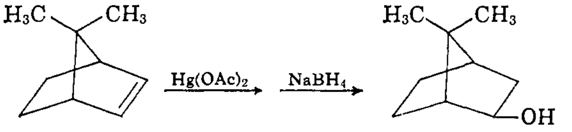
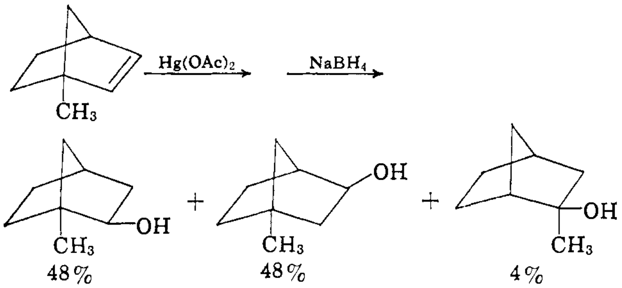
An interesting result was encountered in the oxymercuration of 7,7-dimethylnorbornene (apobornylene). Here the reaction was considerably slower, requiring 15 min for the yellow color[1] to vanish. After a total reaction time of 73 min, there was obtained an 84% yield of alcohol, >99.8% apoisoborneol (III), with no indication of any rearranged product.[6]



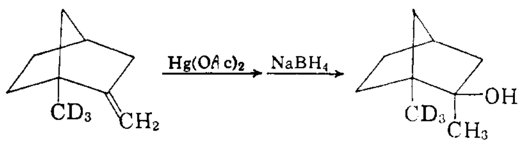
III, yield 84%; >99.8% *exo*

It might be tempting to attribute the marked stereoselectivity observed in these experiments to nonclassical $\sigma$ bridging in the intermediate. However, this appears to be ruled out by the following results. First, 1-methyl-2-norbornene provides in 5 min a 100% yield of product (IV), analyzing for 48% 1-methyl-2-*exo*-norborneol, 48% 1-methyl-3-*exo*-norborneol, and 4% 2-methyl-*exo*-2-norborneol. Evidently, the small amount of tertiary alcohol is the result of the acid produced in the oxymercuration stage, rather than the result of the reaction itself, since oxymercuration–demercuration with added sodium acetate produces 93% product in 1.0 hr, analyzing for 46% 2-*exo*, 53.5% 3-*exo*, and only 0.5% tertiary. Similarly, bornylene forms roughly equal quantities of isoborneol and epiisoborneol.[7]



IV

Second, oxymercuration–demercuration of 1-methyl-$d_3$-2-methylenenorbornane[8] proceeds to give 1-methyl-$d_3$-2-methyl-*exo*-norbornanol without detectable scrambling (V).



V

Consequently, we appear to be faced by the following dilemma. Both the orientation taken by the entering hydroxyl group and the almost exclusive formation of *exo* derivatives, even in the case of apobornylene with its sterically demanding 7,7-dimethyl substituents, are identical with phenomena that in the past have been considered to require bridged nonclassical carbonium ions in this system. Yet the failure to observe either significant rearrangement or scrambling in this reaction does not appear to be compatible with the presence of such bridged intermediates in detectable amounts. Clearly we must now give careful reconsideration to the argument[3,4] that the high stereoselectivity exhibited by the norbornyl and apobornyl cations in solvolysis requires a $\sigma$-bridged formulation for these intermediates.

(6) Prior to our development of the simple oxymercuration–demercuration procedure which is the subject of this group of communications, we learned from T. T. Tidwell and T. G. Traylor that they had oxymercurated 1,4,7,7-tetramethylnorbornene with mercuric acetate in acetic acid and had established the structure of the oxymercuration product. These results are now in the process of publication. Our work in developing the simple combined procedure described in the present communications was greatly facilitated by a full exchange of information with Professor T. G. Traylor, and we wish to acknowledge our debt to him. In turn, we were happy to make available our own unpublished data and procedures on the hydroboration of norbornenes containing sterically demanding and labilizing substituents and to assist Tidwell and Traylor in applying this reaction to 1,4,7,7-tetramethylnorbornene.

