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SPECTROSCOPIC PARAMETERS OF NUCLEOPHILIC AND ELECTROPHILIC REACTIVITY

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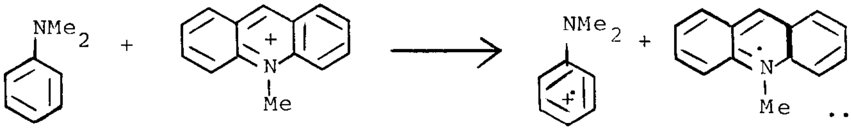
ABSTRACT Reactions of a distinct charge transfer nature (exampled by those between N,N-dimethylaniline and N-methyl cations) are associated with charge transfer bands, in the visible, of energy $h\nu = I - E + C$ where I is the ionisation energy of the nucleophile, E is the electron affinity of the electrophile and C is a correction term. As an example, the reaction between N,N-dimethylaniline and N-methylacridinium chloride is examined in detail. Tables of I are given for anions in adiponitrile solution and of $h\nu$ for cations in dimethylaniline/alcohol solution; low values of I correspond with greater nucleophilic activity and low values of $h\nu$ with greater electrophilic activity.

REACTIONS initiated by charge transfer present difficulties to some theories of reactivity, eg. those in which 'frontier orbitals' play a part.[1,2] Thus the frontier orbitals of the reactants are not necessarily the same as those after transfer has taken place as a result of electron relaxation and correlation taking place as transfer proceeds, an effect well known in photoelectron spectroscopy as 'failure of Koopmans's theorem'. Thus in N_2 the lowest ionisation energy corresponds with the second in the sequence of orbital energies[3] and in bis-Π-allylnickel the thirteenth[4]. Such switchovers are to be expected in 20% or so of cases and lead to the difficulty that the HOMO and the LUMO cannot be identified; for example the first of a series of reactions between N,N-dimethylaniline and N-methylacridinium chloride in ethanolic solution is the charge transfer:



..... 1

Are the frontier orbitals for the reaction following this one (2 below) those of the products of reaction 1 or those of an intermediate stage of transfer? The 'hard/soft' classification allows the prediction of the position of the equilibrium of reaction 2, where the hard H^+ is displaced by soft N,N-dimethylaniline cation,but gives no help with reaction 1 without which the sequence will not be initiated. However alternative parameters of reactivity are offered by Mulliken's equation $h\nu = I - E + C$ (the C term accounts for the fact that, although I and E refer to electron transfer to or from infinity, the equation refers to transfer between close partners and it is convenient to disregard C ie. to treat it as a constant independent of the reactants). The lower I and the greater E the less the energy required for the charge transfer and therefore the more reactive are the partners in the exchange. Measurements of E are generally unavailable especially for the relevant case of species in solution; photoelectron spectroscopy provides values of I for neutral molecules in the gas phase but has only recently given results for such ionic nucleophiles as $SeCN^-$, I^-, etc. in solution[5] - see table 1.

TABLE 1 VERTICAL IONISATION ENERGIES IN ADIPONITRILE SOLUTION, I/eV, and 'SOFTNESS CHARACTER'[1], E^*/eV.

ION	I	E^*	ION	I	E^*	ION	I
NO_2^-	6.8	-	SO_4^{2-}	7.6	-	NO_3^-	8.1
I^-	6.9	-8.31	Br^-	7.6	-9.22	OCN^-	8.2
SCN^-	7.1	-	$S_2O_3^{2-}$	7.8	-	HSO_4^-	9.0
CN^-	7.2	-8.78	SeO_4^{2-}	8.0	-	PF_6^-	>9.0
$SeCN^-$	7.4	-	Cl^-	8.1	-9.94	BF_4^-	>9.0

Klopman's 'softness character' or 'occupied frontier orbital energy' E^* has been given[1] for four of the ions in table 1; for these there is a linear relationship between I and E^*: $E^* = -1.37I + 1.16$. There is also a linear relationship between I and the charge transfer to solvent energy in acetonitrile[6].

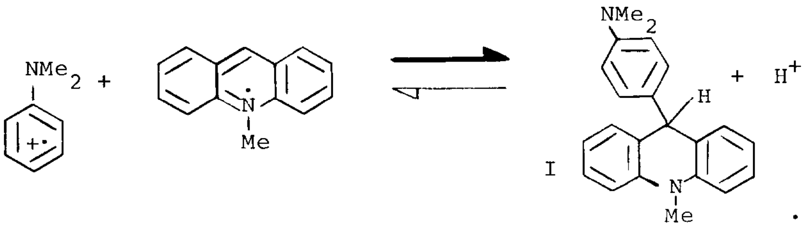
Although accurate values of E cannot be obtained for solutes, relative values of electrophilic reactivity can easily be measured as the energies of the charge transfer peaks in the presence of a common nucleophile like N,N-dimethylaniline which, in alcoholic solution, gives immediate colours due to charge transfer with the cations of table 2.

