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Zelinskii Institute of Organic Chemistry,
USSR Academy of Sciences

ORGANIC CHARGE-TRANSFER COMPLEXES

V. P. Parini

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INTRODUCTION

Organic molecular complexes have been known for a long time, but their systematic study which has resulted in the appearance of special monographs[1,2], is comparatively recent. During the past few years research on molecular complexes has been carried out particularly intensively not only by chemists but also by physicists and biophysicists. These complexes are formed as a result of donor–acceptor interaction between molecules, the so-called charge-transfer complexes, on which many papers have been published during the past decade, including some reviews[3-6]. The search for organic semiconductors has aroused especial interest in charge-transfer complexes. The present paper deals mainly with work on the electrical conductivity of such complexes, and on the probably related magnetic properties.

I. NATURE OF CHARGE-TRANSFER COMPLEXES

Charge-transfer complexes are those formed by molecules or ions, or both, without a covalent bond participating in complex formation. A feature of such complexes is the transfer of an electron from one component (the donor) to the other (the acceptor). The extent of electron transfer can in principle vary from zero to complete transfer, the latter case involving the conversion of neutral molecules to radical-ions The ground state of charge-transfer complexes containing one donor molecule combined with one acceptor molecule is approximately represented by the wave function[7-13]

$$\psi_n(D,A) = a\psi_0\ (DA) + b\psi_1\ (D^+A^-)\ldots, \qquad (1)$$

where D is the donor and A the acceptor; ψ_0 is the wave function for the non-ionic state of D and A, in which they may be linked either by a hydrogen bond, by dipole–dipole interaction forces, or by any others forming part of the classical "van der Waals forces"; ψ_1 is the wave function of the combined state, corresponding to complete transfer of one electron from D to A, and a and b are coefficients. The excited state is represented by the equation

$$\psi_e(D,A) = a^*\psi_1\ (D^+A^-) - b^*\psi_0(DA). \qquad (2)$$

With complexes having a weakly ionic bond, $a \gg b$, $|a| \simeq 1$, and $|b| \simeq 0$, so that

$$\psi_n \simeq \psi_0(DA), \text{ and } \psi_e \simeq \psi_1(D^+A^-),$$

i.e. the excited state is almost completely a diradical-ion. In complexes having a stable ionic bond between the D and A species, $b > a$. Table 1 indicates the relation between the coefficients a and b for several complexes, expressed in terms of the quantity $100b^2/(a^2 + b^2)$. It follows from these data that a is nearly always greater than b.

TABLE 1. Values of $100b^2/(a^2 + b^2)$ for some complexes.

Donor	Acceptor	$\frac{100\,b^2}{a^2+b^2}$	References
Hexamethylbenzene	trinitrobenzene	3.8	14
Stilbene	»	3.5	14
Naphthalene	»	2.8	14
1,2,4,5-Tetramethylbenzene	»	2.1	14
Hexamethylbenzene	chloranil	4.4	14
Benzene	iodine	2.8	9
Benzene	»	8.2	15
Pyridine	»	25	16

When A and D are weak donors and acceptors,

$$\psi_n(D, A) = a\psi_0(D\,A) + b\psi_1(D^+A^-) + c\psi_2(D^-A^+), \qquad (3)$$

where usually $c \ll b$.

With the so-called "self-complexes", which may be formed from identical molecules of aromatic hydrocarbons, $b = c$, since donor and acceptor possess identical properties. The general expression thus obtained is similar to that for the ground state of the hydrogen molecule.

This quantum-mechanical treatment of charge-transfer complexes was developed by Mulliken with reference to their state in solution. The application of these ideas to such complexes in the solid state may suffer certain restrictions or additional conditions. It is clear, however, that the smaller intermolecular distances occurring in the solid state result in greater coulombic forces, and hence in stabilisation of the ionic structure. The deep colour characteristic of many charge-transfer complexes is associated with the presence of excited ionic structures.

