Charge Transfer Complexes of Tropylium and N-Heterocyclic Cations with Aromatic Amines

THE tropylium[1-3] and N-heterocyclic cations[4-6] have been shown to act as electron acceptors in forming complexes of the electron–donor–acceptor type with halide ions and aromatic hydrocarbons as donors. Aliphatic amines form adducts of the σ-complex type with N-heterocyclic cations[7].

Addition of an aromatic amine to a solution of tropylium fluoroborate, N-methylquinolinium or N-methylacridinium perchlorate led to the observation of a new, featureless absorption band in the visible. With p-phenylenediamine

Table 1. CHARGE TRANSFER BAND MAXIMA (NM) FOR AROMATIC AMINE/CATION COMPLEXES

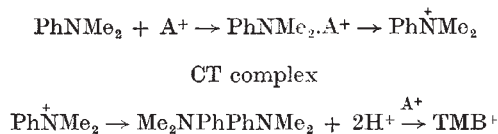| Donor	Acceptor Tropylium	N-methyl-quinolinium	N-methyl-acridinium
Aniline	520a		
N-methylaniline	552b	397c	500a (shoulder)
NN-dimethylaniline	571b	408d	537·5a
NN-diethylaniline	578b	430c	570a
o-toluidine	533·5b		500a (shoulder)

a, In dichloromethane; b, in 50/50 dichloromethane/acetonitrile; c, in acetonitrile; d, in ethanol.

and p-toluidine, this band appeared only transitorily, decaying too rapidly for establishment of its position, while NNN^1N^1-tetramethyl-p-phenylenediamine gave immediately the characteristic absorption and electron spin resonance spectrum of Wurster's blue radical cation. Other amines gave rise to more stable absorption bands, the positions of these being given in Table 1. Plotting $\bar{v}_{max}$ for these bands against the ionization potential of the donor for both amine and aromatic hydrocarbon complexes of the tropylium ion and against $\bar{v}_{CT}$, the charge transfer (CT) band maximum for complexes of chloranil with the same amines gave good linearity in both plots, thus establishing the CT nature of the transition and the complexes as the electron–donor–acceptor type.

The CT bands decayed over a period of time, being less stable in solvents of high polarity, which is in agreement with the observation[8] that carbazole complexes of the tropylium ion are stable in methyl cyanide, the addition of methanol or water leading to formation of carbazole radical cations. Preliminary investigation showed that tropilidene is one of the major products of decomposition of the tropylium complexes. Tropylium is known to abstract hydrogen from tertiary aliphatic amines[9] and from methyltropilidene[10], to form tropilidene. The mechanism in these reactions is postulated as hydride transfer. Kosower[11], however, has suggested that where intermediate CT complex formation occurs, hydride transfer, that is, a two electron transfer process, might alternatively be interpreted as two one electron transfers, electron transfer being followed by hydrogen atom transfer. Observation of electron transfer between tropylium and NNN^1N^1-tetramethyl-p-phenylenediamine and the carbazoles to form the corresponding radical cations lends support to a mechanism for the decomposition of tropylium–amine complexes via the electron transferred form of the CT complex.

The strongest evidence for an electron transfer mechanism was found for complexes of NN-dimethylaniline (DMA) and NN-diethylaniline with the N-methylquinolinium ion. Decay of the CT band in these systems was accompanied by the growth of a characteristic spectrum with three bands in the 440–480 mμ region and three bands in the 900–1,100 nm region. This is identical with the spectrum reported[12] for NNN^1N^1-tetramethylbenzedine (TMB) radical cation. The growth of this spectrum was accompanied by the growth of an electron spin resonance absorption, both being identical to those obtained by bromine oxidation of TMB. DMA also yields TMB and its radical cation on anodic oxidation[13] and we

believe that a similar mechanism is probably operative in the decomposition of the complex—that is, formation of DMA (or DEA) radical cation by electron transfer within the complex, followed by tail-to-tail coupling of the radical cation and elimination of two protons to give TMB. The radical cation of TMB is formed by further electron transfer to the acceptor.

$$PhNMe_2 + A^+ \rightarrow PhNMe_2.A^+ \rightarrow Ph\overset{+}{N}Me_2$$

CT complex

$$Ph\overset{+}{N}Me_2 \rightarrow Me_2NPhPhNMe_2 + 2H^+ \overset{A^+}{\rightarrow} TMB^+$$

Decomposition of the tropylium complexes may occur by a slightly different route, hydrogen atom transfer from the N-alkyl group of the amine to the intermediate tropyl radical giving tropilidene. No electron spin resonance evidence was found for the intermediate arylamine radicals or for the tropyl radical, but this is in accord with the lack of electron spin resonance evidence for these intermediates in anodic oxidation or oxidative dimerization of aromatic amines[14]. We feel that the evidence, although of a preliminary nature, places these reactions in the group where a CT complex plays a definite part as intermediate in the chemical reactions.

T. G. BEAUMONT
K. M. C. DAVIS

Department of Chemistry,
University of Leicester,
Leicester LE1 7RH.

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Effects due to Non-equilibrium pH Conditions in the Radiolysis of Aqueous Systems

DURING studies of the pulse radiolysis of aqueous solutions of pyrimidines and related substances, we have observed the formation of short-lived organic species which are formed by reactions other than those of the free radicals H, OH and e^-_{aq} produced by the radiolysis of the solvent. On the basis of the evidence presented here, we believe that these molecular transient species are the result of acid-base reactions between the pyrimidines and the radiolytic yield of hydroxide ions. These processes, although unlikely to lead to permanent products, are important in the pulse technique where the correct interpretation of a transient absorption is vital.

Nitrous oxide saturated solutions of thymine (T) (10–600 μM) were irradiated with 0·1–2 μs pulses of electrons (2–4 MeV), typical doses being 1 krad/pulse. In these condi-