The Homolysis of C–H Bonds in Carbocations

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The e.s.r. spectra of certain tetra-alkylcyclobutadiene radical cations, of the hexamethylcyclopentadiene radical cation, and of various polycyclic aromatic radical cations, $RH^{\cdot+}$, are observed when the corresponding hydrocarbon cations, RH_2^+, are photolysed in trifluoroacetic acid solvent.

Hydrocarbon radical cations are usually prepared in fluid solution by electron-transfer reactions according to equation (1). The oxidising agents which have been used include H_2SO_4–SO_3, $SbCl_5$, $Co(OCOCH_3)_3$, $Hg(OCOCF_3)_2$, $Tl(OCOCF_3)_3$, $AlCl_3$, XeF_2, and $Ar_3N^{\cdot+}$, sometimes with photoassistance, and the electron-transfer can also be effected electrolytically.[1]

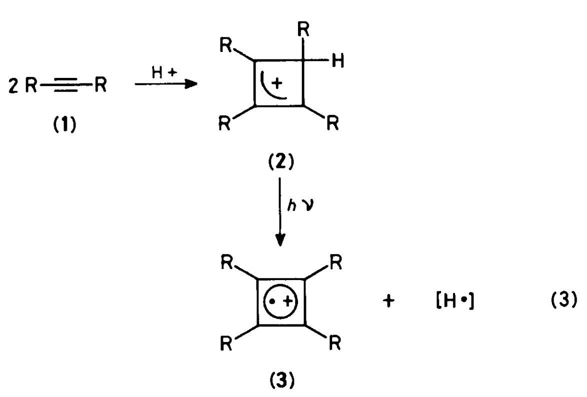
An alternative potential route to radical cations can be based on the homolysis of hydrocarbon cations [equation (2)]. We are not aware of any unambiguous examples of this reaction. Most studies of the photolysis of conjugated carbonium ions have focussed attention on the pericyclic reactions which may occur.[2] Our own generation of the pentamethylcyclopentadiene radical cation by photolysis of pentamethylcyclopentadiene in trifluoroacetic acid[3] might be regarded as an example of reaction (2), but it could alternatively involve protonation of the neutral radical, and the photolytic generation of arene radical cations in sulphuric acid[1] may involve oxidation by H_2SO_4 or SO_3. We now report the observation of the e.s.r. spectra of hydrocarbon radical cations by processes which we believe to provide the first examples of reaction (2).

$$\mathrm{RH} \xrightarrow{-e^-} \mathrm{RH^{\cdot+}} \qquad (1)$$

$$\mathrm{HR^{+}\!-\!H} \longrightarrow \mathrm{RH^{\cdot+}} + [\mathrm{H^{\cdot}}] \qquad (2)$$

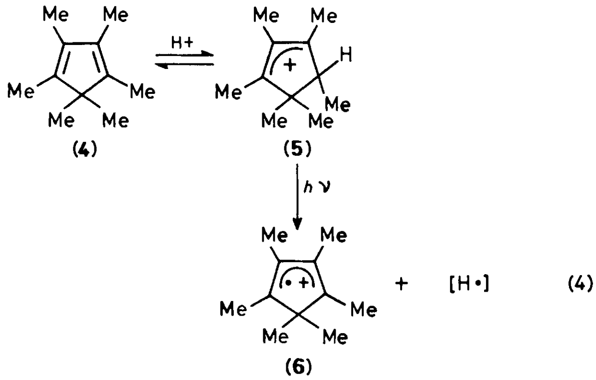
If a solution of di-t-butylethyne (**1**; R = Bu^t) in trifluoroacetic acid is irradiated with u.v. light filtered through Pyrex glass, in the cavity of an e.s.r. spectrometer, a strong spectrum[4,5] of the corresponding radical cation (**3**) is observed. Olah has demonstrated the cyclodimerization of alkynes to give cyclobutenyl cations (**2**) under strong acid conditions,[6] and a reasonable mechanism for the formation of (**3**) is shown in equation (3), analogous to the mechanism which is accepted for the same reaction using aluminium chloride as a Lewis acid.[5,7]