(7) P. von R. Schleyer has informed us that he had observed long ago that the addition of hydrogen chloride to 1-methylnorbornene also proceeds without significant discrimination between the 2 and 3 positions, a result that is difficult to rationalize in terms of the usual $\sigma$-bridged cationic intermediate. We are currently reexamining this observation by our new automatic hydrochlorination procedure[8] in collaboration with Professor Schleyer.

(8) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 466 (1967). We are indebted to Kwang-Ting Liu for this experiment.

(9) Research assistant, 1964–1967, on grants supported by the National Science Foundation (G 19878, GP 6492 X) and the National Institutes of Health (5 ROI-GM-10937).

(10) Postdoctorate research associate on a grant supported by the National Science Foundation (GP 6492 X).

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*Received December 30, 1966*

## The Detection of Trapped Electrons in $\gamma$-Irradiated 3-Methylpentane Glasses by Electron Spin Resonance[1]

*Sir:*

Extensive optical studies by Hamill and his collaborators[2] have provided evidence that trapped electrons are produced by the $\gamma$ radiolysis of 3-methylpentane (3-MP) glasses at 77°K. We now wish to report that trapped electrons can also be readily detected by electron spin resonance (esr) in irradiated 3-MP glasses containing ammonia or trimethylamine (TMA), additives which are capable of functioning as suitable proton acceptors in the radiolysis of hydrocarbons.[3] Because the glasses formed from 3-MP and TMA were transparent and homogeneous over the concentration range of interest (0–20 mole % TMA), this system has been studied in detail.

A narrow intense singlet ($g = 2.002 \pm 0.001$, $\Delta H_{\mathrm{ms}} = 3.5$ gauss) dominates the esr spectrum shown in Figure 1 against a background consisting of the much broader four center lines from the sextet spectrum of 3-MP. The measurements were made with a Varian-4502 9.5-GHz spectrometer employing a 100-kHz modulation frequency and a modulation amplitude of 1.7 gauss. The low-power arrangement of the microwave bridge was used with a total attenuation of 35 db. Repeated irradiations under the same conditions showed that the singlet was not saturated at 35 db, but drastic saturation did set in below 30 db. At any stage during its thermal decay at 77°K, the singlet could be obliterated by exposure to filtered light (saturated potassium dichromate, $\lambda > 540$ m$\mu$) from a tungsten lamp.

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(1) This work was supported by the Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-23.

(2) (a) J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 777 (1964); (b) J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**, 1279 (1966); (c) D. W. Skelly and W. H. Hamill, *ibid.*, **44**, 2891 (1966).

(3) W. R. Busler, D. H. Martin, and F. Williams, *Discussions Faraday Soc.*, **36**, 102 (1963).

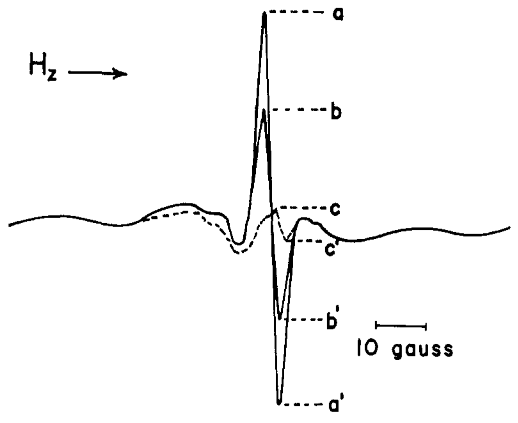

Figure 1. Esr spectra of 3-MP glass containing 3.5 mole % TMA after $\gamma$ irradiation for 10 min (dose = $3 \times 10^{18}$ ev $g^{-1}$) at 77°K and in the dark. Singlet traces aa' and bb' were recorded 3.5 min and 47 min, respectively, after irradiation. Trace cc' (broken line) was recorded after the sample was bleached by weak flashlight for 2 min in a darkened room and shows a residual spike in the center due to resonance of the quartz (Suprasil) tube.

