and propagation steps in the polypropylene oxidation. Bridger and Russell[50] have shown that tertiary hydrogens in a 1,3 arrangement are less reactive to hydrogen abstraction by phenyl radicals than are tertiary hydrogens with a 1,4 (or greater) separation. The lower efficiency of scission in polypropylene than in ethylene–propylene rubber may be a reflection of a lower initiation efficiency in the polypropylene.

If only tertiary hydrogens along the backbone are reacting according to the manner we suggest, then e_s should equal e_i. Our values of e_s for polypropylene and ethylene–propylene rubber are close to the initiation efficiencies for benzoyl peroxide in polymerizations.[51] In poly(ethyl acrylate), however, the scission efficiency is much lower. It has been observed that ester hydrogens are susceptible to oxidation,[52] so it is most reasonable to suppose that $RO_2\cdot$ radicals form on the side chain as well as on the backbone in poly(ethyl acrylate). If $RO_2\cdot$ radicals on the side chain interact and terminate, this will not contribute to the backbone scission that we measure.

The lower value for the composite rate constant $k_3 e_i^{1/2}(RH)/k_6^{1/2}$ for poly(ethyl acrylate) is expected because of the electron-withdrawing nature of the carbethoxy group. The propagating peroxy radical has been shown to be electrophilic.[53] The carbethoxy group might be expected to stabilize a radical formed at the tertiary center. This may be reflected in the lower

activation energy for the composite rate constant for poly(ethyl acrylate). Bolland[54] has reported that resonance stabilization of alkyl radicals formed in the propagation reaction lowers the activation energy for k_3.

It may prove fortuitous that in the cases we have examined, the efficiency of scission approximates the efficiency of initiation of the oxidation chains. Cases may be envisioned in which this might not be so. Termination could occur without scission. Two alkoxy radicals could couple to form a stable peroxide, or secondary peroxy radicals could form along the chain and terminate by a hydrogen-transfer mechanism. Alternatively, scission could occur without termination. The radicals produced by the cleavage of the tertiary alkoxy radical could conceivably have sufficient stability so that propagation reactions, such as hydrogen abstraction or radical addition to reactive double bonds, could compete with termination reactions. Thus in polymers quite different from the vinyl systems studied here, it would not prove surprising if values for e_s are found to be dependent on the kinetic chain length or are found to be much higher or much lower than 0.6.

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(51) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.
(52) A. Fish and A. Waris, *J. Chem. Soc.*, 4513 (1962); 120 (1963).
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[Contribution from the Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia]

Ionization Potentials of Substituted Benzenes and Their Charge-Transfer Spectra with Tetracyanoethylene

By E. M. Voigt and C. Reid

The relation between energy of charge-transfer absorption and ionization potential of the donor molecule in substituted benzene–tetracyanoethylene complexes shows apparent anomalies in the reported literature. By careful analysis of both the previously reported and new data in terms of band width and shape, it is shown that many of the anomalies can be explained. The relationship between the more satisfactory empirical relationship resulting and theoretical expressions which have been put forward is discussed.

Introduction

The energy required for optically induced intermolecular charge transfer (Mulliken[1]) has been discussed theoretically by a number of authors.[2–4] Using the notation of Mulliken and Person,[3] it may be expressed as

$$h\nu_{CT} = W_1 - W_0 + X_1 - X_0 \qquad (1)$$

Here W_0 is the energy of the pure "no-bond" state (D, A) including all interaction terms (electrostatic and van der Waals) except that (X_0) resulting from mixing with the dative state D^+A^-. Similarly W_1 is the energy

of the pure dative state, including van der Waals, and the now very considerable electrostatic term. X_1 represents the additional stabilization resulting from the interaction of the dative with the no-bond state.

We can write W_0 as $W_\infty - G_0$,[5] where W_∞ is the energy of the separated molecules and G_0 includes all but the no-bond–dative interaction.

