Radical Cation of 2,2,3,3-Tetramethylbutane: an Electron Spin Resonance Study

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Summary Exposure of Me_3C–CMe_3 to ^{60}Co γ-rays at 77 K gave $\cdot CMe_3$ radicals [10 lines, $A(^1H) = 22$ G] and a species having at least 17 lines, $A(^1H) = 12$ G, assigned to the radical cation, $Me_3C{\cdot}CMe_3{}^+$.

DESPITE their importance as fundamental electron-loss intermediates, alkane cations have never been well defined by e.s.r. spectroscopy. A singlet having $\Delta H_{\rm ms} = 14$ G and $g = 2{\cdot}002$ has been assigned to the primary cations of 3-methylhexane and 3-methylpentane,[1] and Ceulemans[2] has recently reported the detection of similar singlets for solutions of various alkanes in n-pentane matrices. These relatively broad, featureless lines were not observed directly in the e.s.r. spectra of the irradiated solutions, but were obtained by various subtraction procedures. The spectra do not prove the presence of primary cations, nor do they provide any information about their structures.

The structure of the ethane cation has been the subject of a detailed theoretical treatment,[3] and we have recently reported an *ab initio* calculation for the isoelectronic anion, $B_2H_6{}^-$.[4] For the unrelaxed $C_2H_6{}^+$ cation, having the geometry of the parent molecule, the half-occupied orbital is thought to be $1e_g$ which is a combination of C–H σ-orbitals, but if relaxation involves a lengthening of the C–C bond, the $3a_{1g}$ symmetry orbital rapidly moves above the $1e_g$ orbital. This $3a_{1g}$ orbital is essentially a $2p_x\sigma$(C–C) combination. We have analysed[4] the results of Kasai and McLeod[5] for $B_2H_6{}^-$ anions and find that the $3a_{1g}$ representation is satisfactory.

Our attempts to prepare $C_2H_6{}^+$ cations in conditions suitable for an e.s.r. study have failed. However, it occurred to me that the cation of the hexamethyl derivative, Me_3C–CMe_3 might be more amenable to study. Also, since

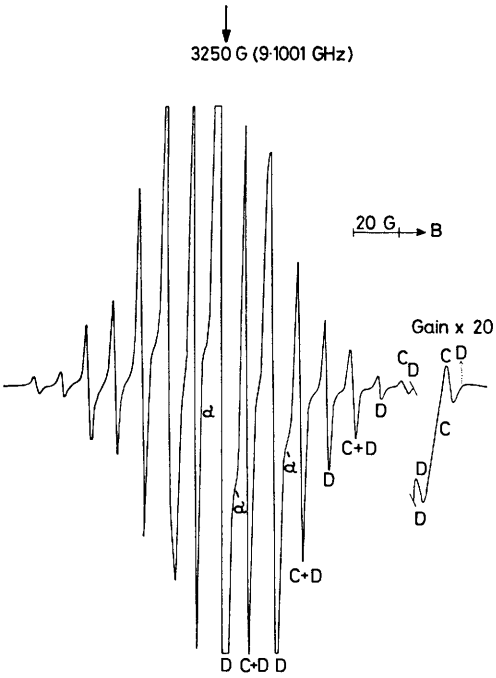

FIGURE. First derivative e.s.r. spectrum for Me_3C–CMe_3 after exposure to ^{60}Co γ-rays at 77 K and annealing to *ca.* 120 K, showing features for radicals B, C, and D. The lines marked α appeared slowly at this temperature and are assigned to a secondary product. The highest field features are shown with increased modulation and gain: similar features were obtained on the low-field side.

the t-butyl radical, $\mathrm{Me_3C\cdot}$ gives a well defined e.s.r. spectrum comprising 10 hyperfine features, it seemed possible that $\mathrm{Me_3C{-}CMe_3^+}$ ions would also display well defined hyperfine features.