In view of the recent finding[4] that carbon dioxide can act as an efficient electron trap in 3-MP to give a sharp line with an almost identical profile ($\Delta H_{\mathrm{ms}}$ = 3.5 gauss) to that shown in Figure 1, the $CO_2\cdot^-$ radical anion was also produced for comparison by $\gamma$ irradiation of 1.8 mole % $CO_2$ in 3-MP under exactly the same conditions as above. The behavior and esr properties of $CO_2\cdot^-$ differed in three respects from that of the singlet described above. (1) Instead of decaying, the $CO_2\cdot^-$ resonance increased about 40% over a period of 1 hr after irradiation. (2) After the intensity of the $CO_2\cdot^-$ resonance had attained a stationary value, esr studies showed that the signal was only saturated at an attenuated power level of 20 db compared to 30–35 db for the TMA–3-MP singlet. (3) The intensity of the $CO_2\cdot^-$ resonance was unaffected by either a weak flashlight or filtered tungsten light. Hence the narrow resonance observed in the TMA–3-MP systems is not due to $CO_2\cdot^-$. The resonances from the $\gamma$ irradiation of empty quartz (Suprasil and Spectrosil) tubes were also examined, but these complex signals are easily differentiated from the singlet on the basis of spectrum shape, relative intensity, decay, and response to light.

To confirm that the narrow line in the TMA–3-MP system is associated with a trapped electron, a mixture of 2.1 mole % methyl iodide and 12.5 mole % TMA in 3-MP was made up at low temperature (to prevent the Menschutkin reaction) and irradiated as before. The narrow line was replaced by the well-known spectrum of the methyl radical, as expected for dissociative electron capture by the halide.[5] Further, the esr spectra of irradiated 3-MP glasses containing either ammonia, dimethoxyethane, or TMA could be superimposed except for the relative height of the singlet, and this observation eliminates the remote possibility that the singlet is due to electron capture by these solutes.

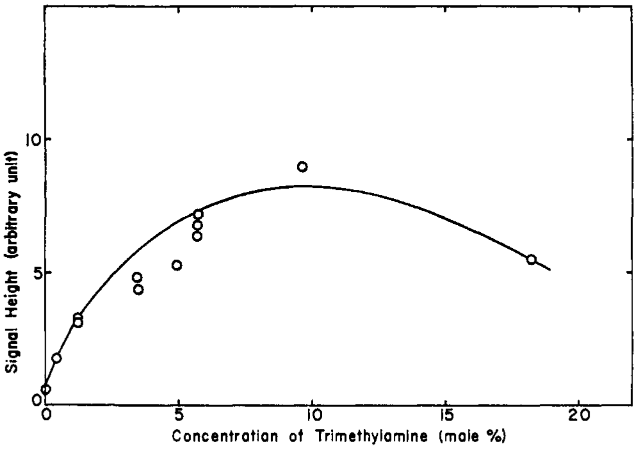

Figure 2. Effect of TMA concentration on the height of the esr singlet produced by $\gamma$ irradiation of 3-MP glasses for 10 min (dose $3 \times 10^{18}$ ev $g^{-1}$) at 77°K. Measurements were made in the dark between 3 and 5.5 min after irradiation.

A plot (Figure 2) of initial signal height against TMA concentration in the glass suggests that a maximum concentration of trapped electrons is formed (for the same dose) in the region of 10 mole % TMA. Qualitatively similar effects have been described by Gallivan and Hamill[6] in their optical work. Only a broad singlet spectrum was produced from the irradiation of TMA alone. A tentative estimate of the $G$ value for trapped electrons may be made on the basis of the relative intensities of the lines due to $e^-$ and $CO_2\cdot^-$. On the assumption that $G(CO_2\cdot^-)$ for 2 mole % $CO_2$ in 3-MP is about 1.6 as for efficient electron scavengers,[2a] then the initial $G(e^-)$ at 10 mole % TMA is *at least* 0.8. Even qualitatively the intensity of the $e^-$ singlet relative to the remaining 3-MP resonance (Figure 1) indicates that the yield of trapped electrons is significant.