Similarly after electron transfer, W_1 is expressed as

$$W_\infty + I_D^v - E_A - G_1$$

Here I_D^v is the vertical ionization potential of the donor, E_A is the electron affinity of the acceptor, and G_1 is again the term involving all D^+A^- interactions except the "resonance" interaction with the "no-bond" state.

Using various simplifying assumptions discussed in

(1) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600, 4493 (1950); **74**, 811 (1952); *J. Chem. Phys.*, **19**, 514 (1951); *J. Phys. Chem.*, **56**, 801 (1952).
(2) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961.
(3) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).
(4) S. P. McGlynn, *Radiation Res. Suppl.*, **2**, 300 (1960).
(5) There is a change from eq. 1 of ref. 3.

ref. 6, we may then write

$$h\nu_{CT} = I_D{}^v - C_1 + \frac{C_2}{I_D{}^v - C_1} \qquad (2)$$

In most cases where C_1 and C_2 have been determined, their values are such that the last term is small for fairly high ionization potentials (>7.5 e.v.), and a linear relation between charge-transfer frequency and vertical ionization potential may result.[7] Our values for tetracyanoethylene (TCNE) and substituted benzenes are $C_1 = 6.10$ e.v. and $C_2 = 0.54$ (e.v.)^2. However, even though the last term is small, C_1, which involves, as well as the electron affinity of the acceptor molecule, all other but the dative–no-bond resonance interaction terms, might well be expected to be quite variable because of changing intermolecular distance, steric or inductive effects of substituent groups, etc. In fact, although the linear relationship has been demonstrated experimentally many times, there are a few quite bad misfits which may be due to the above-mentioned variations.

Foster[8] has shown that a linear relation may be used to determine the electron affinities of organic acceptor molecules. He finds with many aromatic donors and acceptors the relationsh.p

$$h\nu = 0.85 I_D{}^v - e \qquad (3)$$

where e is the apparent electron affinity of the acceptor molecule.

The spectra of TCNE complexes with a number of substituted methylbenzenes do not fit expression 3. Merrifield and Phillips[9] reported that these complexes follow a relationship with different parameters, viz.

$$h\nu = 0.486 I_D{}^v - 1.31 \qquad (4)$$

On the other hand, Kuroda, et al.,[10] have recently published data for polynuclear hydrocarbon–TCNE complexes which almost fit Foster's expression.

$$h\nu = 0.87 I_D{}^v - 4.86 \qquad (5)$$

The authors then included some of Merrifield and Phillips' experimental data and arrived at a final equation

$$h\nu = 0.92 I_D - 5.12 \qquad (6)$$

As mentioned above, discrepancies of this kind may be expected since theory suggests that a linear relationship cannot adequately represent the situation. Nevertheless, we will show that the major error in the above work has been the use of incorrect values for the charge-transfer energy. Superposed peaks arising because of charge transfer from both of two different levels of the donor molecule have not been recognized as such and have caused a substantial shift from the true maximum of the first charge-transfer band.

Experimental

The charge-transfer absorption spectra were studied for TCNE with a large number of substituted benzene donors whose ionization potentials were accurately known from photoionization

(6) G. Briegleb and J. Czekalla, Z. Elektrochem., **63**, 6 (1959); **59**, 184 (1955).

(7) H. McConnell, et al., J. Chem. Phys., **21**, 66 (1953).

(8) R. Foster, Tetrahedron, **10**, 96 (1960).

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

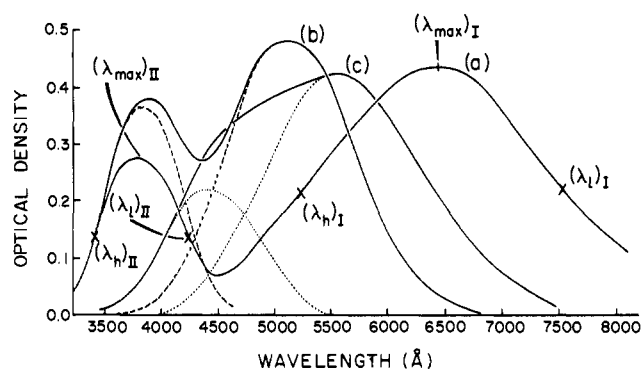(10) H. Kuroda, et al., J. Chem. Phys., **36**, 457 (1962).