The energetics of charge-transfer complexes has been discussed in detail[3]. It is quite obvious that the process of complex formation itself and its energy characteristics depend on the ionisation potential of molecule D and the electron affinity of molecule A. Thus the energy required to raise the complex to an excited state can be written[17]

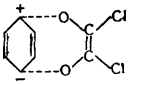
$$h\nu = I - E_a - W,$$

where h is Planck's constant, ν the transition frequency corresponding to charge transfer, I the ionisation potential of the donor, E_a the electron affinity of the acceptor, and W the dissociation energy of the excited state of the complex.

The above views on the nature of charge-transfer complexes are closely related on the one hand to their treatment as purely ionic compounds[18,19], and on the other as resonance hybrids[20] located between the uncombined state D : A and the ionic state $D^+ : A^-$. The possibility has also been considered[21,22] that a condition for the linking of the D and A molecules by free π electrons from the donor is that they should penetrate the potential barrier by a tunnel effect.

The energy of formation of charge-transfer complexes varies from hundreds to several thousand calories per mole.

With regard to the mutual arrangement of D and A molecules in the complex, the superposition of two coplanar molecules suggested for aromatic (including quinonoid) structures has been confirmed in several cases by crystallographic investigations[23-27]. Frequently, however, a different arrangement has been found. Thus, for example, the complex of 1,3,5-trinitrobenzene and anthracene provides an example of such superposition of coplanar D and A molecules[28], whereas the complex of trinitrobenzene with *p*-iodoaniline contains, besides the overlapping layers, alternating D and A molecules arranged in a single layer[29]. In the "self-complex" of *p*-nitroaniline the proximity of the O atom of the nitro-group to a C atom of a neighbouring ring (2.66 Å)[30] led to the hypothesis that acceptor centres may be localised in the substituents, with the formation of chains of "head-to-tail" type. On the other hand, a spectrophotometric investigation of quinhydrone[31] gave no indication of any substantial influence of the hydrogen bond formed here on the transfer of charge or the relative positions of the nuclei. It is very probable that, where the uniform distribution of electron density about the C atoms of the benzene ring is considerably disturbed, there is a tendency for quinonoid structures to be formed with localisation of the active (donor or acceptor) centres. For example, the following structure has been suggested[32] for the complex of benzene with oxalyl chloride:



A linear structure $\geqslant N-Hal-Hal$ has been demonstrated[33,34] for the so-called "onium" complexes formed between a tertiary nitrogen atom and a halogen molecule. Thus both charge-transfer structures in which A and D molecules are superposed and other structures can probably occur.

II. DONORS

The donors in organic charge-transfer complexes are almost exclusively aromatic compounds. With benzene and its derivatives the donor properties of the molecule, and hence the stability of the complex formed with a given acceptor, are determined by the nature of the substituent. The relative stabilities of complexes of benzene derivatives with the silver ion were found to be as follows[35-37] (the numbers in parentheses are relative to the stability of the complex obtained from iodobenzene taken as 5.0): NO_2 (0.19), F (0.46), $COCH_3$ (0.54), $COOC_2H_5$ (0.56), Cl (0.69), Br (0.97), OH (2.19), H (2.41), OCH_3 (2.50), CH_3 (2.63), I (5.00), and $CH=CH_2$ (18.2). With the exception of the last two cases, in which the silver ion apparently gravitates towards the substituent, the stability of the complex is directly linked with the inductive effect of the substituent. The following series has been obtained[38] for the relative stabilities of complex of benzene derivatives with tetranitromethane: H (0.05), CH_3 (0.90), $OCOCH_3$ (1.68), OH (12.28), OC_6H_5 (15.87), OCH_3 (20.41), and OC_2H_5 (20.62). Alkylbenzenes are good donors, and the relative stabilities of the complexes which they form with various acceptors are given in Table 2.

