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PLANAR CATIONIC SYSTEMS AS CHARGE-TRANSFER ACCEPTORS

Martin Feldman[1] and S. Winstein

Department of Chemistry, University of California, Los Angeles, California

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THE tropylium ion I is an interesting acceptor in charge-transfer complex formation, and we recently reported the formation of such complexes with aromatic hydrocarbons.[2] For tropylium iodide a charge-transfer band at 575 m in methylene chloride has been observed by Harmon and coworkers.[3] In comparing tropylium ion with other planar cationic acceptors, we have now also employed iodide ion as the donor, since it has a relatively low ionization potential and its own absorption occurs at low wavelength relative to that of its complexes.

Pyrylium ions have a π-electron system isoelectronic with that of tropylium ion, and we have now compared 2,4,6-trimethylpyrylium II with tropylium in charge-transfer complex formation.[4] The iodide was prepared from the corresponding perchlorate[5] by ion exchange employing Dowex 2-X8 resin in the iodide form. The yellow salt, m.p. ca. 200° (dec.), may be recrystallized from glacial acetic acid and it can be titrated with aqueous silver nitrate (Found, 50.5; calc. % $I^{\ominus}$, 50.8). The 2,4,6-trimethylpyrylium io-

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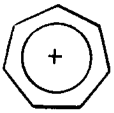
[1] N.S.F. Predoctoral Fellow, 1958-1962.

[2] M. Feldman and S. Winstein, J. Amer. Chem. Soc. 83, 3338 (1961).

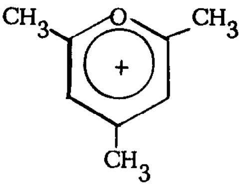
[3] K.M. Harmon, F.E. Cummings, D.A. Davis and D.J. Diestler, J. Amer. Chem. Soc. 84, 120 (1962).

[4] When 2,4,6-trimethylpyrylium perchlorate is added to solutions of anthracene in acetonitrile, there is a change in the absorption spectrum in the vicinity of 400 mμ which indicates the presence of a new band partly obscured by the strong anthracene absorption.

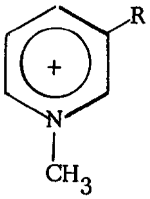
[5] O. Diels and K. Alder, Ber. Dtsch. Chem. Ges. 60, 716 (1927).



I



II



III

a; R = H

b; R = CONH$_2$

dide exhibits a new absorption band in methylene chloride at 452 mμ, which is absent in the spectra of the perchlorate[6] and can be ascribed to charge-transfer absorption.

N-Methylpyridinium ion IIIa is also π-isoelectronic with tropylium, and the charge-transfer spectra of pyridinium iodides have been studied extensively by Kosower[7]. Of special interest is 1-methyl-3-carbamido-pyridinium iodide IIIb (nictonamide methiodide). For this case, Pullman and Pullman[8] have reported that molecular orbital calculations place the lowest unfilled MO of the cation at a very low energy level, corresponding to a high electron affinity, and they ascribe the efficacy of the pyridine nucleotides, such as DPN$^{\oplus}$ and TPN$^{\oplus}$, as oxidative coenzymes to this feature. Our measurements on nicotinamide methiodide in methylene chloride reveal a charge-transfer band at 364 mμ.

The comparison of planar cationic systems may be extended to the N-ethylquinolinium and N-methylacridinium ions.[9] We find that the corresponding iodides in methylene chloride show charge-transfer absorption bands at 422 mμ and 495 mμ, respectively.

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[6] A.T. Balaban, V.E. Sahini and E. Keplinger, Tetrahedron 9, 163 (1960).

[7] E.M. Kosower, J.A. Skorcz, W.M. Schwarz, Jr. and J.W. Patton, J. Amer. Chem. Soc. 82, 2188 (1960) and E.M. Kosower and J.A. Skorcz, Ibid. 82, 2195 (1960) and papers cited therein.

[8] B. Pullman and A. Pullman, Proc. Nat. Acad. Sci., Wash. 45, 136 (1959).

[9] S.F. Mason, J. Chem. Soc. 2437 (1960).