Fig. 1.—Experimental and analyzed charge-transfer bands of methoxybenzenes and TCNE in dichloromethane at 22°: ———, experimental band envelopes of the (a) p-dimethoxybenzene complex, (b) anisole complex, (c) m-dimethoxybenzene complex; ‑‑‑‑‑‑‑‑, analyzed spectrum of b; ...., analyzed spectrum of c. $(\lambda_l)_{I,II}$ and $(\lambda_h)_{I,II}$ = wave length at $^1/_2$ maximum optical density at the low- and high-energy side of bands I and II for the p-dimethoxybenzene complex.

data.[11] Measurements were made on a Cary Model 14 recording spectrophotometer thermostated at 22°. The solvent used throughout was dichloromethane (Eastman Kodak Spectrograde and Fisher Certified Reagent). Tetracyanoethylene from Eastman Kodak was twice recrystallized from chlorobenzene and twice sublimed. All other reagents were commercially obtained and subsequently purified by recrystallization or distillation until melting or boiling points were within 1° of the literature values ("Handbook of Chemistry and Physics," 41st Ed.).

The absorption cells used were a pair of tared, stoppered quartz cells of 1-cm. path length. Samples were prepared immediately before measurement by mixing TCNE–dichloromethane solutions (10^{-3} M) with donor–dichloromethane solutions (10^{-2} to 10^{-1} M), to give charge-transfer bands having optical densities of 0.4 to 0.5. In the reference beam was placed a donor–dichloromethane solution at the same concentration as in the sample cell.

Analysis of Spectra.—Most of the complexes studied showed broad, more or less overlapping charge-transfer bands. Single (noncomposite) bands showed some asymmetry, the intensity on the high-energy side maximum falling off more slowly than on the low-energy side. They followed fairly well a relation put forward by Briegleb and Czekalla[12]

$$\frac{\bar\nu_h - \bar\nu_l}{2(\bar\nu_{max} - \bar\nu_l)} \simeq 1.2 \qquad (7)$$

where $\bar\nu_h$ and $\bar\nu_l$ refer to frequency at half the maximum intensity on the high- and low-energy side of the peak located at $\bar\nu_{max}$.

Assuming this relationship for the overlapping transitions of composite bands to define their shapes, and taking as half-width the value for the most nearly related complex showing a simple, or only slightly overlapping, band, composite bands were decomposed into their components. If the overlap was very great, the additional difficulty of deciding on the relative intensities of the two components arose. Where overlap was small, however, we found the ratio q_1 = optical density of the second band/optical density of the first band $\lesssim 1$ for almost all cases investigated, and this provided a guide for the difficult, closely overlapping cases.

Figure 1 shows typical decompositions for bands with little, moderate, and strong overlap. The estimated accuracies for the three cases are (a) ±50–100 cm.$^{-1}$ for weakly overlapped bands if they lie at the red end of the spectrum falling to ±200 cm.$^{-1}$ for transitions in the blue and near ultraviolet; (b) ±200 cm.$^{-1}$ for moderate overlap at the red end, the error again almost doubling in the blue; (c) for strong overlap, errors are larger but vary much from case to case. The individual error limits are given in ref. 13.

(11) (a) K. Watanabe, et al., "Final Report on Ionization Potential of Molecules by a Photoionization Method," Dec., 1959; (b) W. C. Price, et al., Proc. Roy. Soc. (London), **A258**, 459 (1960).

(12) G. Briegleb and J. Czekalla, Z. physik. Chem. (Frankfurt), **24**, 37 (1960).

(13) E. M. Voigt, J. Am. Chem. Soc., **86**, 3611 (1964).