TABLE 2 PEAK ENERGIES OF CHARGE TRANSFER BANDS IN THE VISIBLE ABSORPTION SPECTRA OF CATIONS IN 5M, ETHANOLIC N,N-DIMETHYLANILINE, hν/eV[7]. The cations were in the chloride form. The colour of a fresh solution (due to charge transfer) and of an aged solution differs if a reaction ensues.

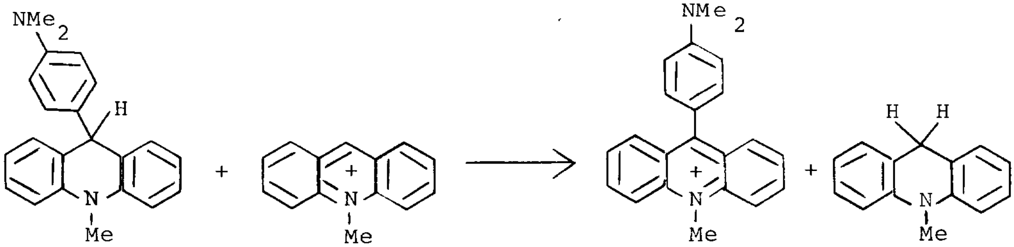
ION	hν	fresh colour	aged colour
N-methylphthalazinium	3.22		
N-methylquinolinium	3.01		
N-methylpyridazinium	2.95		
N-methylphenanthridinium	2.91		
N-methylpyrazinium	2.85		
N-methyl-1,5-naphthyridinium	2.66		
N-methylquinoxalinium	2.50	pink	blue
N-methylcinnolinium	2.42	pink	colourless
N-methyl-1,4,5-triazanaphthalenium	2.42	pink	blue
N-methyl-3,4-benzacridinium	2.42	pink	colourless
N-methylacridinium	2.35	brown	blue
N-methylphenazinium	2.17	green	orange

In connection with table 2 it is noteworthy that reactions between N,N-dimethylaniline and the cations occur only if the value of hν is 2.5 eV or less. Values of electron affinity can be calculated and hν is found to be related linearly to them[7].

In order to confirm the nature of the reactions a detailed study was made of one : that between N-methylacridinium chloride and N,N-dimethylaniline.



I 2



II 3

The overall products of the reaction were established by refluxing N-methylacridine and an excess of N,N-dimethylaniline in ethanol for one hour and isolating N-methylacridan from the blue solution so obtained in 50% yield; addition of ether to the refluxed mixture produced a blue-black precipitate identical (IR and UV) with a sample of II prepared from the base[8] by reaction with methyl iodide. The kinetics of the reactions were established by monitoring the visible spectrum at room temperature over a period of days.

An initial encounter (reaction 1) produces a charge transfer complex[9] as evidenced by the immediate brown colouration ($h\nu = 2.35$ eV) obtained upon mixing the reactants. It is not necessarily implied that a large proportion of the molecules are complexed[10]. Reaction 2 causes the rapid fading of the brown colour, the rate law being d(absorbance)/dt $\propto$ -[N-methylacridinium] x [N,N-dimethylaniline]. The use of p-deuterio-N,N-dimethylaniline reduced the rate by the factor 2.06.

Reaction 3 was monitored by the appearance of the blue colour of II (575 nm) and the rate law was found to be (where { } denotes initial concentration): d(absorbance)/dt $\propto$ {N-methylacridinium}^{2}/[N,N-dimethylaniline] which is consistent with reaction 2 being an equilibrium lying to the right. Thus the concentration of N-methylacridinium at equilibrium was proportional to [I]/[N,N-dimethylaniline]. In fact the equilibrium was driven to the right by the use of a large excess of N,N-dimethylaniline ie. 5M as compared with about 10^{-3} M for the N-methylacridinium chloride; under these conditions reaction 2 produced an equilibrium concentration of I proportional to the intitial N-methylacridinium concentration. P-deuteration of N,N-dimethyline did not affect the rate of reaction 3.

The above sequence resembles that postulated for many anodic substitution reactions[11]:

$$\mathrm{ArH} \xrightarrow[\text{anode}]{} \mathrm{ArH}^{+}\cdot + e^{-}$$

owed by,

$$\mathrm{ArH}^{+}\cdot + (\text{nucleophile})^{-} \longrightarrow \mathrm{Ar}\begin{smallmatrix}\nearrow \text{nucleophile}\\ \searrow \mathrm{H}\end{smallmatrix}$$

$$\mathrm{Ar}\begin{smallmatrix}\nearrow \text{nucleophile}\\ \searrow \mathrm{H}\end{smallmatrix} \xrightarrow[\text{anode}]{} \text{Ar-nucleophile} + \mathrm{H}^{+} + e^{-}$$

ich the anode, an electrophile after all, replaces N-methylacridinium in 1 and 3 .

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