Table 1 summarizes the positions of the cation-iodide charge-transfer bands in methylene chloride and the energy of the transitions in electron-volts (E_{CT}). Other effects being equal, the change in the energy of the charge-transfer transition of complexes with the same donor will reflect the difference in electron affinities of the acceptors, a large transition energy characterizing a low electron affinity.[10] The transition energies relative to that of tropylium iodide are given as ΔE_{CT} values in Table 1, and these provide an inverse measure of electron affinities relative to tropylium ion.

Another measure of relative electron affinities is polarographic reduction potentials, and charge-transfer absorption frequencies should correlate with polarographic reduction potentials.[11] For all of the cations except 2,4,6-trimethylpyrylium, polarographic half-wave potentials ($E_{1/2}$) are available either in the older or very recent literature, and these are listed in Table 1. For the pyrylium perchlorate we obtained a half-wave reduction potential of -0.85 volts vs. the saturated calomel electrode (sce) using a Sargent XXI Recording Polarograph and 0.05 M acetate buffer with 0.003 per cent Triton X-100 to suppress maxima. Comparison of diffusion currents of tropylium perchlorate and trimethylpyrylium perchlorate at concentrations of 5×10^{-4} M indicates that the latter is also a one-electron reduction (assuming identical diffusion constants).

While the half-wave potentials for the irreversible reductions reflect other effects in addition to electron affinity (e.g. solvation energy), it is probable that for a series of similar cations the relative potentials will be a measure of readiness to accept an electron. In Table 1 the half-wave potentials in water relative to tropylium ion ($\Delta E_{1/2}$) are compared

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[10] G. Briegleb and J. Czekalla, <u>Angew. Chem.</u> **72**, 401 (1960).

[11] M.E. Peover, <u>Nature, Lond.</u> **191**, 702 (1961).

TABLE 1

Iodide	λ, mμ (CH_2Cl_2)	E_{CT} (e/V)	$-E_{1/2}$ (vs. sce)	ΔE_{CT}	$\Delta E_{1/2}$
Tropylium	575[3]	2.16	0.25-0.27[14]	0	0
2,4,6-Trimethylpyrylium	452	2.74	0.85	0.58	0.58-0.60
N-Methylpyridinium	367[a] 374[a]	3.38[9] 3.32[7]	1.47-1.50[15]	1.22 1.16	1.20-1.24
Nicotinamide methiodide	364[12]	3.41	1.59-1.62[15]	1.25	1.32-1.37
N-Ethylquinolinium	422[13]	2.94	0.8[16]	0.78	0.55
N-Methylacridinium	495[13]	2.50	0.67[b,17]	0.34	0.40-0.42

[a] Solvent, $CHCl_3$ with 1% EtOH.
[b] Average for several concentrations of acridine at low pH.

with the ΔE_{CT} values. It is obvious that there is parallelism between ΔE_{CT} and $\Delta E_{1/2}$, the correlation being especially good for the isoelectronic tropylium, pyrylium and pyridinium cations which have approximately the same size.

One may conclude from the charge-transfer spectrum of nicotinamide methiodide and from the half-wave potential that this cation has a much lower electron affinity than tropylium. The Pullmans[8], treating the cation

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[12] E.M. Kosower and S.W. Bauer, [J. Amer. Chem. Soc. **82**, 2191 (1960)] report this band in pyridine at 370 mμ.

[13] Mason[9] gives these bands as 420 and 500 mμ, respectively, in $CHCl_3$ with 1% EtOH.

[14] P. Zuman, J. Chodkowski, H. Potěšilová and F. Šantavý, Nature, Lond. **182**, 1535 (1958) and P. Zuman, J. Chodkowski and F. Šantavý, Coll. Czech. Chem. Comm. **26**, 380 (1961); **27**, 759 (1962).

[15] K. Schwabe, Polarographie und Chemische Konstitution Organischer Verbindungen pp. 180, 182, 254. Akademie Verlag, Berlin (1957).

[16] D.J. Casimir, A.J. Harle and L.E. Lyons, J. Chem. Soc. 5297 (1961).

[17] R.C. Kaye and H.I. Stonehill, J. Chem. Soc. 27 (1951).

as a 10 π-electron system with an assumed set of Coulomb and exchange integrals, calculated that the lowest unfilled MO of this pyridinium cation has an energy level (E-α) equal to -0.356 β. Simple LCAOMO calculation for tropylium gives (E-α) equal to -0.445 β for its lowest unfilled MO. It is not surprising that these MO approximations fail to reflect adequately the relative electron affinities of the cations.

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