exhibited by the selectively deuterated compounds, has led to the tentative assignment of a structure for the radicals that accompany the radiation decomposition process.

Experimental

Compounds Used.—The choline chloride used in this work was the Eastman Kodak Co. "white label" product; it was recrystallized from ethanol–ether solution. Its identity was checked by elemental analysis (Calcd.: C, 43.1; H, 10.1. Found: C, 43.1; H, 10.3.). Its nuclear magnetic resonance (n.m.r.) spectrum is shown in Fig. 1. The deliquescent nature of choline chloride necessitated storing it in a vacuum desiccator over P_2O_5 and handling it in a drybox. The radiation decomposition studies were made with 5 to 10 mg. of finely ground sample in a sealed, evacuated tube. Before the sample tubes were sealed, the sample was dried by heating at 100° for 0.5 hour at a pressure of 100 μ or less.

The selectively-deuterated compounds were prepared as follows (details are recorded elsewhere)[6]

(1) $CD_3CO_2D \longrightarrow CD_3CO_2Ag \xrightarrow{Br_2,\ CCl_4} CD_3Br \xrightarrow{NH_2CH_2CH_2OH} [(CD_3)_3NCH_2CH_2OH]^+Br^- \longrightarrow [(CD_3)_3NCH_2CH_2OH]^+Cl^-$

The product was characterized by its C and H analysis (Calcd.: C, 40.4; H, 15.6. Found: C, 40.5; H, 14.9) and its n.m.r. spectrum (Fig. 1).

(2) $CD_3CO_2D \xrightarrow{Br_2,\ PBr_3} BrCD_2CO_2D \xrightarrow{C_6H_5COBr} BrCD_2COBr \xrightarrow{C_2H_5OH} BrCD_2CO_2C_2H_5 \xrightarrow{(CH_3)_2NH} (CH_3)_2NCD_2CO_2C_2H_5 \xrightarrow{LiAlH_4} (CH_3)_2NCD_2CH_2OH \xrightarrow{CH_3I} [(CH_3)_3NCD_2CH_2OH]^+I^- \longrightarrow [(CH_3)_3NCD_2CH_2OH]^+Cl^-$

The product was characterized by its C and H analysis (Calcd.: C, 42.4; H, 11.4. Found: C, 42.5; H, 11.5) and its n.m.r. spectrum (Fig. 1).

(3) $[(CH_3)_3NCH_2CD_2OH]^+Cl^-$ was prepared by the same route as reaction 2 (above) except that the starting material was ordinary acetic acid, and $LiAlD_4$ was employed instead of $LiAlH_4$. The product was characterized by its C and H analysis (Calcd.: C, 42.4; H, 11.4. Found: C, 42.7; H, 11.2) and by its n.m.r. spectrum (Fig. 1).

Irradiation Procedures and ESR Spectra.—The crystalline choline chloride and its deuterio analogs were irradiated with a 4.5 Mev. linear electron accelerator. This apparatus and the techniques for using it to irradiate samples at low temperatures were described previously.[4,7] The use of the electron accelerator enabled us to avoid the problem of F centers in the glass interfering with the e.s.r. measurements. Our irradiations were performed on 5- to 10-mg. samples in evacuated Pyrex tubes (3 mm. o.d., about 12 cm. long). The sample was irradiated (at $-170 \pm 20°$) in one end of the tube and the e.s.r. determinations were made (at room temperature) after the sample had been tapped down to the other end. (The glass at the unirradiated end of the tube was found to accumulate no detectable electron spins during the irradiations.) Between irradiations and the spin-resonance or percentage decomposition determinations, all samples were stored at $-196°$.

The above procedure is not easily adaptable to single-crystal work, where alignment of the crystal in the external magnetic field is necessary. Consequently, the spectra described in this report were all obtained on polycrystalline material. This procedure seems in order in view of the e.s.r. spectral changes known to occur when single crystals of irradiated choline chloride are rotated, in the spectrometer cavity, about their transverse axis (with the axis of rotation perpendicular to the external magnetic field).[8] When the long axis (choline chloride crystallizes in long, orthorhombic needles) was perpendicular to the external field, the spectrum was very similar to that of a polycrystalline sample; the only apparent difference was a slightly improved resolution.

