

each metal atom may be attained through a rhenium-rhenium triple bond (in addition to the three postulated<sup>17</sup> bridging H atoms). This anion would then be related to our tetranuclear species in a manner analogous to the relation between the N<sub>2</sub> molecule and the P<sub>4</sub> tetrahedron. Compound I and the salt of H<sub>3</sub>Re<sub>2</sub>(CO)<sub>6</sub><sup>1-</sup> thus represent a common link between these two extreme types of substitution reactions, the substitution of H<sup>-</sup> by CO as carried out by Ginsberg and coworkers on ReH<sub>9</sub><sup>2-</sup> and the substitution of H<sup>-</sup> for CO on Re<sub>2</sub>(CO)<sub>10</sub> studied by our group.

**Acknowledgment.** We are grateful to Dr. J. R. Holmes for assistance in obtaining the Raman spectra and for valuable discussions.

(18) Research Fellow of the Alfred P. Sloan Foundation, 1968-1970.

H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley  
Contribution No. 2327, Department of Chemistry  
University of California, Los Angeles, California 90024

Melvyn R. Churchill<sup>18</sup>  
Department of Chemistry, Harvard University  
Cambridge, Massachusetts 02138  
Received November 4, 1968

### Electron Spin Resonance Evidence on the Nature of Trapped Positive Holes in $\gamma$ -Irradiated 3-Methylpentane Systems at 77°K

Sir:

Production of positive holes in organic glasses by high-energy radiation has been studied extensively by Shida and Hamill<sup>1</sup> by optical methods. They have shown that positive charge resulting from ionization of the matrix can be trapped by suitable scavengers. The optical method, however, does not permit an unequivocal identification of the nature of the positive hole; *i.e.*, it cannot distinguish between species such as a radical cation RH<sup>+</sup>, a carbonium ion R<sup>+</sup>, a protonated ion RH<sub>2</sub><sup>+</sup>, or a dimeric radical cation such as (RH)<sub>2</sub><sup>+</sup>.

Use of electron spin resonance should provide a method to distinguish between these possible species. To the knowledge of the authors, however, esr studies of positive holes in organic glasses of aliphatic hydrocarbons do not seem to have been very successful.<sup>2</sup>

This report presents the result of an esr study of  $\gamma$ -irradiated 3-methylpentane (3-MP) glasses containing small amounts of tetramethylethylene (TME) which gives direct evidence regarding the nature of the positive hole.

The samples were prepared from purified materials (in some cases with CO<sub>2</sub> added), cooled to liquid nitrogen temperature, and subjected to <sup>60</sup>Co  $\gamma$  irradiation at a dose rate of  $1.3 \times 10^{18}$  eV g<sup>-1</sup> min<sup>-1</sup>. Esr measurements were carried out with a Model V-4502 Varian spectrometer.

Figure 1a shows the esr spectrum of 3-MP glass containing 0.3 mole % TME and 0.2 mole % CO<sub>2</sub> after irradiation with a dose of  $3.9 \times 10^{18}$  eV g<sup>-1</sup>. The spectrum can be attributed to three paramagnetic

species. The strong central line deviating slightly toward high field from the free-spin value is attributable to CO<sub>2</sub><sup>-</sup>. This assignment is confirmed by the splitting into two lines when <sup>13</sup>CO<sub>2</sub> is used.<sup>3</sup> Furthermore, six lines with an average spacing of 22.5 G may be attributed to the 3-MP radical as suggested in ref 4; they cause the lifting and lowering of the spectrum at low and high fields, respectively. Superimposed on this group is a set of 13 lines equally spaced at 16.7 G; 9 of them can be discerned in Figure 1a. The full set can be obtained at a ten times higher dose and high instrument gain.

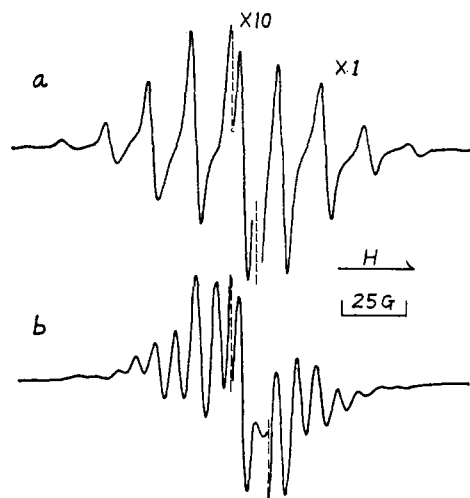


Figure 1. Esr spectra of  $\gamma$ -irradiated 3-MP glasses containing TME and CO<sub>2</sub> at a dose of  $3.9 \times 10^{18}$  eV g<sup>-1</sup>: (a) 0.3% TME, (b) 10% TME. The central parts of the spectra were recorded at reduced sensitivity.

