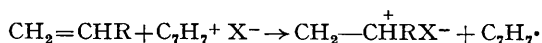


Electron-transfer Reactions with the Tropylium Cation

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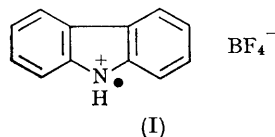
RECENTLY we have shown that tropylium salts are very useful initiators for the cationic polymerisation of several vinyl monomers.¹ The mechanism suggested for initiation in these polymerisations involves oxidation of vinyl monomer by the tropylium cation:



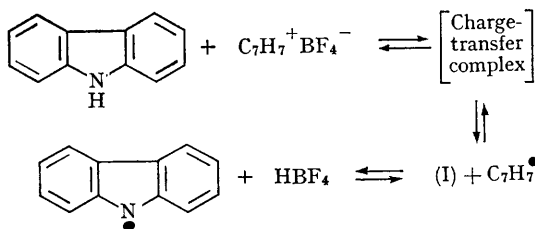
In order to characterise one-electron transfers to tropylium cation we have investigated the oxidation of a series of compounds, which do not polymerise, but which have structures similar to the donor groups (R) present in the polymerisable olefins. *N*-Vinylcarbazole polymerises very readily when treated with catalytic quantities of tropylium fluoroborate ($\text{C}_7\text{H}_7^+\text{BF}_4^-$) in acetonitrile,^{1,2} and consequently it was convenient to study the reactions of carbazole, and *N*-methylcarbazole with tropylium cation.

Addition of carbazole to $\text{C}_7\text{H}_7^+\text{BF}_4^-$ in dry acetonitrile at room temperature resulted in the immediate formation of a red, 1:1-charge-transfer complex³ (λ_{max} . 430 m μ ϵ_{max} . 3514). The carbazole-tropylium complex was stable for many days in acetonitrile but on addition of methanol or water, the absorption band of the charge-transfer complex slowly disappeared and was replaced by another band with maximum at 506 m μ . If solutions of the carbazole-tropylium complex in acetonitrile were poured into excess of methanol the longer wavelength band was formed immediately and, after evaporation, red violet crystals separated; these had elemental analysis figures suggesting a compound [$\text{carbazole}^+-\text{BF}_4^-$] and this structure (I) was confirmed by infrared and

ultraviolet spectroscopy. Solutions of (I) in acetonitrile did not show a detectable e.s.r. signal but crystalline (I) gave a weak, single line, e.s.r. spectrum with $g \approx 2.0$. This evidence indicates that the material is probably a Wurster-salt type of radical-cation, *i.e.* (I).



Wurster-salts of secondary amines are formed most readily in acidic media^{4,5} and this presumably explains why hydroxylic molecules must be added to the acetonitrile solutions in order to form (I), otherwise (I) would dissociate into H^+ and a carbazole radical.⁴



The fluoroboric acid formed by partial hydrolysis of $\text{C}_7\text{H}_7^+\text{BF}_4^-$ is apparently sufficient to permit

¹ C. E. H. Bawn, C. Fitzsimmons, and A. Ledwith, *Proc. Chem. Soc.*, 1964, 391.

² C. E. H. Bawn, A. Ledwith, and M. Sambhi, unpublished results.

³ M. Feldman and S. Winstein, *J. Amer. Chem. Soc.*, 1961, **83**, 3338.

⁴ J. Weiss, *Trans. Faraday Soc.*, 1946, **42**, 116.

isolation of (I). Confirmation of this mechanism was obtained by treating *N*-methylcarbazole with $C_7H_7^+BF_4^-$ in *dry* acetonitrile to give initially a charge-transfer complex (λ_{max} . 430 m μ) which slowly oxidised to the radical-cation (λ_{max} . = 520 m μ). In this case the radical-cation has no labile proton and is therefore stable in neutral solution.

Further confirmation of the ease with which tropylium cation oxidises donor molecules was obtained by studying its reactions with the Wurster amine, *NNN'*-tetramethyl-*p*-phenylenediamine. The Wurster-type, radical-cation of this amine is well known^{5,6} and has characteristic absorption maxima in acetonitrile at 564 m μ and

614 m μ . Reaction between this diamine and $C_7H_7^+BF_4^-$ in acetonitrile or between the diamine and $C_7H_7^+SbCl_6^-$ in dichloromethane was stoichiometric and immediately yielded solutions of the diamine radical-cation. Best results were obtained by using an excess of the diamine and in this way a value for ϵ_{614} of 7030 was obtained. Literature values for ϵ_{614} vary in the range 1,000—12,000.

Preliminary results have indicated that tropylium ion can be used to oxidise a wide range of unsaturated molecules which contain heteroatoms.

The authors are indebted to Mr. D. Cowley for measuring e.s.r. spectra.

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⁵ L. Michaelis, *J. Amer. Chem. Soc.*, 1931, **53**, 2953; L. Michaelis, M. P. Schubert, and S. Granicki, *J. Amer. Chem. Soc.*, 1939, **61**, 1981.

⁶ R. Foster and T. J. Thompson, *Trans. Faraday Soc.*, 1962, **58**, 860.