It is seen from Table 2 that accumulation of methyl groups strengthens the donor properties of the benzene ring. In the opinion of several workers[42] introduction of larger alkyl groups weakens the complex by preventing donor and acceptor from coming together.

The donor properties and the capacity for complex formation of aromatic nitrogen compounds of the amine type, pyridine, quinoline, and their derivatives are well known.

Polycyclic aromatic hydrocarbons are active donors. Stilbene and diphenylpolyenes[43,44] give 1 : 2 complexes with

TABLE 2. Relative stabilities of complexes of alkylbenzenes with various acceptors (benzene = 1.00).

Donor	Acceptor				
	Ag^+ [35,37,39,40]	iodine [39]	tetranitromethane [38]	HF [41]	tetracyanoethylene [42]
Benzene	1.00	1.00	1.00	1.00	1.00
Toluene	1.09	1.09	20.0	7.0	1.87
o-Xylene	1.31	1.82	143	12.2	—
m-Xylene	1.36	2.09	143	290	—
p-Xylene	1.09	2.09	143	12.2	3.80
1,2,4-Trimethylbenzene	—	—	—	700	—
1,2,3-Trimethylbenzene	—	—	—	770	—
1,3,5-Trimethylbenzene	0.74	5.50	465	145000	8.65
1,2,4,5-Tetramethylbenzene	0.93	4.25	590	1560	27.1
1,2,3,4-Tetramethylbenzene	—	—	—	4450	—
1,2,3,5-Tetramethylbenzene	—	—	—	178000	—
Pentamethylbenzene	—	5.90	800	320000	61.5
Hexamethylbenzene	—	9.10	1120	1080000	—
Ethylbenzene	1.22	—	26	—	—
Hexaethylbenzene	—	0.88	—	—	—
Propylbenzene	1.31	—	—	—	—
Isopropylbenzene	1.26	—	18.5	—	—

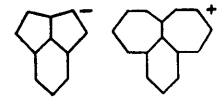
1,3,5-trinitrobenzene, which suggest that the benzene rings act in this case as independent donors; however, the donor properties of such systems become stronger as the polyene chain becomes longer. The ionisation potential of fused--ring hydrocarbons falls, and hence their capacity for complex formation increases, not with increase in the total number of fused rings but as quinonoid rings accumulate in the molecule [45]. Thus the ionisation potential falls from 9.24 eV for benzene to 4.39 eV for graphite, the latter substance showing an extremely great capacity for complex formation [46]. The ionisation potentials of several donors are given in Table 3.

The importance of the ionisation potential of the donor was confirmed by the fact that, in a series of complexes of iodine with various donors, the frequency of the electronic absorption band corresponding to charge transfer varies linearly with this ionisation potential [50]. Since in polycyclic aromatic systems the fall in ionisation potential is accompanied by an increase in electron affinity, when such systems react with alkali metals as donors they also exhibit the properties of acceptors, forming negatively charged radical-ions. Many alkali-metal complexes can initiate anionic polymerisation [51]. Metals like magnesium, aluminium, zinc, and even copper can act as donors with sufficiently strong acceptors, such as tetracyanoethylene, for example [52].

TABLE 3. Ionisation potentials of some donors.

Donor	Ionisation potential, eV	References
Benzene	9.24	47
Naphthalene	8.12	47
Anthracene	7.4	48
Naphthacene	7.0	48
Toluene	8.82	47
1,3,5-Trimethylbenzene	8.39	47
1,2,4,5-Tetramethylbenzene	8.3	47
Hexamethylbenzene	7.85	48
Aniline	7.70	47
NN-Dimethylaniline	7.3	48
NNN'N'-Tetramethyl-*p*-phenylenediamine	6.5	48
Pyridine	9.23	47
Trimethylamine	7.82	47
Potassium	4.34	49
Sodium	5.14	49
Copper	7.72	49

Aromatic structures which cannot exist as neutral molecules, of the type



etc., should show a very strong tendency to form charge--transfer complexes [53].

