

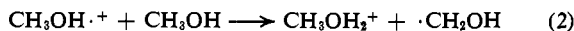
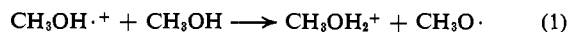
Communications to the Editor

Electron Spin Resonance Studies of Radical Trapping in the Radiolysis of Organic Liquids. I. Evidence for the Primary Formation of the Methoxy Radical in Methanol¹

Sir:

Although the technique of "spin trapping"² (radical trapping followed by esr identification of a more stable adduct radical) has been employed successfully in recent years for the study of free-radical intermediates in chemical reactions,²⁻⁴ its application to radiation chemistry seems to have been limited heretofore to the irradiation of solids⁵ and aqueous solutions.⁶ We now wish to report on the utilization of this technique to resolve the persistent problem of primary radical formation in the radiolysis of deaerated liquid methanol.^{7,8}

It has been widely suggested⁷ that the facile ion-molecule reactions 1 and 2 contribute to radical forma-



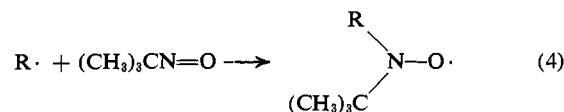
tion in the radiolysis of methanol. Mass spectroscopic studies^{9,10} show that these reactions occur with about equal probability in the vapor, but this result may not apply to the liquid phase where strong hydrogen bonding is present. Accordingly, information is desirable about the initial distribution of radicals in the liquid. Previous studies^{7,8} have provided abundant evidence for the participation of the hydroxymethyl radical in the radiation chemistry of liquid and solid methanol, but it has been recognized⁷ that this radical could also be produced by other processes including the secondary reaction 3 from a methoxy radical precursor. How-



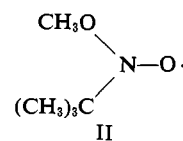
ever, definitive proof of methoxy radical formation has been lacking although its intermediacy was inferred from the analysis of reaction products derived from the radiolysis of benzene-methanol mixtures¹¹ and, more

recently, from the pulse radiolysis detection of an oxidizing species.¹²

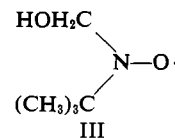
In this work we have used 2-methyl-2-nitrosopropane ((CH₃)₃C—N=O, I) as a radical trap^{3,4} to produce nitroxide radicals according to reaction 4. The esr



hyperfine structure of these nitroxides is generally characteristic of the trapped radical and identification is straightforward, as described below. Figure 1 shows esr spectra recorded after γ irradiation of solutions containing different concentrations of I in methanol at -78° . The upper spectrum obtained at the higher scavenger concentration ($10^{-1} M$ based on complete dissociation of the dimer¹³) consists almost exclusively of a ¹⁴N triplet of 1:3:3:1 quartets indicating hfs from three equivalent hydrogens in the trapped radical. Assignment of these lines to the methoxy *tert*-butyl nitroxide II follows from the magnitude of the



nitrogen splitting which is characteristic of alkoxy radical addition to I^{4b} and from the close correspondence of the hyperfine constants $a^{\text{N}} = 29.7 \text{ G}$ and $a^{\text{H}} = 1.6 \text{ G}$ to the values of 29.4 and 1.4 G reported^{3b} for the similar nitroxide radical produced by methoxy radical addition to 2-methyl-2-nitrosobutan-3-one. The lower spectrum in Figure 1 corresponding to the smaller scavenger concentration of $10^{-2} M$ shows that the lines from II are now accompanied by another prominent set of components (¹⁴N triplet of 1:2:1 triplets) which are readily identified as belonging to the hydroxymethyl *tert*-butyl nitroxide III, the values of the hyperfine con-



stants, $a^{\text{N}} = 14.5 \text{ G}$ and $a^{\text{H}} = 4.1 \text{ G}$, being in good agreement with those previously reported for this radical.^{4b,14} Comparison of the two spectra shows that lines from III are barely discernible in the upper spectrum.