Results and Discussion

The main contribution of this work is to arrive at fairly accurate, lowest charge-transfer energies by decomposing hitherto unrecognized overlapping bands into their components. Examples of some such bands have already been reported.[9,14] Merrifield and Phillips found two different absorption maxima for the p-xylene and the durene–TCNE complexes, but only single peaks, with abnormally large half-widths for the toluene and o- and m-xylene complexes. The usual half-widths are remarkably constant around 5–6 × 10³ cm.⁻¹ while that for o-xylene, for example, is 6.8 × 10³ cm.⁻¹.

Some of the complexes investigated in the present work give apparent half-widths as great as 8.2 × 10³ and result in serious errors if used undecomposed. A summary of the results is given in Table I.

As an example, the charge-transfer band for chlorobenzene–TCNE as reported[7] lies at a higher frequency than that for benzene–TCNE, while the donor photoionization potentials are 9.07 and 9.245 e.v., respectively; i.e., the order of charge-transfer energies is the reverse of that expected. In our own spectrum, decomposition of the wide band (half-width 7.9 × 10³ cm.⁻¹) into two components, moves the first maximum for this complex to 24,900 cm.⁻¹ (Merrifield and Phillips' value was 26.5) while our value for the benzene case is 25,800 cm.⁻¹. The correct order is therefore restored.

One or two similar anomalies have been reported in the literature. Iodine gives a reversed order from that expected with benzene and bromobenzene,[15] and some brominated hydrocarbons give undecomposed charge-transfer bands with several acceptors (I_2, tetrachlorophthalic anhydride, TNB, etc.), all at higher energies than those of the benzene complexes, while ionization potentials predict the reverse.[16]

When such anomalies occur (and a number of other cases, recorded in Table I, have been found during the course of this work), it is found that the higher-energy component has been shifted more to the blue relative to benzene than has the low-energy component moved to the red. This is understandable in terms of Orgel's[17] approach to the origin of double charge-transfer bands. In suitably substituted benzenes, the degeneracy of the highest filled (E_1) level of benzene is lifted because of different interaction between the substituents (s) and the two degenerate orbitals. The blue shift is often two to three times as great as that to the red. However, the effect of splitting is not always to reverse the direction of the shift expected relative to benzene. We therefore take the anomalous band width as the main criterion of splitting (see Table I). Furthermore, observation of two peaks for the corresponding para isomers of many disubstituted benzenes confirms this assumption, as do the data for the monohalogenated benzenes. The latter show a steadily increasing band width going from fluoro- to bromobenzene while the iodo compound shows two clearly separated peaks.

There is, of course, no certainty that all double charge-transfer bands in complexes have their origin in this splitting. In the case of heterocyclic donors, which will be dealt with in a later paper, the possibility of n and π donation must be considered. New bands are

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(15) R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., **74**, 4500 (1952).
(16) T. M. Spotswood, Australian J. Chem., **15**, 278 (1962).
(17) L. E. Orgel, J. Chem. Phys., **23**, 1352 (1955).

TABLE I
CHARGE-TRANSFER SPECTRA OF SUBSTITUTED BENZENE–TCNE COMPLEXES[a]