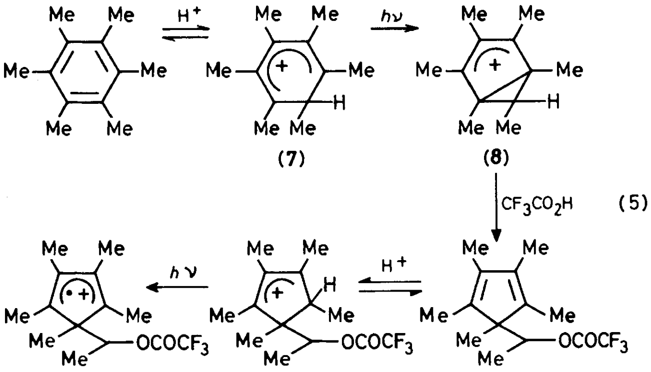
Di-1-adamantylethyne similarly reacts to show the spectrum of the tetra-1-adamantylcyclobutadiene radical cation (**3**; R = 1-Ad)[8] and a mixture of di-1-adamantylethyne and dimethylethyne gives $Ad_4C_4^{\cdot+}$ and *cis*-$Me_2Ad_2C_4^{\cdot+}$, a(6H) 7.9 G† at −50 °C. Under these conditions we have obtained the radical $Ad_4C_4^{\cdot+}$ with a half-life of more than 1 hour at −8 °C, whereas the same radical generated with aluminium chloride in dichloromethane has $t_{\frac{1}{2}}$ *ca.* 3 min at −55 °C.[8]



If a solution of hexamethylcyclopentadiene (**4**) in trifluoroacetic acid is photolysed, a strong spectrum of the corresponding radical cation (**6**) is observed, a(2Me) 14.4, a(2Me) 4.0, a(2Me) 1.3 G. The parent hydrocarbon (unlike pentamethylcyclopentadiene[3]) does not show the formation of any radicals in the absence of the acid, and we conclude that again we are observing the homolysis of a carbonium ion (**5**), as shown in equation (4).

When polycyclic arenes such as anthracene or pyrene are photolysed in trifluoroacetic acid, they show the familar spectra[1] of the corresponding radical cations. Again, it seems likely that the reactions are proceeding according to equation (2). Hexamethylbenzene, however, behaves differently. When it is irradiated in trifluoroacetic acid it shows a spectrum, not of the known hexamethylbenzene radical cation [a(6Me) 6.45 G],[9] but instead one which can be interpreted in terms of the hyperfine coupling constants a(2Me) 11.51, a(2Me) 4.25, ΔH_{pp} 0.6 G. These values suggest that we are





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† 1 G = 10^{-4} T.

again observing the formation of a butadiene radical. The reaction which we believe to be occurring is shown in equation (5).

The symmetry allowing disrotatory ring closure (**7**) → (**8**) is sterically possible, and has been shown to occur in the presence of $ClSO_3H$[10] or FSO_3H,[11] and the ring opening to give a cyclopentadiene has been demonstrated for the heptamethyl analogue of (**8**).[12] Thereafter, the reaction follows the route of equation (4).

We believe that the homolysis of the many further types of carbocations which are known will provide a prolific source of radical cations.

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References

1 Landolt-Börnstein, 'Magnetic Properties of Free Radicals,' Vol. II/1, 1964; Vol. II/9c2, 1979.
2 *E.g.* R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, 1974, **96**, 6409; P. A. Christensen, Y. Y. Huang, A. Meesters, and T. S. Sorensen, *Can. J. Chem.*, 1974, **52**, 3424.
3 J. L. Courtneidge, A. G. Davies, and S. N. Yazdi, *J. Chem. Soc., Chem. Commun.*, 1984, 570.
4 H. Bock, B. Roth, and G. Maier, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 209.
5 J. L. Courtneidge, A. G. Davies, E. Lusztyk, and J. Lusztyk, *J. Chem. Soc., Perkin Trans. 2*, 1984, 155.
6 G. A. Olah, J. S. Staral, R. J. Spear, and G. Liang, *J. Am. Chem. Soc.*, 1975, **97**, 5489.
7 Q. B. Broxterman, H. Hogeveen, and D. M. Kok, *Tetrahedron Lett.*, 1981, **22**, 173.
8 Q. B. Broxterman, H. Hogeveen, and R. F. Kingma, *Tetrahedron Lett.*, 1984, **24**, 2043.
9 R. M. Dessau, S. Shih, and E. I. Heiba, *J. Am. Chem. Soc.*, 1970, **92**, 412.
10 V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 1969, 389.
11 R. F. Childs, M. Sakai, B. D. Parrington, and S. Winstein, *J. Am. Chem. Soc.*, 1974, **96**, 6403.
12 R. F. Childs, M. Zeya, and R. P. Dain, *Can. J. Chem.*, 1981, **59**, 76.