Parallel results were obtained from experiments with CH₃OD and CD₃OD at -78° . As expected, the esr spectra of the nitroxides produced from CH₃OD

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(2) (a) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **90**, 5909 (1968); (b) *ibid.*, **91**, 4481 (1969); (c) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

(3) (a) C. Lagercrantz and K. Torssell, *Acta Chem. Scand.*, **22**, 1935 (1968); (b) S. Forshult, C. Lagercrantz, and K. Torssell, *ibid.*, **23**, 522 (1969); (c) C. Lagercrantz, *J. Phys. Chem.*, **75**, 3466 (1971).

(4) (a) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, **90**, 7141 (1968); (b) M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. B*, 395 (1970); (c) M. J. Perkins, *Chem. Soc., Spec. Publ.*, No. 24, 97 (1970).

(5) C. Lagercrantz and S. Forshult, *Nature (London)*, **218**, 1247 (1968).

(6) (a) K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **72**, 3387 (1968); (b) D. Behar and R. W. Fessenden, *ibid.*, **76**, 1710 (1972).

(7) F. S. Dainton, G. A. Salmon, and P. Wardman, *Proc. Roy. Soc., Ser. A*, **313**, 1 (1969).

(8) G. R. Freeman in "Actions Chimiques et Biologiques des Radiations," Vol. 14, M. Haissinsky, Ed., Masson et Cie., Paris, 1970, Chapter II, p 73.

(9) J. C. J. Thynne, J. K. Amenu-Kpodo, and A. G. Harrison, *Can. J. Chem.*, **44**, 1655 (1966).

(10) D. J. Hyatt, E. A. Dodman, and M. J. Henchman, *Advan. Chem. Ser.*, No. 58, 131 (1966).

(11) A. Ekstrom and J. L. Garnett, *J. Phys. Chem.*, **70**, 324 (1966).

(12) F. S. Dainton, I. Janovsky, and G. A. Salmon, *Chem. Commun.*, 335 (1969).

(13) (a) The compound exists as a trans dimer in the solid state: see I. T. Millar and H. D. Springall, "The Organic Chemistry of Nitrogen by the late N. V. Sidgwick," Clarendon Press, Oxford, 1966, Chapter 10, p 343. (b) The monomer-dimer equilibrium in methanol is being studied by nmr spectroscopy. Contrary to a previous statement,^{8b} we find that photoactivation is not necessary to bring about the dissociation of the dimer at -80° .

(14) I. H. Leaver and G. C. Ramsay, *Tetrahedron*, **25**, 5669 (1969).

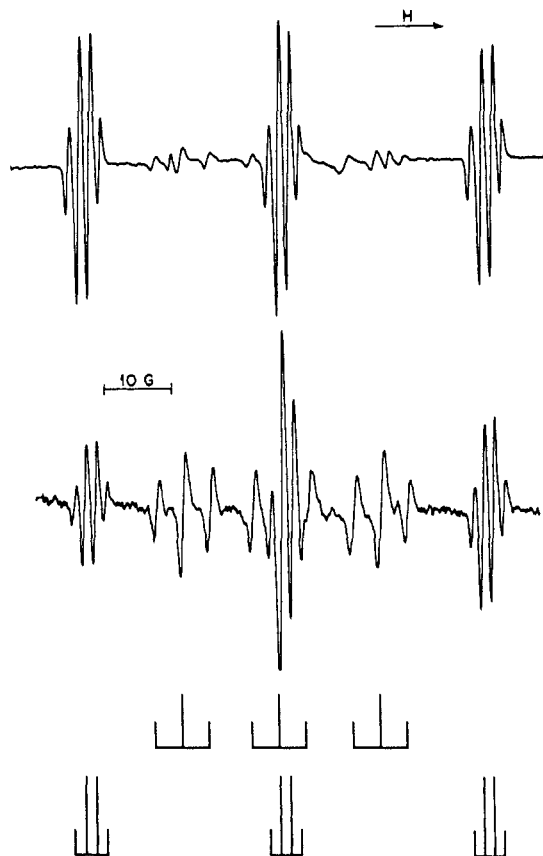


Figure 1. ESR first-derivative spectra of methanol solutions of 2-methyl-2-nitrosopropane recorded at -80° after γ irradiation for 10 min (dose, 0.07 Mrad) at -78° . The upper and lower spectra refer to concentrations of 10^{-1} and 10^{-2} M, respectively. In addition to the components indicated by the stick diagram (see text), the upper spectrum shows a triplet ($a^N = \text{ca. } 16.2$ G) of very weak lines; these lines were also observed before γ irradiation and belong to di-*tert*-butyl nitroxide formed during preparation of the sample.