(5) R. M. Lemmon, *et al.*, *J. Am. Chem. Soc.*, **80**, 2730 (1958).

(6) R. O. Lindblom, University of California Radiation Laboratory Report No. UCRL-8910, October 19, 1959.

(7) R. M. Lemmon and D. F. Mosier, *Rad. Res.*, **4**, 373 (1956).

(8) B. Fingerman and R. M. Lemmon, University of California Radiation Laboratory Report No. UCRL-8698, March, 1959, p. 13.

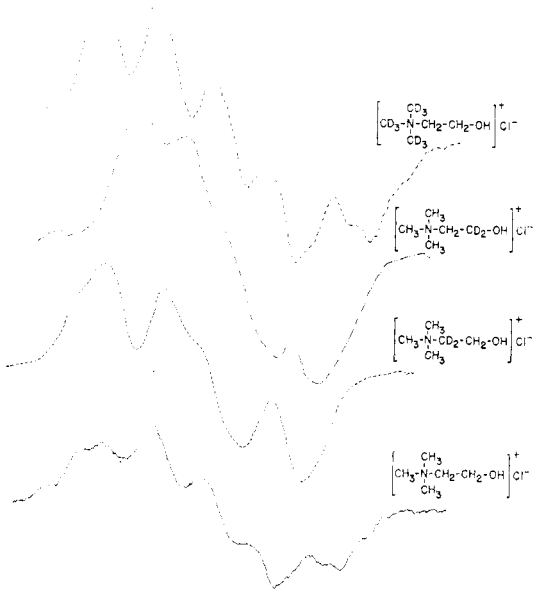


Fig. 2.—E.s.r. spectra of irradiated choline chloride and its deuterated analogs.

When the long axis was parallel to the field, a complex and only partially resolved thirteen-line spectrum appeared.

The e.s.r. spectra were taken at a frequency of 9.3 kmc./sec. on a spectrometer similar to the one developed by Beringer and Castle.[9]

Radical Concentration.—The quantitative e.s.r. measurements were made by comparing simultaneously the signal from the sample with the signal from a standard. The standard was a solid solution of Mn^{++} in purified MgO. This solid solution was dispersed as a finely ground powder in a polyethylene cylinder that surrounded the sample. This standard was very stable and gave a sharp six-line spectrum with practically no signal at the points of the sample signal maximum. It was used as a secondary standard and calibrated with an aqueous $MnCl_2$ solution which was treated as the primary standard.[6]

Radiation Damage.—Since almost all (> 95%) of the decomposed choline is accounted for in the chemical forms of trimethylamine and acetaldehyde,[3] we chose the measurement of the amine as the most convenient and sensitive index of radiation damage in these experiments. It was determined by adding (in a vacuum-type Tomkin–Kirk cell[6]) excess base to a weighed portion of the irradiated choline chloride. The evolved trimethylamine was absorbed in standard H_2SO_4 and the acid was titrated to determine the amount of amine evolved. The results obtained by these analyses are in good agreement with those obtained by the Reineckate method.[4]

Calculations.—The G-value is calculable from the dose and decomposition by the expression

$$G = P(69.0)/D_m$$

where

P = percentage decomposition of the choline chloride
D_m = radiation dose given the sample in megarads (10^8 ergs/g.)

The dose, D_m, was calculated from $D_m = 0.185Q_s$, where Q_s is the electron density (μ coulombs/cm.^{2}) put through the sample. This dose calculation is derived from the Feather relationship[10] and is intended for thin samples in a uniform beam. It ignores back scatter and secondary electrons from the windows and sample holder. Although there may be significant errors (possibly as much as ±20%) in the absolute dosimetry, the relative dosimetry should be quite accurate.

Results and Discussion

Radical Structure.—In Fig. 2 are shown the e.s.r. spectra of irradiated samples of choline chloride and its deuterated analogs. All of the spectra were taken at room temperature since preliminary work showed that the resolution at that temperature was better than at −170° (Fig. 3). Temperatures higher than room temperature accelerate the rate of disappearance of the radical and, consequently, were not used. The spectrum of irradiated $[(CH_3)_3NCH_2CH_2OD]^+Cl^-$ was also determined and was found to be very similar to that of the undeuterated compound.