Donor[b]	c	Transition I — $\bar{\nu}_{max} \times 10^3$, cm.⁻¹	$\bar{\nu}_{1/2}$[d]	Transition II — $\bar{\nu}_{max} \times 10^3$, cm.⁻¹	$\bar{\nu}_{1/2}$[d]	q_I[e]
Benzene (a)		25.8	5.8	...	...	..
Anisole (b)	O	19.7	...	25.8	...	0.83
	A	19.7	5.0	26.1	5.5	0.77
o-Dimethoxybenzene (b)	O	16.9	...	23.2	...	0.58
	A	16.9	5.3	23.3	5.8	0.50
m-Dimethoxybenzene (c)	O	18.3	...	20.8	...	0.86
	A	17.9	5.2	22.7	5.8	0.51
p-Dimethoxybenzene (a)		15.7	5.9	26.3	6.0	0.56
1,2,3-Trimethoxybenzene (a)		19.4	6.3	..	...	..
1,2,4-Trimethoxybenzene (b)	O	14.6	...	22.7	...	0.33
	A	14.6	6.1	23.4	5.7	0.26
p-Methylanisole (a)	O	17.8	...	25.3	...	0.72
	A	17.8	4.8	25.3	5.5	0.72
o-Methylanisole (b)	O	18.3	...	23.8	...	0.8
	A	18.3	4.7	23.9	5.4	0.8
m-Methylanisole (b)	O	18.8	...	23.4	...	0.8
	A	18.8	4.6	24.0	5.5	0.84
p-Chloroanisole (a)	O	19.5	...	28.0	...	0.67
	A	19.5	5.7	28.1	5.9	0.65
o-Chloroanisole (b)	O	20.3	...	24.4	...	0.96
	A	20.1	4.8	25.7	5.7	0.9
p-Bromoanisole (a)	O	19.3	...	28.1	...	0.67
	A	19.3	5.7	27.9	6.0	0.65
o-Bromoanisole (b)	O	20.1	...	24.9	...	1.0
	A	19.7	4.8	25.4	5.6	0.9
Thioanisole (a)	O	17.5	...	26.5	...	0.3
	A	17.5	4.6	26.0	5.1	0.26
Styrene (b)	O	20.7	...	25.2	...	0.83
	A	20.8	4.9	25.9	5.4	0.8
Biphenyl (b)	O	20.0	...	25.6	...	1.2
	A	20.0	4.9	25.7	Uncertain	
Mesitylene (a)		21.4	5.3	..	...	..
Bromobenzene (c)	O	25.4	8.2	..	...	..
	A	24.6	4.8	28.2	5.9	0.8
p-Dibromobenzene (b)	O	23.8	...	29.7	...	0.99
	A	23.7	5.4	29.5	6.0	0.93
Chlorobenzene (c)	O	26.4	7.9	..	...	..
	A	24.9	4.6	28.3	5.4	0.9
p-Dichlorobenzene (b)	O	24.9	...	29.8	...	0.9
	A	24.5	5.4	29.7	6.0	0.87
o-Dichlorobenzene (c)	O	26.8	7.9	..	...	..
	A	25.0	4.7	28.7	5.4	0.8
m-Dichlorobenzene (c)	O	27.6	7.8	..	...	..
	A	25.4	4.6	28.6	5.4	0.9
1,3,5-Trichlorobenzene (a)		28.1	6.5	..	...	..
p-Chlorotoluene (b)	O	22.7	...	26.3	...	0.91
	A	22.3	4.7	27.1	5.4	
p-Bromotoluene (b)	O	22.2	...	26.2	...	0.87
	A	21.8	4.6	26.6	5.4	0.8
o-Bromotoluene (c)	NA	24.3	7.9	..	...	..
o-Chlorotoluene (c)	NA	24.7	7.1	..	...	..
Fluorobenzene (c)	NA	27.8	7.0	..	...	..
Benzonitrile (c)	NA	30.9	...	..	...	..
Trifluoromethylbenzene (c)	NA	30.5	...	..	...	..
Iodobenzene		22.3	4.6	27.9	6.0	1.0

[a] Solvent, CH_2Cl_2; temp., 22°; acceptor, TCNE. [b] a, b, and c refer to type of spectrum as denoted in Fig. 1 and specified in the text. [c] O = observed, A = analyzed, NA = not analyzed. [d] $\bar{\nu}_{1/2}$ = half-width of the charge-transfer band. [e] q_I = ratio of optical densities, max. II/max. I.

also possible as a result of the presence of complexes other than 1:1. This possibility is ruled out in our work by the unchanged intensity relationships found on
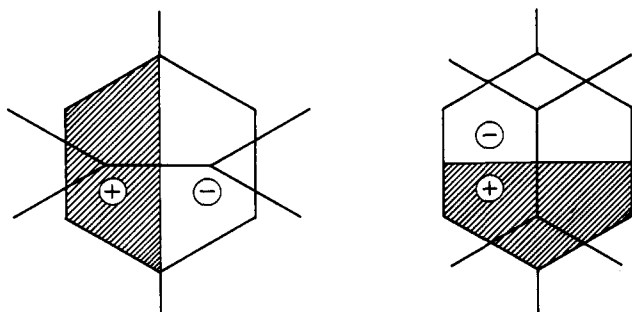
Fig. 2.—The two orientations of TCNE and p-dimethoxybenzene which make the charge-transfer transition allowed from the two highest filled levels of the aromatic ring.