were virtually identical with those described from CH_3OH . In the case of CD_3OD , the spectra were again easily analyzed since the simple triplets from the anticipated nitroxides corresponding to II and III can be readily distinguished by virtue of the large difference in the ^{14}N splittings.

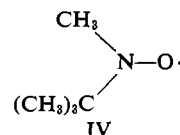
The ESR spectra were always recorded at -80° immediately after γ irradiation of the samples at -78° for 10 min (dose = 0.07 Mrad). The signal due to II decreased very slowly at this temperature, whereas the signal from III remained constant, ruling out the possibility of interconversion between these two isomeric nitroxide radicals. At higher temperatures the decay of II was especially marked, and when the entire experiments were carried out at 25° only the spectrum of III was observed irrespective of the scavenger concentration. The thermal instability of alkoxy nitroxides has been noted previously.¹⁵ Consequently, no conclusions can be drawn about the radiolysis mechanism from radical trapping experiments carried out with I above -80° .

The concentration dependence of the ESR results at -80° strongly indicates that the hydroxymethyl radical

(15) A. Mackor, Th. A. J. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Lett.*, 385 (1967).

arises almost entirely from the secondary reaction 3 in competition with the scavenging of methoxy radicals by reaction 4. A similar competition was previously suggested¹² to explain the high concentration (10^{-1} M) of iodide ion necessary for complete scavenging of the oxidizing species, presumed to be the methoxy radical, in methanol radiolysis.

Evidently the methoxy radical is the most abundant primary radical produced in the radiolysis of liquid methanol. In order to probe the mechanism of its formation, further experiments were carried out using 10^{-1} M solutions of I containing a high concentration (1–5 mol %) of methyl bromide, an excellent electron scavenger.¹⁶ The ESR results showed that the formation of II was unaffected by the presence of the methyl bromide, while additional lines belonging to the spectrum of methyl *tert*-butyl nitroxide^{3b, 4b} IV were easily



identified. The appearance of IV in this system is diagnostic of methyl radical formation through electron scavenging by the methyl bromide,¹⁶ and therefore these results show that the methoxy radical does not originate from electron attachment or ion recombination processes. It follows that the present work is entirely consistent with the formation of the methoxy radical by reaction 1 and that relative to the gas-phase results, reaction 2 is much less important than reaction 1. Consequently, it would appear that the hydrogen bonding in the liquid phase facilitates the selective transfer of the hydroxyl hydrogen in the primary ion-molecule reaction.

These results illustrate the potential usefulness of the spin-trapping technique as applied to the radiolysis of organic liquids where more than one type of radical is commonly produced.¹⁷ Mention should also be made of the fact that no nitroxide radicals originated from a radiation-induced decomposition of I, in contrast to the photolysis at certain wavelengths.²⁰ Finally, the high sensitivity of the technique means that results can be obtained at relatively low irradiation doses (<0.1 Mrad), thereby avoiding the risk of complications resulting from the buildup of radiolysis products.

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(16) (a) J. M. Warman, K.-D. Asmus, and R. H. Schuler, *Advan. Chem. Ser.*, No. 88, 25 (1968); (b) E. D. Sprague and F. Williams, *J. Chem. Phys.*, 54, 5425 (1971).

(17) R. A. Holroyd in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley, New York, N. Y., 1968, Chapter 7, p 413.

(18) Fellow of the Consejo Nacional de Investigaciones Científicas y Técnicas, Republic of Argentina.

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Jorge A. Wargon,¹⁸ Ffranco Williams*¹⁹

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

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