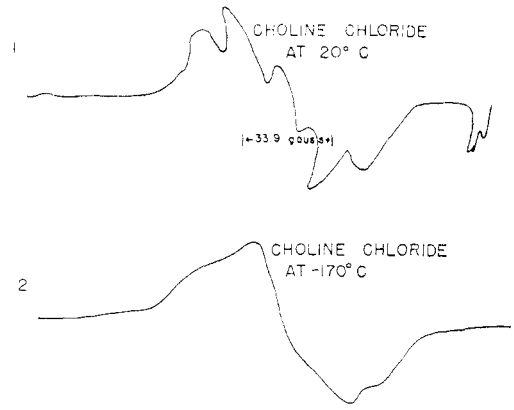


Fig. 3.—E.s.r. spectra of irradiated choline chloride at room temperature and at −170°.

The e.s.r. spectrum of irradiated choline chloride (undeuterated, bottom line) shows five peaks with an intensity ratio of about 1-3-3-3-1; no nitrogen splitting is apparent. If the unpaired electron showed a hyperfine interaction with four equivalent hydrogen atoms, the expected intensity ratio would be in the binomial distribution of 1-4-6-4-1. The 1-3-3-3-1 distribution more nearly approximates the case of an interaction with three protons having interaction constants of 1,1,2 (*i.e.*, an intensity ratio 1-2-2-2-1). Another possibility is an interaction with the nitrogen and two equivalent protons; this could give an intensity ratio of 1-3-4-3-1. However, the only hypothesis consistent with the e.s.r. spectra from the deuterated choline chlorides (discussed below) is that of roughly equivalent interactions between the unpaired electron and four hydrogen atoms. The failure to observe the 1-4-6-4-1 distribution may be attributed to two factors. The first and most important is the diffuse, overlapping line structure of the spectrum; the second is that the coupling constants with the four protons are probably not exactly equal.

The e.s.r. spectrum obtained from the methyl-deuterated choline chloride (Fig. 2, top line) has nearly all the characteristics of the irradiated normal compound. It differs only in having more distinct hyperfine structure. This indicates that part of the less distinct hyperfine structure in the undeuterated (normal) compound is due to diffuse, weak interactions of the unpaired electron with the nine methyl-group hydrogens. This is consistent with the observation that irradiated choline chloride shows decreased resolution at −170°. The lower temperature would result in less motional narrowing,[11] *i.e.*, a smearing out of hydrogen hyperfine interactions.

(9) R. Beringer and J. G. Castle, *Phys. Rev.*, **78**, 581 (1950).
(10) L. E. Glendenin, *Nucleonics*, **2**, No. 1, 12 (1948).
(11) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworth Scientific Publications, London, 1958, p. 120.

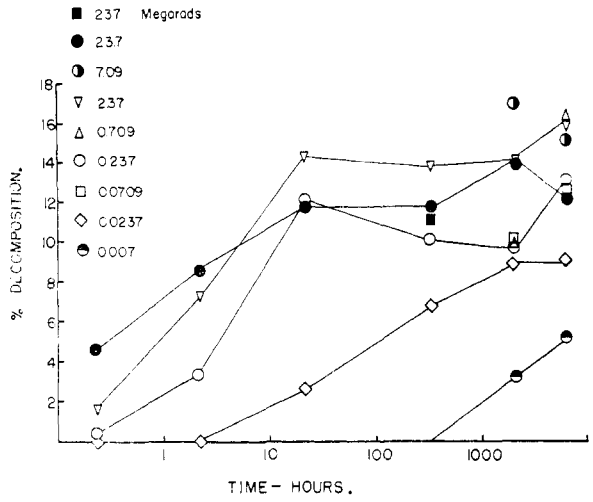


Fig. 4.—Decomposition (%) of irradiated choline chloride as a function of chain-propagation time and radiation dose.