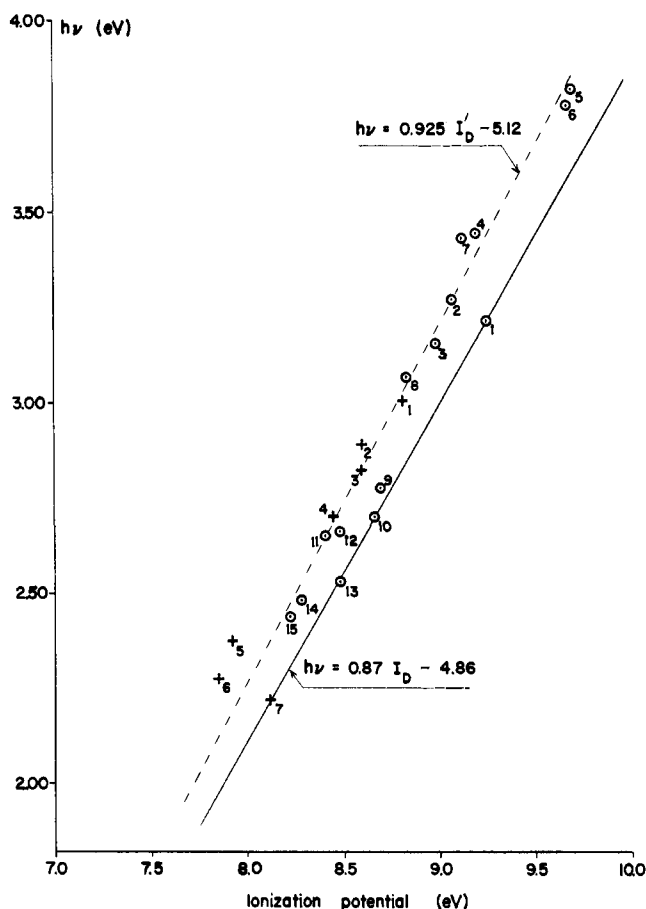Fig. 3.—Charge-transfer energy of various substituted benzenes with TCNE plotted against ionization potential of donor (solvent, CH_2Cl_2; temp., 22°). Donors: (a) (⊙, present authors [Table I]): 1, benzene; 2, chlorobenzene; 3, bromobenzene; 4, fluorobenzene; 5, benzonitrile; 6, trifluoromethylbenzene; 7, m-dichlorobenzene; 8, o-chlorotoluene; 9, p-chlorotoluene; 10, p-bromotoluene; 11, mesitylene; 12, 1,2,3-trimethoxybenzene; 13, styrene; 14, biphenyl; 15, anisole. (b) (+, from ref. 6): 1, toluene; 2, o-xylene; 3, m-xylene; 4, p-xylene; 5, pentamethylbenzene; 6, hexamethylbenzene; 7, naphthalene (photoionization potentials from ref. 11).

dilution. More subtle forms of isomeric complex might be possible involving different orientations of the TCNE relative to the substituent positions. In fact, if a model is chosen in which TCNE is placed symmetrically with the C–C bond parallel to the plane of the ring and with a fixed orientation, very different intensities for the two bands might be expected if the complex retains C_{2v} symmetry (Fig. 2). Since, in the cases examined, intensities rarely differ by more than a factor of two, a single rigid symmetrical model seems therefore to be ruled out in such cases. The possibility of a model in which the TCNE rotates in a plane parallel to that of the benzene ring so that both transitions become allowed seems not unreasonable and seems more likely than any explanation involving stable isomeric complexes which would inevitably have closely similar energies.

