The only possible explanation of the observed effects is that ionic conductivity in these fused salts is a polyorder process, the ions moving in groups or by means of some chain mechanism, such as a charged hole moving through many ionic diameters with a single activation step. Other mixtures are currently under investigation.

TABLE I

RELATIVE MOBILITY AND CATION TRANSPORT NUMBER IN KNO₃–LiNO₃ MIXTURES

Total charge passed, ~800 coulombs; $T = 360–370°$

Ratio, K:Li anode, originally	Ratio K:Li, cathode after electrolysis	Transport no of cations
10	10.6	0.61
5	4.95	.60
3	3.06	.60
2	2.11	.64
1	1.06	.74
0.50	0.550	.75
.33	.361	.78
.20	.204	.80
.10	.106	.85

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TROPYLIUM ION–AROMATIC HYDROCARBON CHARGE-TRANSFER COMPLEXES

Sir:

In working with solutions of tropylium[1] perchlorate[2] or tetrafluoroborate[2] in various solvents, we have observed that addition of aromatic hydrocarbons gives rise to new absorption bands in the ultraviolet and visible regions of the spectrum (Table I). It is proposed that the new bands are charge-transfer absorption bands due to charge-transfer complexes[3] of tropylium ion with the various hydrocarbons as donors. The general evidence in favor of this interpretation may be summarized as follows.

(i) A plot of the frequencies of the new absorption bands vs. the frequencies reported for the same aromatic hydrocarbon donors and trinitrobenzene[4] as acceptor leads to a fair straight line with a slope near unity. Similarly, straight lines are obtained when the frequencies observed for tropylium ion are plotted against those observed with iodine[5a] or tetracyanoethylene[6] as acceptors. Since the frequencies of charge-transfer absorption for a series of donors with any one acceptor change nearly linearly with the ionization potential of the donors,[7] straight lines can be expected for

(1) (a) W. E. Doering and L. H. Knox, J. Am. Chem. Soc., **76**, 3203 (1954); (b) W. E. Doering and H. Krauch, Angew. Chemie, **68**, 661 (1956).

(2) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, J. Am. Chem. Soc., **79**, 4557 (1957).

(3) R. S. Mulliken, ibid., **72**, 600 (1950).

(4) A. Bier, Rec. Trav. Chim., **75**, 866 (1956).

(5) (a) H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., **71**, 2703 (1949); (b) R. L. Scott, Rec. Trav. Chim., **75**, 787 (1956).

(6) R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc., **80**, 2778 (1958).

(7) (a) R. Foster, Nature, **183**, 1253 (1959); (b) G. Briegleb and J. Czekella, Z. Elektrochem., **63**, 6 (1959).

the plots of charge-transfer absorption frequencies observed with one acceptor vs. those observed with another.

TABLE I

Donor[a]	ClCH₂CH₂Cl[b] mμ	CH₃CN[b] mμ
Benzene	305(sh)	(c)
Toluene	325	310(sh)
m-Xylene	...	330
p-Xylene	340	323
Mesitylene	365	350[d]
Naphthalene	430	395(sh)
2-Methylnaphthalene	472	...
Phenanthrene	425(sh)	...
Anthracene	530	487
Pyrene	535	...