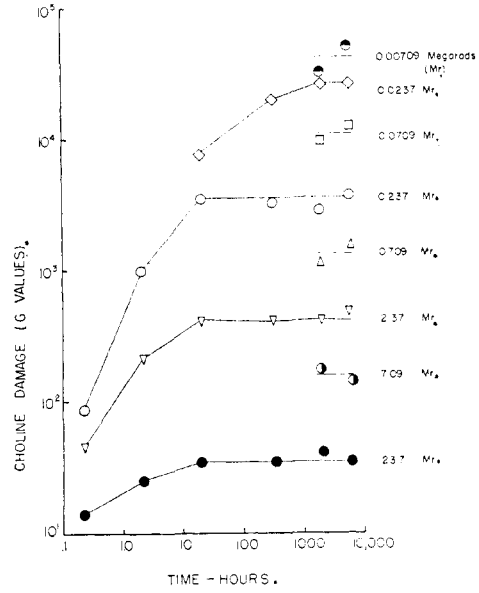


Fig. 5.—*G*-Values of irradiated choline chloride as a function of chain-propagation time and radiation dose.

Deuteration of choline chlorine in either the O-methylene or N-methylene position reduces the five-line e.s.r. hyperfine spectrum to a three-line spectrum typical of an unpaired electron interacting with two hydrogens. The almost equal hyperfine splitting indicates that the unpaired-electron density is only slightly greater at the O-methylene carbon than at the N-methylene carbon. In both the methylene hydrogen spectra there is also a hint that the methylene hydrogens are not exactly equivalent. Especially in the O-methylene case (third spectrum from the top in Fig. 3) a splitting to four lines is suggested.

The following model for the radicals is consistent with the observed e.s.r. spectrum:

$$[(CH_3)_3NCH_2CH_2OH]^+Cl^- \rightsquigarrow$$

$$(CH_3)_3\overset{+}{N}\cdot\cdot CH_2CH_2OH\cdots Cl^-$$

$$\updownarrow$$

$$(CH_3)_3\overset{+}{N}\cdot CH_2CH_2\dot{O}H\cdots Cl^-$$

Failure to find a recognizable hyperfine spectrum from the nitrogen radical is attributed to excessive broadening by the nine protons and/or coupling between the positive nitrogen and the crystal lattice. Failure to observe any effect from the hydroxyl hydrogen can be attributed to hydrogen bonding to the chloride ion. Evidence for this kind of bonding in choline chloride has already been obtained.[12] The observed e.s.r. spectrum has been attributed to a single radical because the observed one-thousand-fold decay in radical concentration caused no significant change in the e.s.r. spectrum.

This hydrogen bonding, or various crystal-field forces, could also provide the necessary activation energy to prevent immediate recombination of the radicals. The model is consistent with the known major products of irradiation: trimethylamine hydrochloride and acetaldehyde.

Chemical Studies.—The dependence of the radiation damage on both the initial dose and the post-irradiation chain propagation time are shown in Figs. 4 and 5. Figure 4 expresses the radiation sensitivity in terms of the percentage of decomposition observed. The more usual representation of the radiation sensitivity as a *G*-value is shown in Fig. 5. Since the *G*-value represents damage per unit dose, it is a measure of the decomposition chain length. The data at low damage levels (*i.e.*, less than 10%) does not appear to be unusual. However, at about 12% decomposition some process intervenes that makes further decomposition difficult; in fact, no decomposition greater than 17% was observed. This upper limit to observable decomposition was quite unexpected and its explanation probably lies in the strains caused by the decomposition. An ionic crystal structure with 12% of its cations chemically altered must be under considerable strain, and this strain may block the chain decomposition. The dependence of the radiation sensitivity of choline chloride on its crystal form has been observed recently. Serlin[13] has reported that choline chloride at 150° loses its extreme radiation sensitivity, and Collin[14] has interpreted this as the result of a phase change which occurs spontaneously at about 75°. The absence of a dose saturation effect in experiments where a continuous room temperature irradiation was used[4] can best be explained in terms of radiation annealing.[15]

E.s.r. Studies.—An effort was made to study the radical concentrations by e.s.r. spectroscopy over the same range of dose and chain-propagation times as those covered with the chemical radiation-damage studies. The cumulative nature of the chemical damage allowed chemical studies to be made at much lower radiation doses and longer propagation times (*i.e.*, lower radical concentra-

(12) M. E. Senko and D. H. Templeton, *Acta Cryst.*, **13**, 281 (1960).

(13) I. Serlin, *Science*, **126**, 261 (1957).

(14) R. L. Collin, *J. Am. Chem. Soc.*, **79**, 6086 (1957).

