Theoret. chim. Acta (Berl.) 10, 86—89 (1968)

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Aromatic Hydrocarbon-Carbonium Ion Molecular Complexes

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Received December 11, 1967

Molecular complexes of aromatic hydrocarbons and carbonium ions are described according to Mulliken's donor – acceptor theory. Estimations of electron affinities of several cations are deduced from charge-transfer transition energies and the indepently measured electron affinity of the tropylium ion.

The nature of charge-transfer complexes of aromatic hydrocarbons and carbonium ions, first exemplified by our study of tropylium ion complexes [1], was examined recently by Paldus and Polák [2], who used for a model the interaction of ethylene with the methyl cation. Although calculations of this type are worthwhile, we believe that there is significant value in describing the complexes according to the donor-acceptor theory of Mulliken [3], as elaborated by Briegleb [4].

Experimental evidence for the validity of the donor-acceptor treatment has been provided by the linear relationship between the ionization potential of the donor and the energy of the complex absorption band, for complexes of a given acceptor, as required by eq. 1:

$$E_{\mathrm{CT}} = h\nu = I_{\mathrm{D}} - E_{\mathrm{A}} + C\,. \tag{1}$$

I_{D}, the ionization potential of the donor, may be obtained from a variety of experimental methods, but E_{A}, the electron affinity of the acceptor, and C, a sum of interaction terms for the ground and excited states of the complex, may only be estimated from an assumption of the geometry of the complex. Values of electron affinities derived from charge-transfer spectra and estimations of C have been presented by Briegleb [5]. Complexes of the tropylium ion with aromatic donors are of theoretical interest because tropylium is an acceptor whose electron affinity has been measured directly. The evaluation of the Rydberg spectrum of the tropyl radical by Thrush and Zwolenik [6] gives an ionization potential of the radical (or the electron affinity of the tropylium cation) of 6.24 eV [1].

For several complexes of the tropylium ion, the variation of the energy of the charge-transfer band with ionization potential [8] of the donor is given in Table 1,

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[1] Electron impact measurements give a value of 6.60 eV [7].

and shown graphically in Fig. 1. The linear relationship of unit slope confirms that the complexes are of the donor-acceptor type, and allows the direct evaluation of C (Eq. 1) since E_A for tropylium is known. Two donors which deviate from the line are p-xylene and durene, but the large band-widths in the spectra of their complexes with tropylium [1b] suggest that the observed bands are in fact coalesced double bands. Complexes of these donors with other acceptors are well known to display double bands [4]. The energy of the first charge-transfer transition for each of these donors would thus be lower than the value given in Table 1, and a better fit with the correlation line would be expected.

Table 1. *Charge-transfer maxima (eV) of some tropylium ion complexes*[a]

Donor	I_D[b]	E_{CT}
1. Toluene	8.81	4.01
2. m-Xylene	8.59	3.76
3. p-Xylene	8.44	3.85
4. Mesitylene	8.41	3.55
5. Anisole	8.22[c]	3.35
6. Naphthalene	8.14	3.11
7. Durene	8.05	3.41
8. Hexamethyl-benzene	7.85	2.98
9. Anthracene	7.38	2.54

[a] Fluoroborate salt, solvent acetonitrile. [b] eV, from Ref. [8].
[c] K. Watanabe, T. Nakayama, and J. Mottl, "Final Report on Ionization Potentials of Molecules," U.S. Dept. Comm. 158317 600.

