Carbonium Ion Charge-transfer Complexes

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FELDMAN and WINSTEIN have recently observed[1,2] charge-transfer complex formation between various stable organic cations and aromatic hydrocarbons. We have found that relatively reactive carbonium ions also exhibit this phenomenon, and that under certain conditions complete electron transfer from donor to acceptor can occur.

The mixing of dichloromethane solutions of various carbonium ions (*e.g.* substituted di- and tri-phenylcarbenium, xanthylium, and tropenylium ions) with solutions of pyrene or other aromatic hydrocarbons give coloured solutions which exhibit bands in the visible or infrared not found in the spectra of either component. The spectra of carbonium ion–pyrene solutions were studied qualitatively; the results are given in the Table.

Charge-transfer absorptions of pyrene–carbonium ion complexes

Acceptor[a]	λ_{max} (nm.)	ν_{max} (10^3 cm.$^{-1}$)	$E_{\frac{1}{2}}$ (red.) (V *vs.* S.C.E.)
Hydroxytropenylium	450	22·2	−0·41[c]
Methoxytropenylium	480	20·8	−0·27[c]
t-Butyltropenylium	503	19·9	
Tropenylium	535	19·7	−0·21[c]
Bromotropenylium	585	17·1	+0·01[c]
Chlorotropenylium	605	16·5	+0·04[c]
Cyanotropenylium	680	14·7	
Xanthylium	660	15·2	
p-Methoxyphenyldiphenylcarbenium	575	17·4	+0·05[d]
Tris-(*p*-tolyl)carbenium	640	15·6	+0·07[f]
Di(*p*-methoxyphenylcarbenium	675	14·8	
Triphenylcarbenium	710	14·1	+0·27[e]
Tris-(*p*-t-butylphenyl)carbenium	705	14·1	
p-Methoxyphenylphenylcarbenium	725[b]	13·8	
p-Nitrophenyldiphenylcarbenium	790[b]	12·6	+0·42[f]
Tris-(*p*-chlorophenyl)carbenium	820[b]	12·2	+0·34[f]

[a] The fluoroborate salts were employed except for those measured in CH_2Cl_2–$CF_3 \cdot CO_2H$ which were trifluoroacetates.

[b] Measured in CH_2Cl_2–$CF_3 \cdot CO_2H$.

[c] K. M. Harmon, Ph.D. Thesis, University of Washington, Seattle, Washington, 1958 (MeCN solvent).

[d] E. D. Jenson and R. W. Taft, *J. Amer. Chem. Soc.*, 1964, **86**, 116 (MeCN solvent).

[e] R. Breslow, W. Bahary, and W. Reinmuth, *J. Amer. Chem. Soc.*, 1961, **83**, 1763 (MeCN).

[f] Unpublished work of R. G. Johnston, University of Washington ($MeSO_3H$ solvent), with the method of S. G. Wawzonek, R. Berkey, and D. Thomson, *J. Electrochem. Soc.*, 1956, **103**, 513.

From these data it can be seen that these carbonium ions are powerful π-acceptors: the ν_{max} of the pyrene–Ph_3C^+ solution is very close to that of the pyrene–tetracyanoethylene complex,[3] and those of $(p\text{-}ClC_6H_4)_3C^+$ and $(p\text{-}NO_2C_6H_4)Ph_2C^+$ appear further into the infrared.

For a given donor molecule, ν_{max} for complexes of a series of similar acceptors should correlate with the electron affinities of the acceptors.[1,4,5] Electron affinity data are available only for the tropenylium ion[1] so this comparison cannot be made. However, electrochemical reduction potential data are available for these cations, and these can be correlated with ν_{max} (Figure). The reduction potential data are relatively crude, most having been obtained by polarography at a dropping-mercury electrode, not all in the same solvent, and cannot be taken to represent the true reversible redox potential.‡ Thus we cannot hope for better than a rough correlation of $E_{\frac{1}{2}}$ (red.) with ν_{max} and such is observed. Were good *reversible* redox potential data for a single solvent system available, a better ν_{max} –$E_{\frac{1}{2}}$ correlation could be expected.

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‡ This is especially true since the combination of tropenyl radicals, at least, is known to be fast (F. R. Hunter, *Diss. Abs.*, 1966, **27**, 4309b).

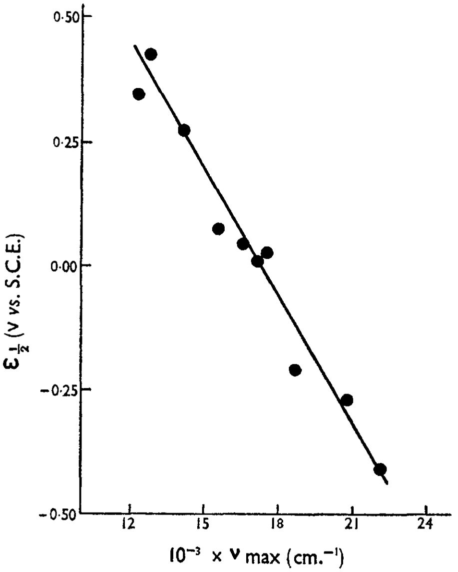

FIGURE. *Correlation of* $E_{\frac{1}{2}}$ *(red.) with* ν_{max} *(charge-transfer).*

Certain of the carbonium ions, particularly Ph_3C^+ and its derivatives, appear from their reduction potentials to be fairly strong oxidizing agents. Indeed, some seemed capable of oxidizing the more easily oxidized polynuclear aromatics to their respective cation-radicals, particularly under illumination (strong room light was sufficient). Thus Ph_3C^+ oxidized perylene and tetracene; $(p\text{-}Cl{\cdot}C_6H_4)_3C^+$ (prepared from the alcohol and $H_3O^+BF_4^-$ in CH_2Cl_2–$CF_3{\cdot}CO_2H$) oxidized pyrene and anthracene. In each case the cation-radicals were identified by their absorption spectra;[6] that of perylene gave a well defined e.s.r. spectrum.§ The cation-radicals of perylene, tetracene, and pyrene were stable in the CH_2Cl_2–$CF_3{\cdot}CO_2H$ medium employed in these latter experiments, but that of anthracene was not.

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