(15) G. J. Dienes and G. H. Vineyard, "Radiation Effects in Solids," Interscience Publishers, Inc., New York, N. Y., 1957, pp. 51 and 64.

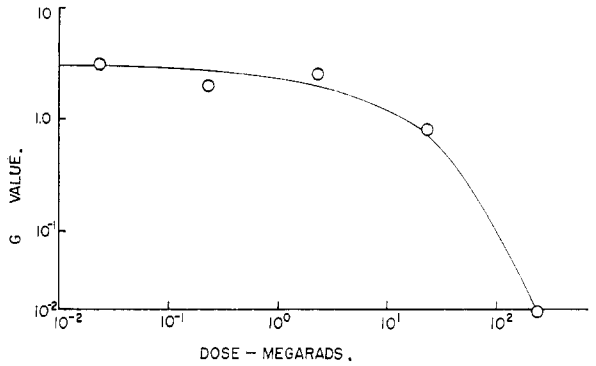


Fig. 6.—Radical G-values as a function of dose.

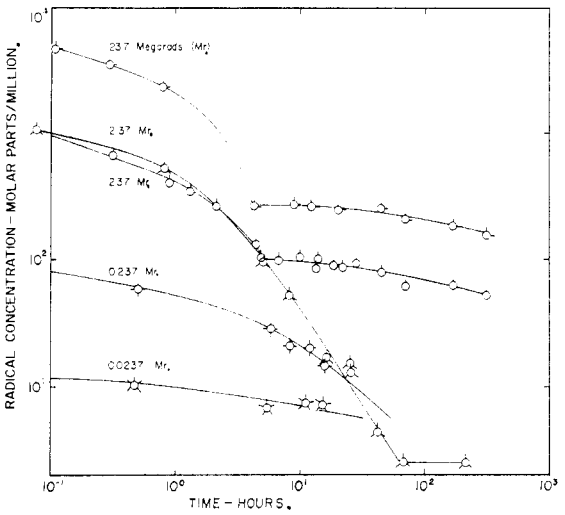


Fig. 7.—Radical concentrations in irradiated choline chloride as a function of radiation dose and chain propagation time.

tions) than those at which the radicals could be observed with the e.s.r. spectrometer. Figure 6 shows the G-values for radical production as a function of dose. Figure 7 shows the radical concentrations as a function of radiation dose and propagation time. The order of the radical decay reaction was determined by abstracting the decay rate data from Fig. 7 at points before the appearance of the damage-saturation effect, that is, before the abrupt reduction of the radical decay rates. The decay rates appear in Fig. 8 in a log–log plot against the radical concentration. The slope indicates a 3/2 order reaction and is evidence that the radicals are not intermediates in the chain decomposition reaction. An intermediate in the chain decomposition would, of necessity, have a first- or second-order decay constant. It would be first order if the apparent decay was a rearrangement to a radical that escaped observation and second order if a dimeric disproportionation or a dimerization were the termination step. A kinetic model first proposed by Rice and Herzfeld[16] provides a reasonable explanation for our observed 3/2 order for the radical decay. Figure 9 shows the model we tentatively propose for the choline decomposition reaction. Figure 10 shows the corresponding integrated

(16) F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

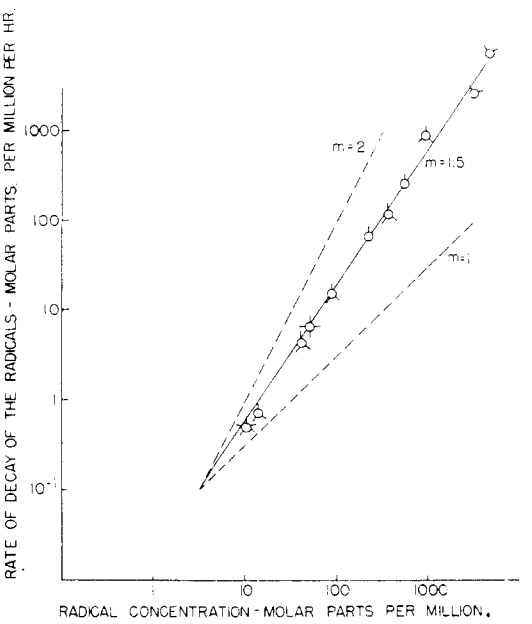


Fig. 8.—Radical decay rate as a function of radical concentration in irradiated choline chloride.