Let us now return to the ionization potential vs. charge-transfer relationship. Figure 3 shows the kind of result obtained with undecomposed bands, in the ionization potential range 7.5–9.5 e.v. Two lines have been drawn through these points, one corresponding to Kuroda's relationship for polycyclic hydrocarbons, the other given by

$$h\nu = 0.925 I_D^v - 5.12 \qquad (8)$$

which is close to that found by the above author when Merrifield and Phillips' data were included.

In Fig. 4 are plotted the "true" first charge-transfer band energies, obtained by our decomposition method vs. ionization* potential, over a more restricted range (8.2–9.25 e.v.). We find a best line for all TCNE complexes except that with benzene given by

$$h\nu_{CT} = 0.83 I_D^v - 4.42 \qquad (9)$$

which fits Briegleb's "best" parabolic relation, as well as having the first parameter close to that given by Foster[8] in his more general relationship (eq. 3). Figure 4 also includes a line through benzene and naphthalene corresponding to Kuroda's relationship (eq. 5). Other aromatics are not included, since photoionization potentials are not available, but the fit of the available data to this line may be found in Kuroda's paper.[10]

Although the use of undecomposed bands has been responsible for a good many of the reported deviations, there are a few cases due to incorrect ionization potentials. The recently reported photoionization values for penta- and hexamethylbenzenes give a better fit than do the old values quoted by Briegleb and Czekalla[6] which were used by Kuroda. Some of Merrifield and Phillips' ionization potentials[9] are also inaccurate,

adding to the discrepancies caused by composite maxima.

Much has been written on the ionization potential vs. charge-transfer energy relationship, and in view of the theoretical complexities, the empirical linear plots must be used with caution.[2–4] However, if rather stringent conditions are met we may expect the correlation to hold, and hence predict the otherwise unobtainable ionization potentials of involatile substances. The most important conditions to be met are:

(1) The obvious one that spectra to be compared should be obtained under as nearly identical conditions of solvent, temperature, and solute concentrations as is possible, and ionization potentials used should all be the photoionization values.

(2) Donation should be from orbitals of similar type. For example, one could hardly expect to predict the n-ionization potential of a heterocyclic n-donor from the corresponding charge-transfer band using a plot based on π-donors.

(3) There must be no steric factors (e.g., very bulky substituents on a benzene ring) which might hinder the attainment of comparable geometry to that of the reference complexes.
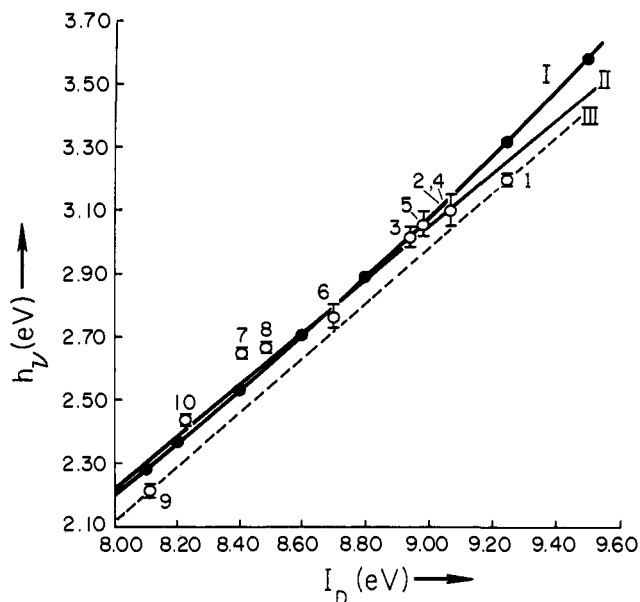
Fig. 4.—Analyzed ν_{max} values for the lowest charge-transfer band of various substituted benzenes with TCNE plotted against ionization potential of the donor: I, "theoretical" curve $h\nu_{CT} = I_D - 6.10 + 0.54/(I_D - 6.10)$; II, best experimental line $h\nu_{CT} = 0.83I_D - 4.42$ showing vertical error limits; III, Kuroda's line drawn through the points for benzene (1) and naphthalene (9): 2, chlorobenzene; 3, p-dichlorobenzene; 4, o-dichlorobenzene; 5, bromobenzene; 6, p-chlorotoluene; 7, 1,3,5-trimethylbenzene; 8, 1,2,3-trimethylbenzene; 10, anisole.