III. ACCEPTORS

Many inorganic substances are known as acceptors in charge-transfer complexes, among them being notably chlorine [54], bromine [55-58], iodine [55,57-67], hydrogen halides [41,68-71], aluminium chloride [72,73], ferric chloride [46,74,75], and the chlorides of antimony [74,76,77], tin [74,76], and titanium [78,79]. Other compounds which must be mentioned are sulphur dioxide [80-82], sulphuryl chloride [82,83], and water [84].

Among organic compounds used are anhydrides of di- and poly-carboxylic acids, *e.g.* maleic [20,83,85-87], phthalic [83], and mellitic [88] anhydrides, as well as acid chlorides such as oxalyl [32,83], fumaroyl [83], and phthaloyl [83] chlorides.

TABLE 4. Electron affinity of some acceptors [128].

Acceptor	Electron affinity, eV
Maleic anhydride	0.5
Trinitrobenzene	0.6
Iodine	0.8
Chloranil	1.35
Tetracyanoethylene	1.6

Halogenated derivatives have also been investigated, for example, chloroform [89,90], carbon tetrachloride and tetrabromide [91-93], and chloromaleic [85] and tetrachlorophthalic [94,95] anhydrides.

Among nitro-derivatives we must mention tetranitromethane [20,38], nitrobenzene and dinitrobenzenes [96-100], 1,3,5-trinitrobenzene [15,19,26,101-105], picric acid [101,103,106-109], picryl chloride [102,110-112], and styphnic acid [76]; among nitriles are 1,3,5-tricyanobenzene [96], tetracyanoethylene [42,52,113-115], and 7,7,8,8-tetracyanoquinodimethane [116-118].

An important group of acceptors are the quinones: *o*-[119] and *p*-benzoquinones [23,103,111,112,119-123] and their derivatives – chloranil [20,23,31,111,112,119,124], bromanil [23,113,119], and iodanil [113,119], – and also naphthaquinones [23] and substituted anthraquinone and phenanthraquinone [125].

Substituents in the benzene ring affect the properties of acceptors, as in the case of donors. In substituted quinones the tendency to complex formation varies [126] in the following sequence: chloroquinone > benzoquinone > > toluquinone > xyloquinone > duroquinone. Among the 4-substituted 1,3-dinitrobenzenes the acceptor strength decreases in the order [127] Cl > Br > OH > H > CH_3 > NH_2. The inductive effect of the substituent is quite evident in all cases.

The approximate electron affinities of several acceptors are given in Table 4.

IV. METHODS OF INVESTIGATING CHARGE-TRANSFER COMPLEXES AND SOME OF THEIR PROPERTIES

The following methods are generally used both to establish the actual fact of complex formation and to study the properties of the resulting complex: investigation of solubility in and distribution between various solvents, measurement of vapour pressure, plotting of melting point–composition curves for mixtures of donor and acceptor, spectrophotometric measurements, determination of dipole moments, viscosity measurements, radiofrequency spectroscopy, investigation of electrical conductivity both of solutions of the complexes and of the solid complexes themselves. We shall consider briefly optical methods, which are most often employed, and which have so far been the most important in research on charge-transfer complexes.

1. Optical Studies on Charge-Transfer Complexes

Spectrophotometry is an extremely convenient method for ascertaining the formation of a complex and also for determining its composition and the equilibrium constant of the reaction

$$D + A \rightleftharpoons \text{charge-transfer complex.}$$

The displacement of electron density accompanying the formation of such a complex corresponds to a considerable bathochromic change in the absorption and also to an increase in its intensity. Measurements of the shift in the absorption maxima in the electronic spectra and also of the optical density of solutions of the complexes are widely used for the investigation of such systems, notably of the picrates[129,130], complexes of stilbene and diphenylpolyenes with trinitrobenzene[44], complexes of aromatic nitro-compounds with hydrocarbons and amines[131-136], complexes of maleic anhydride[124,137] and of tetracyanoethylene[42]. Izmail'skii and his coworkers have made an extensive investigation of the optical properties of aromatic systems containing donor and acceptor groups, both insulated from one another and linked together by a system of conjugated bonds[138-146]. It is quite obvious that charge-transfer complexes are formed in these cases. The formation of such complexes is very probable in the so-called aggregation of dyes[147,148], and also in several cases of solvatochromism[149-154].