[a] ca. 0.5 M. [b] Tropylium fluoroborate concentration ca. 10^{-3} M. [c] Under 275 mμ band of tropylium ion. [d] Identical band observed with tropylium perchlorate.
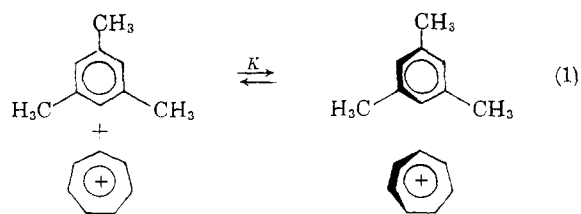
(ii) The wave lengths of the new bands listed in Table I are of the correct order of magnitude for charge-transfer absorptions. Theoretical considerations[3,7b,8] suggest that $h\nu$ for charge-transfer absorption of aromatic hydrocarbon–tropylium ion complexes should be approximated by the difference between the ionization potential of the donor and the electron affinity of the acceptor. This is because classical interactions and wave-mechanical exchange forces in the ground and excited states can be expected[7b] to make only small contributions to $h\nu$. In the LCAOMO first approximation (neglecting overlap) $h\nu$ thus turns out to be 1.445β, 1.063β and 0.859β for benzene, naphthalene and anthracene as donors, respectively.[9] An estimate of an appropriate value for the exchange integral, β, may be obtained from the 275 mμ band of tropylium ion, assuming this transition involves excitation of an electron from the highest energy bonding π-orbital to the lowest-energy anti-bonding one ($h\nu = 1.692\beta$). On this basis, charge-transfer absorption bands for tropylium ion complexes with benzene, naphthalene and anthracene are predicted at 322, 438 and 540 mμ, respectively. These are in very good general agreement with observed bands in ethylene chloride solvent at 305, 430 and 530 mμ, respectively.[10]

(iii) With mesitylene concentrations in the 0.1–0.65 M range and a tropylium tetrafluoroborate concentration of 1.3×10^{-3} M in acetonitrile, a Benesi–Hildebrand plot[5] of the observed absorbances at 350 mμ, assuming 1:1 complex formation as in equation 1, leads to a good straight line. The intercept and slope of the plot lead to an equilibrium constant, K, of 0.67 l. mole^{-1} at 25.0° and an extinction coefficient for the complex equal to 1850.

(8) S. P. McGlynn, Chem. Reviews, **58**, 1113 (1958).

(9) (a) E. Hückel, Z. Physik, **70**, 204 (1931); (b) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie., Paris, France, 1952, p. 187–199.

(10) The shift to shorter wave lengths accompanying the change from ethylene chloride to acetonitrile as solvent (Table I) seems in line with the general interpretation [see e.g., E. Kosower, J. Am. Chem. Soc., **80**, 3523 (1958)]. In ethylene dichloride, ion pairing must be quite important, and it is not yet clear how this affects complexing and the solvent sensitivity of the charge-transfer band.

$$\underset{\substack{+}}{\overset{CH_3}{\underset{H_3C \quad CH_3}{\bigcirc}}} \quad \overset{K}{\rightleftarrows} \quad \overset{CH_3}{\underset{H_3C \quad CH_3}{\bigcirc}} \qquad (1)$$

While there are a number of aromatic hydrocarbon charge-transfer complexes, the tropylium ion-aromatic complexes appear to be the first directly observed in which the acceptor is a carbonium ion. On the basis of the observed K value for mesitylene-tropylium ion complex formation, tropylium ion as an acceptor compares favorably with other π-acids. The present charge-transfer complexes of the stable tropylium ion are instructive models for possible reaction intermediates containing π,π-interacting aromatic hydrocarbon and carbonium ion species.[11]

In principle, olefins should conceivably be able to replace aromatic hydrocarbons as donors toward tropylium ion. While such complexing of tropylium ion with olefins has not yet been examined thoroughly, visible colors are produced on addition of tropylium salt to a solution of *trans*-stilbene, isoprene or tropilidene.[12]

Regarding charge-transfer complexes of tropylium ion with simpler donors such as halide ion, Doering[1] has suggested that the sequence of colors of the crystalline tropylium halides indicates a charge-transfer process. Also, Harmon[13] has ascribed a band for tropylium bromide in methylene chloride at 401 mμ to a charge-transfer transition. However, with halide ion donors charge-transfer complex formation tends to be followed or accompanied by more deep-seated reactions. For example, Dauben[2] has reported that tropylium iodide decomposes on standing to tropylium triiodide and other products. Also, we have observed that addition of tetrabutylammonium bromide to tropylium salt in ethylene dichloride gives rise to rapid formation of tribromide ion. We have similar indications that thiocyanate ion is oxidized by tropylium ion.

(11) Of related interest is the demonstration by A. K. Colter and S. S. Wang that acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate is accelerated by small concentrations of aromatic hydrocarbons [page 22-O of Abstracts, 139th Meeting of the American Chemical Society, St. Louis, Mo., March 21–30, 1961].