The intensity ratio of lines 1-3 and 11-13 in the complete set is 0.078:1:5.2 and 5.6:1:0.073.<sup>5</sup> The relative intensities of lines 4-10 cannot be determined accurately because of the superposition of the 3-MP radical spectrum. Nevertheless, the presence of 13 lines and the intensity ratios found for the outer lines agree quite well with a paramagnetic species with 12 equivalent protons, with corresponding ratios of 0.083:1:5.5...5.5:1:0.083. The result agrees with what may be expected for a species such as a TME radical ion.

The charge of the ion may be inferred from the following observations. In the presence of CO<sub>2</sub> the 13-line spectrum is stabilized; that is, even after 24 hr its intensity is little changed. In the absence of CO<sub>2</sub> both the trapped electron and the radical-ion signal decay within several minutes; their rate of decay is considerably increased by illumination of the system with infrared light. When a positive charge scavenger is added to the TME-CO<sub>2</sub>-3MP system (0.1 mole % N-methyldiphenylamine<sup>6</sup>), the TME radical-ion spectrum

(3) P. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **44**, 1845 (1966).

(4) K. Fueki and Z. Kuri, *J. Am. Chem. Soc.*, **87**, 923 (1965); M. Shirom, R. F. C. Claridge, and J. E. Willard, *J. Chem. Phys.*, **47**, 286 (1967).

(5) The intensity ratios of lines at the low and high field are normalized to the intensities of lines 2 and 12, respectively.

(6) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).

(1) T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 5376 (1966).

(2) C. F. Luck and W. Gordy, *ibid.*, **78**, 3240 (1956); P. B. Ayscough, A. P. McCann, C. Thomson, and D. C. Walker, *Trans. Faraday Soc.*, **57**, 1487 (1961).

is reduced by about one-third. The effects of these additives on the TME radical ion agree qualitatively with the results obtained by Shida and Hamill<sup>1</sup> for radical cations.

The value of the coupling constant,  $a_H = 16.7$  G, lends further qualitative support for the presence of the TME radical cation. According to Symons<sup>7</sup> the coupling constant of a  $\beta$  proton is related to the  $Q_\beta$  value by

$$a_\beta = Q_\beta \left( \rho_C^0 - \frac{Na_\beta}{502} \right)$$

where  $\rho_C^0$  is a formal charge density on the  $\alpha$  carbon (+0.5), and  $N$  is the number of  $\beta$  protons. For TME<sup>+</sup> we obtain  $Q_\beta = 55.6$  G. Although not in quantitative agreement with the data of Hulme and Symons,<sup>3</sup> this result approaches the large  $Q$  values expected by these authors for organic radical cations.

By comparison of the center of the 13-line spectrum with that of the methyl radical spectrum (obtained by radiolysis of CH<sub>3</sub>I in the TME-3-MP system), the  $g$  value was found to be  $2.0025 \pm 0.0003$ . Unfortunately, there exists no theory for the shift of  $g$  values for alkyl-substituted hydrocarbon radical ions or experimental data with which this value could be compared. It is, however, interesting that within the relatively large limit of error the  $g$  value for the proposed TME<sup>+</sup> coincides with the corresponding values for aromatic cations.<sup>8</sup>

It is interesting to note that, at higher TME concentrations under otherwise the same conditions as given for Figure 1a, the spectrum of Figure 1b is obtained showing an average line separation of 7.8 G. This is about one-half of the separation found for TME<sup>+</sup>. In the absence of CO<sub>2</sub> this species is also sensitive to optical and thermal bleaching. Possibly, at higher concentrations the formation of a dimeric radical cation (TME)<sub>2</sub><sup>+</sup> occurs as discussed by Edlund, *et al.*,<sup>10</sup> for benzene-silica gel systems.

**Acknowledgment.** We wish to thank Professor Milton Burton for helpful discussions.

(7) M. C. R. Symons, *Tetrahedron*, **18**, 333 (1962).

(8) R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1120 (1965).

(9) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

(10) O. Edlund, P.-O. Kinell, A. Lund, and A. Shimizu, *ibid.*, **46**, 3679 (1967).

(11) On leave from the Government Industrial Research Institute of Nagoya, Nagoya, Japan.

(12) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-647.