The decay of the trapped electrons appears to be a function of TMA concentration, but at 10 mole % the rate is sufficiently slow that the initial signal intensity is almost linear with dose for irradiation times up to 20 min ($6 \times 10^{18}$ ev $g^{-1}$). Kinetic measurements show that the time for half-decay, $t_{1/2}$, decreases from 2 hr to 30 min as the TMA concentration is reduced from 9.6 to 1.2 mole %, and, unexpectedly, the decay curve for 3.5 mole % TMA is remarkably similar to that obtained by optical studies on *pure* 3-MP (Figure 2 of ref 2b) with $t_{1/2} \simeq 45$ min. As reported previously,[7] the esr spectrum of pure 3-MP shows a faint singlet. In the present work, quantitative measurements on pure 3-MP were rendered difficult by the overlapping quartz signal of comparable intensity but $t_{1/2}$ is estimated to be about 5 min in this case.

The present esr observations may be reconciled with the optical results of Hamill, *et al.*,[2,6] if it is supposed that a proton scavenger modifies the environment of the trapped electron so as to make the latter more readily observable by the esr technique. From an intercomparison of this work and the optical results[2,6] relating to yields and decay in pure 3-MP, it does not appear that the effect of added TMA is simply interpretable in terms of arresting the rate of electron recombination, either by positive charge trapping or through decreased electron mobility in the matrix, although the esr data alone would suggest that one or both of these effects contribute to some degree. It is

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

(5) (a) D. W. Skelly, R. G. Hayes, and W. H. Hamill, *ibid.*, **43**, 2795 (1965); (b) R. F. C. Claridge and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 4992 (1965).

(6) J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**, 2378 (1966).

(7) K. Tsuji, H. Yoshida, and K. Hayashi, *ibid.*, **46**, 810 (1967).

conceivable that a fundamental change may occur in the esr relaxation mechanism when the trapped electron is divorced[8] from its conjugate 3-MP cation by the act of proton transfer (or charge transfer generally). In this connection it is interesting to note that *strong* esr spectra due to trapped electrons in irradiated organic glasses[9] have been observed hitherto only in cases where the parent cation almost certainly undergoes a change of identity by reaction with the matrix.

(8) By "divorced" we do not mean physical separation in this instance.

(9) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, 43, 876 (1965); *J. Phys. Chem.*, 70, 2379 (1966).

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## The Mechanism of Fluorine-19 Exchange in the $TiF_4 \cdot 2$(Donor) Complexes

*Sir:*

The temperature dependence in the fluorine-19 nmr spectra of solutions of *cis* $TiF_4 \cdot 2$(donor) complexes has been noted.[1] The low-temperature (slow exchange) spectra of these complexes consist of two triplets of equal intensity due to the two $F^{19}$ environments which contain two nuclei each[1,2] (see Figure 1). As a solution is warmed the fine structure of the spectrum is lost; the peaks broaden and then collapse into a single resonance. These observations show that there is a temperature-dependent exchange of fluorine nuclei between the nonequivalent sites. We wish to report evidence that this exchange involves both inter- and intramolecular exchange processes. The data indicate that the exchange mechanism consists of dissociation of a donor molecule followed by anharmonic vibration of a nonrigid intermediate formed by the dissociation.

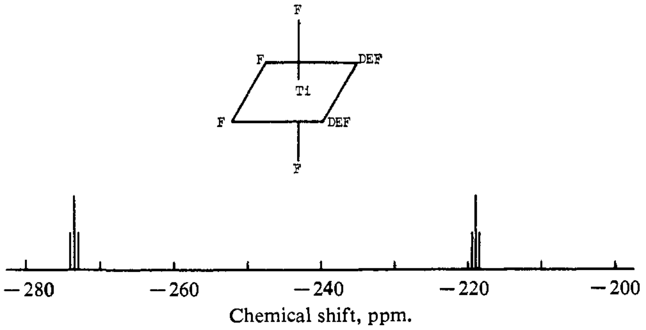

Figure 1. Diagrammatic representation of the $F^{19}$ nmr signals observed for $TiF_4 \cdot 2DEF$ (DEF = N,N-diethylformamide) in acetonitrile at −10°. The chemical shifts are expressed in parts per million displacements from the resonance of external $CF_3CO_2H$.