kinetic equations. In this model, the observed radicals have the role of an initiator for the decomposition mechanism and not the role of an intermediate.

$$\text{Cho} \rightsquigarrow \text{Cho}^* \xrightarrow{\text{fast}} \cdot\text{Cho}\cdot \quad \text{biradical formation (0)}$$

$$\cdot\text{Cho}\cdot + \text{Cho} \xrightarrow{k_1} (\text{CH}_3)_3\overset{+}{\text{N}}\text{H} + \text{AcH} + (\text{CH}_3)_3\overset{+}{\text{N}}\cdot + \text{AcH}_2\cdot \quad \text{initiation (1)}$$

$$\text{AcH}_2\cdot + \text{Cho} \xrightarrow{k_2} (\text{CH}_3)_3\overset{+}{\text{N}}\text{H} + \text{AcH} + \text{AcH}_2\cdot \quad \text{propagation (2)}$$

$$\text{AcH}_2\cdot + \cdot\text{Cho}\cdot \xrightarrow{k_3} (\text{CH}_3)_3\overset{+}{\text{N}}\text{H} + \text{AcH} + \text{AcH}_2\cdot \quad \text{pre-termination (3)}$$

$$\text{AcH}_2\cdot + (\text{CH}_3)_3\overset{+}{\text{N}}\cdot \xrightarrow{k_4} \text{Cho} \quad \text{termination (4)}$$

$$\text{Cho} = (\text{CH}_3)_3\overset{+}{\text{N}}\text{CH}_2\text{CH}_2\text{OH}$$

$$\text{Cho}\cdot = (\text{CH}_3)_3\overset{+}{\text{N}}\cdot \cdot\text{CH}_2\text{CH}_2\text{OH}\text{---}\text{Cl}^- \quad \text{(the e.s.r. obsd. radical)}$$

$$\text{CH}_2\text{CH}_2\dot{\text{O}}\text{H}\text{---}\text{Cl}^-$$

$\text{AcH}_2\cdot = \text{CH}_3\cdot\text{CHOH}$; $\text{AcH} = \text{CH}_3\text{CHO}$

Fig. 9.—A kinetic model for choline chloride radiation damage.

The following hypothesis summarizes our current ideas of the sequence of events in irradiated choline chloride. Initially, the radiation acts to excite a choline chloride molecule. The excited molecule has antibonding orbitals that lead to the fissure of the nitrogen-to-methylene bond. After the breaking of this bond, the radical fragments are stabilized by hydrogen bonding and crystal cage effect. The ethanol fragment of the biradical gives rise to the observed e.s.r. signal. The $(\text{CH}_3)_3\text{N}\cdot^+$ is not seen because of excessive broadening by the

nine protons. The $AcH_2\cdot$ radicals are not seen because they have only a very low concentration compared to that of the observed radical (·Cho·). The observed radical reacts either with its cage (to propagate the decomposition reaction) or terminates with another radical that propagates into the vicinity.

The data points in Fig. 4 below 6% and for times less than 100 hr. give a reasonable fit to eq. IV of Fig. 10. The data at higher damage levels fall in the dose saturation region, and thus no kinetic information can be obtained from this region. The data at longer times fall in a separate group. Here, $k_1t/2$ is, presumably, no longer $<< 1$; *i.e.*, the simplifying assumptions for eq. IV are no longer valid. At the present time there are not sufficient data to solve for the rate constants in eq. III.

A steady state approximation gives:

$$AcH_2\cdot = \sqrt{k_1/k_4}\,(\cdot Cho\cdot)^{1/2} \qquad I$$

$$d(\cdot Cho\cdot)/dt = -k_1(\cdot Cho\cdot) - k_a\cdot\sqrt{k_1/k_4}\,(\cdot Cho\cdot)^{3/2} \qquad II$$