T. Ichikawa,<sup>11</sup> P. K. Ludwig

Department of Chemistry and the Radiation Laboratory<sup>12</sup>  
of the University of Notre Dame, Notre Dame, Indiana

Received November 8, 1968

#### Studies of Stable Free Radicals. IV. The Origin of Asymmetry and Rate of Symmetrization of a Spin-Labeled $\alpha$ -Sulfonyl Carbanion

Sir:

It is recognized that asymmetry at carbon atoms bearing a sulfone grouping is often retained in the

corresponding  $\alpha$ -sulfonyl carbanion.<sup>1</sup> However, the absolute rates of racemization of these asymmetric carbanions are unknown, and with one exception only rates relative to protonation have been measured.<sup>2</sup> Further, the reason for the asymmetry remains in dispute. Evidence has been given in support of pyramidal carbanions,<sup>3</sup> but there are cogent arguments that maintenance of asymmetry results primarily from coulombic restrictions to rotation in  $\alpha$ -sulfonyl carbanions, whether planar or pyramidal.<sup>4</sup> We present here evidence bearing on these points.

Treatment of the stable radical I, R = CH<sub>2</sub>Cl,<sup>5,6</sup> with aqueous sodium phenylsulfinate and potassium iodide yielded I, R = CD<sub>2</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>.<sup>6</sup> This sulfone gave typical nitronyl nitroxide esr spectra of five triplets produced by coupling with two equivalent nitrogens and two  $\alpha$  hydrogens ( $a_N = 7.85$ ,  $a_H = 1.77$  G, H<sub>2</sub>O). Dissolution of this radical in aqueous 6 *N* KOH produced solutions of II having nine-line esr spectra resulting from coupling with two nonequivalent nitrogens [ $a_N(\text{av}) = 8.55$  G]. No additional coupling was evident except for expected line broadening ( $\sim 0.9$  G) from unresolved coupling with the methyl hydrogens ( $\sim 0.2$  G).<sup>7b</sup> Neutralization of this solution regenerated the original five-triplet pattern. In weakly alkaline deuterium oxide the sulfone gave the expected five-singlet spectrum of I, R = CD<sub>2</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, and addition of more alkali again gave the nine-line pattern. Slightly diminished line widths ( $\sim 0.75$  G) in this spectrum suggest possible coupling of  $\sim 0.2$  G by the  $\alpha$  hydrogen in II. Warming of alkaline solutions of II caused collapse of the nine-line pattern to five lines expected by averaging of the spin densities on the nonequivalent nitrogens. This averaging was not produced by proton exchange since the residual five-triplet pattern observed in less basic, incompletely ionized solutions of the sulfone failed to collapse on heating.

The nonequivalence of the nitrogens in II must arise from asymmetric solvation or polarization of the normally symmetric nitronyl nitroxide grouping by an asymmetrically distributed charge in the side chain. Possible structures which could account for this asymmetry include IIa, IIb, and IIc, each of which would be expected to have nonequivalent nitrogens provided there is restricted rotation about the C<sub>2</sub>-C <sub>$\alpha$</sub>  bond. Among these alternatives, planar carbanion IIa appears unlikely by several considerations. (1) Attachment of the  $\alpha$  hydrogen directly to the radical  $\pi$ -electron system in IIa should cause stronger  $\alpha$ -hydrogen hyperfine interaction than the  $< 0.2$  G observed (*cf.* I, R = CH=CHC<sub>6</sub>H<sub>5</sub>,<sup>5,6</sup>  $a_{H\alpha} = a_{H\beta} = 1.5$  G). (2) Compari-

(1) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 105; (b) D. J. Cram, W. D. Nielsen, and B. Rickborn, *J. Am. Chem. Soc.*, **82**, 6415 (1960); (c) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961).

(2) Rates of symmetrization of the configurationally constrained 2,2-dimethyl-1-phenylsulfonylecyclopropyl anion in DMSO-THF have recently been measured by nmr. However, ion-pair dissociation rather than inversion or rotation is probably rate controlling in this solvent: A. Ratajczak, F. A. L. Anet, and D. J. Cram, *ibid.*, **89**, 2072 (1967).

(3) D. J. Cram and A. S. Wingrove, *ibid.*, **84**, 1496 (1962); (b) *ibid.*, **85**, 1100 (1963).

(4) (a) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Letters*, 515 (1962); (b) E. J. Corey and T. H. Lowry, *ibid.*, 793, 803 (1965).

(5) See ref 7 for method of synthesis of nitronyl nitroxides.

(6) Satisfactory combustion analysis and mass spectrum.

(7) (a) J. H. Osiecki and E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 1078 (1968); (b) D. G. B. Boocock, R. Darcy, and E. F. Ullman, *ibid.*, **90**, 5945 (1968); (c) D. G. B. Boocock and E. F. Ullman, *ibid.*, **90**, 6873 (1968).