The coalescence temperature ($T_c$) of the spin–spin triplets in the spectrum of $TiF_4 \cdot 2DEF$ (DEF ≡ N,N-diethylformamide) was determined as a function of the concentration of excess amide in acetonitrile solutions. The graph of $T_c$ *vs.* [DEF] (see Figure 2) shows that the addition of excess amide slows the rate of fluorine exchange. Variation of the concentration of $TiF_4 \cdot 2DEF$ in acetonitrile does not change $T_c$.

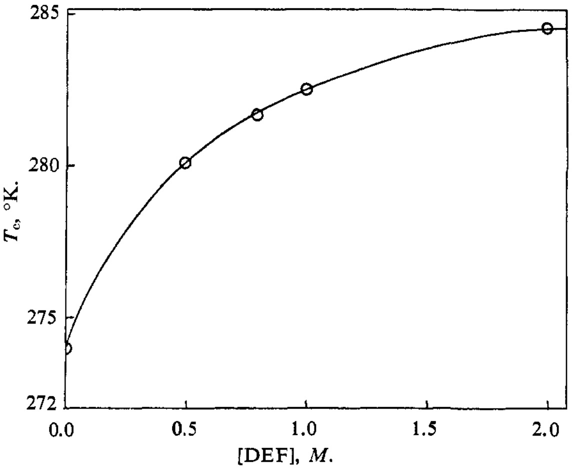

Figure 2. $T_c$ *vs.* [DEF] for 1 *M* $TiF_4 \cdot 2DEF$ solutions in acetonitrile (DEF = N,N-diethylformamide).

Coalescence of a spin–spin multiplet occurs when the exchange rate becomes large enough to satisfy the condition

$$Jt \simeq 1 \qquad (1)$$

where $J$ is the spin–spin coupling constant (radians/sec) and $t$ is the average lifetime (sec) of a fluorine-19 spin state. After exchange occurs, the probability that the two $F^{19}$ nuclei in either environment of a $TiF_4 \cdot 2D$ complex will have changed their spin state is $^5/_8$. Therefore, at $T_c$ the pseudo-first-order rate constant,[3] $\kappa$, is given by

$$\kappa = \frac{8}{5t} \simeq \frac{8}{5}J$$

Using the value for $J$ (38 cps) obtained from the low-temperature spectrum of $TiF_4 \cdot 2DEF$ gives 370 $sec^{-1}$ for $\kappa$.

The loss of fine structure and subsequent collapse of the two peaks were attributed to a rapid base (donor molecule) exchange.[1] It has been shown[4] that donor exchange does occur in these solutions. Since nucleophilic displacement reactions are generally not observed in solutions of transition metal complexes,[5] this exchange would be expected to occur *via* a dissociation mechanism. The rapid equilibrium

$$TiF_4 \cdot 2D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TiF_4 \cdot D + D$$

would be established. However, this equilibrium cannot be sufficient to produce fluorine equivalence because such a mechanism requires that the mean lifetime, $\tau$ $(= 1/\kappa)$, evaluated from the fluorine-19 nmr spectra[6] be independent of the donor concentration. This is contrary to the experimental data (Figure 2).

The dissociation must, therefore, be followed by a subsequent reaction which scrambles the fluorines. One such reaction could be the formation of a *trans* complex.[7] One would then have

$$TiF_4 \cdot 2D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TiF_4 \cdot D + D$$

$$D + TiF_4 \cdot D \xrightarrow{k_t} D \cdot TiF_4 \cdot D$$

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(1) E. L. Muetterties, *J. Am. Chem. Soc.*, 82, 1082 (1960).

(2) R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, 2, 1002 (1963).

(3) H. M. McConnell, *J. Chem. Phys.*, 28, 430 (1958).

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(5) R. G. Pearson, D. N. Edington, and F. Basolo, *J. Am. Chem. Soc.*, 84, 3233 (1962).

(6) A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, 67, 280 (1963).

(7) D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, 601 (1966).