These expectations seem to have been fulfilled. Directly after exposure to ^{60}Co γ-rays at 77 K, the pure material gave an e.s.r. spectrum comprising four sets of features (see Table): (A) outer parallel and perpendicular features assigned to radicals trapped in pairs, (B) a broad central triplet assigned to $\mathrm{H_2\dot{C}CR_3}$ radicals, (C) a set of 10 relatively narrow lines assigned to $\mathrm{Me_3C\cdot}$ radicals, and (D) a poorly defined set of lines overlapped by those from $\mathrm{Me_3C\cdot}$ radicals, having about half the coupling constant for $\mathrm{Me_3C\cdot}$ radicals and *ca.* twice the number of lines. Features for the radical pairs were rapidly lost on annealing, but those for (C) and (D) narrowed appreciably as shown in the Figure. Fifteen features for radical D were well defined, and two more could be detected at high gain. The only reasonable structures for D are the σ^* anion, $\mathrm{Me_3C\dot{-}CMe_3^-}$ or the σ cation $\mathrm{Me_3C\cdot CMe_3^+}$. Almost certainly the $\mathrm{Me_3C\cdot}$ radicals were formed by dissociation of one of these ions.

$$\mathrm{Me_3C\dot{-}CMe_3^-} \rightarrow \mathrm{Me_3C\cdot} + \mathrm{:C\,Me_3^-} \qquad (1)$$

or

$$\mathrm{Me_3C\cdot CMe_3^+} \rightarrow \mathrm{Me_3C\cdot} + \mathrm{CMe_3^+} \qquad (2)$$

The structure of the σ^* anion is expected to retain the near tetrahedral configuration of the two central carbon atoms. In that case, the ^{1}H hyperfine coupling is expected to be smaller than half the value for the planar[6] (or nearly planar[7]) t-butyl radical. However, for the cation, both halves of the molecule are expected to be nearly planar since $\mathrm{CMe_3^+}$ cations are certainly planar. In that case a slight increase is expected because of the positive charge effect on hyperconjugation,[8] and hence a value slightly greater than half that for $\mathrm{Me_3C\cdot}$ radicals is expected. The latter result was observed experimentally (Table) and hence I favour assignment of spectrum D to the cations.

TABLE. E.s.r. data for radicals formed in γ-irradiated $\mathrm{Me_3C{-}CMe_3}$

Centre	Structure	^{1}H Hyperfine coupling[a]
A	Radical-pairs[b]	sets of lines with $A = 6$ G
B	$\mathrm{H_2\dot{C}CR_3}$	3 lines; *ca.* 22 G
C	$\mathrm{Me_3C\cdot}$	10 lines; 22 G
D	$\mathrm{Me_3C\cdot CMe_3^+}$	17 lines;[c] 12 G

[a] In Gauss; G = 10^{-4} T. In all cases, g was very close to the free-spin value. [b] $2D_z = 560$ G. [c] 19 lines, inferred from the relative intensities and an assumed binomial distribution.

In order to check this, some carbon tetrachloride was dissolved in the hydrocarbon prior to irradiation. The e.s.r. spectrum at 77 K gave clear evidence for electron capture by $\mathrm{CCl_4}$ molecules.† On annealing above 77 K these features broadened reversibly and a very narrow multiplet became well resolved. Fifteen lines separated by 12 G, with the correct intensity distribution for a binomial set of 19 lines, were detected, clearly assignable to radical D. There was no indication of the presence of $\mathrm{Me_3C\cdot}$ radicals.

These results strongly support the concept that the parent anions dissociate to give $\mathrm{Me_3C\cdot}$ radicals (equation 1) whilst the cations remain stable. They also fit in well with our suggested structure for $\mathrm{B_2H_6^-}$ anions, comprising two planar $\mathrm{BH_3}$ units held loosely together by a single σ-electron.

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† I think the species first formed is the $\mathrm{\cdot CCl_4^-}$ anion. This species was converted into $\mathrm{\cdot CCl_3}$ radicals on annealing. These results will be reported later. Direct anion formation is also unlikely in view of the low electron affinities of such hydrocarbons. It should be mentioned that on cooling to *ca.* 4 K the e.s.r. spectrum of $\mathrm{Me_3C\cdot}$ radicals in a neopentane matrix undergoes a reversible change to give a 19-line spectrum having half the spacing (M. Iwasaki, K. Toriyama, K. Nunome, M. Kukaya, and H. Muto, *J. Phys. Chem.*, 1977, **81**, 1410). This change, attributed to a tunnelling motion of the three methyl groups, is unlikely to be responsible for the present spectrum since the normal spectrum of $\mathrm{Me_3C\cdot}$ is observable at 77 K, and the 12 G spectrum is not lost on annealing but actually becomes better defined.

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