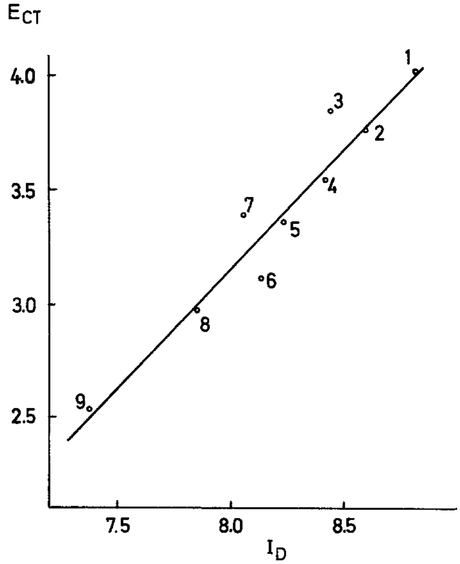

Fig. 1. Variation of E_{CT} with I_D for tropylium ion complexes. The numbers correspond to the donors in Table 1. The graph fits the equation $E_{CT} = (1.05 \pm 0.05)\, I_D - (5.23 \pm 0.65)$. Excluding points 3, 6 and 7 yields $E_{CT} = (1.03 \pm 0.01)\, I_D - (5.05 \pm 0.13)$

From the intercept of Fig. 1 and the measured value of E_A, C has a value of 1.2 eV. This is the sum of donor-acceptor interaction in the ground and excited states of the complex, including resonance stabilization of the ground state and destabilization of the excited state, ion-induced dipole interactions and specific solvent effects [9]. Determination of the heats of formation of the complexes would be valuable in the dissection of C, but these measurements are complicated by the disparate solubility requirements of the hydrocarbon donors and ionic acceptor.

A unique advantage of treating carbonium ion complexes as described here is that it makes possible the evaluation of electron affinities of other cations from relatively simple measurements of charge-transfer spectra. Provided that the charge-transfer bands are in an accessible region, a comparison of transition energies of complexes of a given donor with two cations will give the relative electron affinities of the cations. Since the electron affinity of tropylium has been determined, a comparison with complexes of tropylium will give an absolute value of the electron affinity of a particular cation. Table 2 lists charge-transfer maxima for several cations with various aromatic donors, as well as calculated electron affinities of the cations. It should be noted that these cations are rather complex, and direct determination of the ionization potentials of the corresponding radicals presents an extremely difficult experimental problem.

We wish to emphasize that only relatively stable carbonium ions will form molecular complexes with aromatic donors; by and large, the reaction of a carbonium ion with an aromatic hydrocarbon yields an alkylated aromatic. Even tropylium readily alkylates phenoxide ions [10], ferrocene [11] and N,N-dimethylaniline [12]. The ionization potential of the latter compound, 7.14 eV [8], lies between that of anthracene and phenothiazine (Tables 1 and 2), compounds which are not alkylated by tropylium. This indicates that theories of aromatic substitution in which electron-transfer is held to be important [13, 14] are questionable, and a knowledge of the behavior of other carbonium ions in this regard would be desirable.

Table 2. *Charge-transfer maxima (eV) of complexes of organic cations*

Cation	Donors					
	Durene	Hexamethylbenzene	Pyrene	Anthracene	Phenothiazine	Electron affinity
Tropylium[a]	3.20	2.84	2.32	2.34	1.85	6.24[g]
Dibenzo[*a*,*d*]tropylium[b]	2.78	2.38	1.86		1.53	6.7
1-ethoxyphenalenium[c]			1.84	1.74	1.53	6.7
N-methylacridinium[d]			2.46	2.40		6.1
Pyridinium ions:						
1-methyl-3,4,5-tricyano-[e]		2.45	2.00			6.6
1-benzyl-3-carbamido-[f]			3.02	3.18		5.5
1-benzyl-3-acetyl-[f]			2.92			5.6
1-benzyl-3-cyano-[f]			2.82			5.7

[a] Fluoroborate salt, solvent ethylene dichloride. Ref. [1b]. [b] Fluoroborate salt, solvent methylene chloride. J. A. Jackson, M. S. Thesis, Howard University, 1966. [c] Fluoroborate salt, solvent methylene chloride. D. A. Robinson, unpublished results, Howard University. [d] Perchlorate salt, solvent methylene chloride. P. R. Hammond, Nature **201**, 922 (1964). [e] Perchlorate salt, solvent not given. K. Wallenfels and W. Hanstein, Angew. Chem. Internat. Ed., **4**, 869 (1965). [f] Chloride salt, solvent dioxane-water, 6:4 v/v. G. Cilento and D. L. Sanioto, Arch. Biochem. Biophys. **110**, 133 (1965). [g] Ref. [6].

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