(4) Overlapped charge-transfer bands must be decomposed as in the present work.

(5) As a result of meeting the above conditions (and any other relevant ones), the change in donor ionization potentials must be the predominant variable as the donor changes. This condition is fairly well met, for example, in the case of the polycyclic aromatics, but less so for many substituted benzenes, where there may be substantial changes in charge distribution with little variation in ionization potential.

TABLE II
IONIZATION POTENTIALS OF SOME SUBSTITUTED BENZENES FROM THEIR CHARGE-TRANSFER ENERGIES WITH TCNE[a]

Substituted benzene donor	$h\nu_{CT}$, e.v.	I_D, e.v.[b]
1-Bromo-2-methoxy-	2.45	8.3
1-Bromo-4-methoxy-	2.39	8.2
1-Chloro-2-methoxy-	2.49	8.3
1-Chloro-4-methoxy-	2.43	8.2$_5$
1,4-Dibromo-	2.95	8.9
1,2-Dimethoxy-	2.09	7.8
1,3-Dimethoxy-	2.22	8.0
1,4-Dimethoxy-	1.96	7.7
1-Methyl-2-methoxy-	2.27	8.1
1-Methyl-3-methoxy-	2.33	8.1
1-Methyl-4-methoxy-	2.22	8.0
Thiomethoxy-	2.17	7.9
1,3,5-Trichloro-	3.47	9.5
1,2,4-Trimethoxy-	1.81	7.5
1,2,3-Trimethoxy-[c]	2.41	8.2

[a] Calculated from eq. 8.　[b] ±0.15.　[c] Unexpectedly high charge-transfer energy, probably due to steric effects in the donor.

In Table II we give a few examples of ionization potentials derived in this way from eq. 9. Because this is an average line relating many different TCNE complexes, the error is inevitably high. The results may be useful, however, for molecules too volatile for direct ionization potential measurement. We believe that accuracy may be improved by obtaining the reference line from a group of donors closely related to the one under investigation, and propose to test this matter further. At present, however, our line for the methylated, halogenated, and methoxybenzenes, while they appear to show some differences, are very nearly within the limits of experimental error. They have, therefore, not been included or used in this paper.

Electron Donor Ability of 7-Oxabicyclo[2.2.1]heptane

By Milton Tamres, Scott Searles, Jr., and John M. Goodenow

The thermodynamic constants for the complexation of 7-oxabicyclo[2.2.1]heptane with iodine in n-heptane were determined by a study of the temperature dependence of the perturbed iodine absorption in the visible region and the charge-transfer (CT) band in the ultraviolet region. The hydrogen-bonding interactions of this ether with methanol-d and with phenol were measured by the respective O–D and O–H shifts. Nuclear magnetic resonance data for the δ-shift and for the $J_{C^{13}-H}$ coupling constant of the α-protons were determined. Comparable data were taken for the four-, five-, and six-membered ring saturated cyclic ethers. The composite data indicate an electron donor ability of 7-oxabicyclo[2.2.1]heptane which is less than that of oxetane, but somewhat greater than that of tetrahydrofuran and terahydropyran. This relative order differs from that found from pKₐ measurements in aqueous acid, which show the bridged ether to be the weakest base. This difference is attributed to a solvation effect.

Introduction

Studies on hydrogen bonding[1] and on iodine complexation[2,3] with saturated cyclic ethers showed their basicity order to be four- > five- > six- > three-mem-

(1) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).
(2) M. Brandon, M. Tamres, and S. Searles, *ibid.*, **82**, 2129 (1960).
(3) M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960).

bered ring.[1] These results have been attributed to a change in electron distribution around the atoms in the ring with change in ring size.

Recently, Arnett and Wu[4,5] have measured directly the pKₐ's of a number of saturated ethers in sulfuric

(4) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1680 (1962).
(5) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1684 (1962).