(12) Immediate color formation from tropylium ion and 7-methyltropilidene already has been noted by Kenneth Conrow during tropylium ion-catalyzed isomerization of 7-methyltropilidene [*J. Am. Chem. Soc.*, **83**, 2343 (1961)].

(13) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

(14) N.S.F. Predoctoral Fellow, 1958–1962.

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EVIDENCE FOR COÖRDINATION OF MONOPHENYL DIIMIDE WITH HEME PROTEINS

Sir:

It has been reported that the reaction of ferrihemoglobin (Hb$^+$) and phenylhydrazine results in reduction of Hb$^+$ to ferrohemoglobin (Hb) and
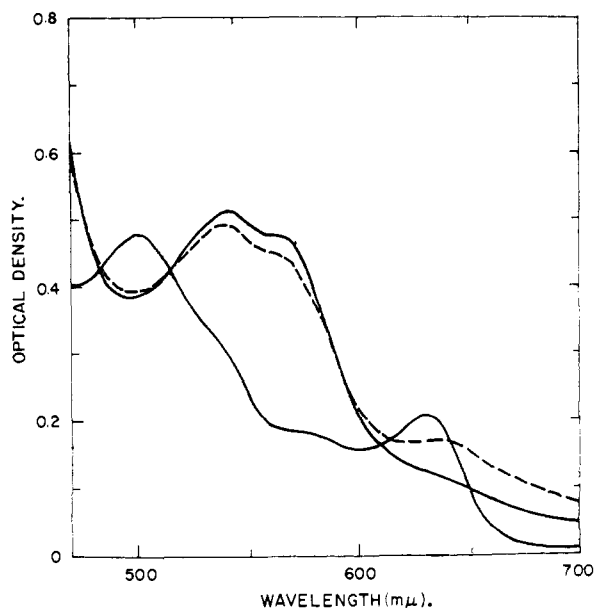

Fig. 1.—Absorption spectra of solutions 0.05 mM in heme at pH 6.8. The Hb$^+$ spectrum has maxima at 631 and 500 mμ. The other spectra are those of the compounds of oxidized phenylhydrazine with Hb (broken line) and Hb$^+$ (solid line).

oxidation of phenylhydrazine to benzene and nitrogen.[1] We observed, however, that addition of excess phenylhydrazine to a solution of Hb$^+$ resulted in a brownish solution, the absorption spectrum of which differed from those of Hb, Hb$^+$, or of a mixture of only these compounds. This observation led to experiments reported below, which indicate that an oxidation product of phenylhydrazine coördinates with both Hb and Hb$^+$ to form compounds having characteristic absorption spectra.

Bovine hemoglobin in phosphate buffer of pH 6.8, $\Gamma/2$ 0.1, was used in these experiments. Solutions of Hb, Hb$^+$, and HbCO were prepared as previously described.[2] Absorption spectra of samples 0.05 mM in heme were recorded with the Cary Model 14M spectrophotometer. Oxidized phenylhydrazine was prepared by mixing solutions of phenylhydrazine and K$_3$Fe(CN)$_6$ at concentrations up to 10 mM and 20 mM, respectively. At higher concentrations the mixed solutions became turbid. It was found that two moles of ferricyanide are reduced per mole of phenylhydrazine oxidized. In order to prevent interconversion between the ferrous and ferric compounds of hemoglobin, excess of phenylhydrazine and ferricyanide were added to solutions for experiments with Hb and Hb$^+$, respectively.

Addition of oxidized phenylhydrazine to Hb$^+$ in presence of oxygen resulted in a compound with an absorption maximum at 541 mμ. This compound and Hb$^+$ have isosbestic points at 609 and 516 mμ. The same compound was the major

(1) H. H. Rostorffer and J. R. Totter, *J. Biol. Chem.*, **221**, 1047 (1956).
(2) H. A. Itano and E. Robinson, *Biochim. et Biophys. Acta*, **29**, 545 (1958).