Integrating this, substitution in the propagation eq. 2 and integrating again gives

$$Cho - Cho_0 = \frac{k_1k_2t}{k_3} - 2\frac{k_2}{k_3}\log\left\{\left(\frac{k_3}{\sqrt{k_1k_4}}\right)(\cdot Cho_0\cdot)^{1/2}(e^{k_1t/2} - 1) + e^{k_1t/2}\right\} \qquad III$$

where Cho_0 = initial concn. of choline

$Cho_0\cdot$ = initial concn. of ·Cho·

In two limiting cases this simplifies

where $\frac{k_1t}{2} \ll 1$ $\quad Cho - Cho_0 \approx -\left(k_2\sqrt{\frac{k_1}{k_4}}\,(\cdot Cho_0\cdot)^{1/2}t\right)$ IV

where $\frac{k_1t}{2} \gg 1$ $\quad Cho - Cho_0 \approx \frac{-2k_2}{\sqrt{k_1k_4}}\,(\cdot Cho\cdot)^{1/2}$ V

Fig. 10.—Integration of the kinetic model for choline chloride radiation damage.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, N. J.]

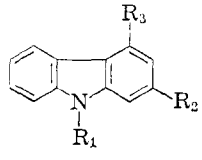
Thermal Reactions of Substituted Aryl Azides: The Nature of the Azene Intermediate

BY GERALD SMOLINSKY

RECEIVED DECEMBER 2, 1960

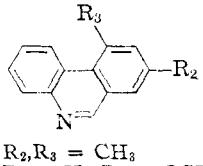
Six aryl azides were prepared and thermally decomposed. In two cases, *o*-azidocumene (XIX) and *o*-azidophenylcyclohexane (XX), the pyrolysis products were identified as 3-methyl-2,3-dihydroindole (XX) and hexahydrocarbazole, respectively. It is proposed that these products were formed by insertion of an azene group into the C–H bond of a primary and secondary carbon, respectively. The mechanism of these reactions is discussed in terms of a singlet or triplet azene intermediate.

In an earlier paper it was reported that the decomposition of 2-azido-2′,4′,6′-trimethylbiphenyl (I) resulted in the formation of 2,4,9-trimethylcarbazole (II) and 8,10-dimethylphenanthridine (III), presumably *via* the azene intermediate IV.[1] The present work was undertaken with the hope of gaining some insight into the electronic nature of the reacting azene intermediate—specifically as to whether this species behaves as an electrophile having a paired electronic configuration (–N:) or as a diradical –N.)·



I, $R_1,R_2,R_3 = CH_3$
VIII, $R_1 = OCH_3$; $R_2,R_3 = H$
X, $R_1 = OH$; $R_2,R_3 = H$
XII, $R_1,R_2,R_3 = OCH_3$
XIV, $R_1 = CH_3$; $R_2 = H$; $R_3 = OCH_3$

II, $R_1R_2R_3 = CH_3$
IX, $R_1,R_2 = H$; $R_3 = OCH_3$

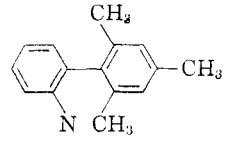


III, $R_2,R_3 = CH_3$
XVI, $R_2 = H$; $R_3 = OCH_3$

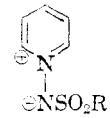
(1) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960).

It appears that in the substitution reaction of aromatic nuclei by the azene formed from thermal decomposition of benzenesulfonyl azide, the intermediate reacts as an imino diradical.[2] Supporting this conclusion is the observation that methyl acrylate and acrylonitrile polymerized at 110° in the presence of small amounts of decomposing benzenesulfonyl azide; the polymerization of acrylonitrile was inhibited by the presence of traces of hydroquinone or *p*-benzoquinone.[3]

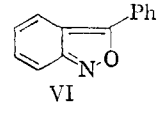
The following reactions can be explained by postulating an electrophilic azene intermediate. Decomposition of arenesulfonyl azides in pyridine



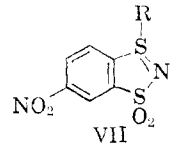
IV



V



VI



VII

(2) J. F. Heacock and M. T. Edmison, *ibid.*, **82**, 3460 (1960); O. C. Dermer and M. T. Edmison, *ibid.*, **77**, 70 (1955); O. C. Dermer and M. T. Edmison, *Chem. Revs.*, **57**, 77 (1957).

(3) K. Ziegler, W. Deparade and H. Kuhlhorn, *Ann.*, **567**, 151 (1950); K. Ziegler, W. Deparade and W. Meye, *ibid.*, **567**, 141 (1950).