Infra-red spectroscopy has been employed to investigate the donor–acceptor interaction of aromatic compounds with halogens[151-157] and hydrogen halides[158-160], of pyridine with iodine[106], and also of aniline[161], dimethylaniline, and acenaphthene[162] with aromatic nitro-compounds.

The infra-red spectra, Raman spectra, and also X-ray structure analysis indicate that the formation of a charge-transfer complex involves some weakening of the interatomic bonds both in the donor molecule and in the acceptor molecule[3].

The luminescence spectra of such complexes show[163-165] that the resulting D....A bond affects the character of the luminescence by the donor.

2. Investigations of the Magnetic Properties of Charge-Transfer Complexes

Determinations of magnetic susceptibility by the static method have shown that the diamagnetism of many complexes is even greater than the additive value[105,122,166].

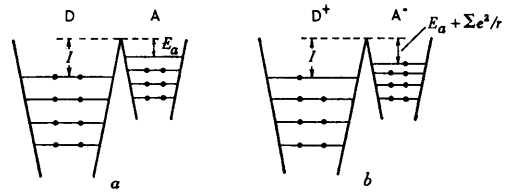


Fig.1.

The increase in the diamagnetism of the charge-transfer complexes with trinitrobenzene corresponds to the fall in the ionisation potential of the donor in the series naphthalene–phenanthrene–anthracene[96]. This fact is probably connected with the increasing delocalisation of the electrons in complexes of non-ionic type. For such charge-transfer complexes, $a \gg b$ in Eqn. (1).

With complexes of predominantly ionic type, D^+A^-, the energy required for excitation to the triplet level should be small, and the charge-transfer complex may be paramagnetic even at room temperature. A sharp fall in diamagnetism has been noted in the formation of charge-transfer complexes of bromine and iodine with polycyclic aromatic hydrocarbons.

The presence of temperature-independent paramagnetism has been established in such charge-transfer complexes by the method of electron spin resonance. The calculations showed that, for the complex of violanthrene with iodine, the faster contribution of the diradical-ion state is ~ 14%.[167] The presence of paramagnetism has been shown in this way in the complexes of *NNN'N'*-tetramethyl-*p*-phenylenediamine with *p*-benzoquinone and its tetrahalogeno-derivatives and also with tetrabromo-*o*-benzoquinone[119,168]. Paramagnetism had been detected previously[169] in the complex of *NN*-dimethylaniline with chloranil. According to Bijl *et al.*[119], the complex of *NNN'N'*-tetramethyl-*p*-phenylenediamine with chloranil contains 0.4% of the diradical form, while that with tetrabromo-*o*-benzoquinone, which has a considerably higher redox potential, contained 80%. Over the temperature range 6°–300°K the paramagnetism of the resulting complexes satisfies the Curie law, which suggests that the diradical state is in this case, as in several others[161], not an excited but the ground state.

More recent work[170] has shown that the contribution of the diradical-ion form in the charge-transfer complexes of dimethylaniline and *NNN'N'*-tetramethyl-*p*-phenylenediamine with chloranil, bromanil, and iodanil reaches 17%. However, the integral intensity of the electron spin resonance signal of these complexes, and also its form and width, change when the complexes are stored either in air or in an inert atmosphere. These changes are supposed to be due to the decomposition and reformation of the complexes during storage. A change with time in the concentration of the paramagnetic species, and in the colour of the charge-transfer complexes, has also been noted in other work[171]. Furthermore, it has been found that the form of the electron spin resonance signals depends on the mode of preparation and isolation of the specimens of the complex investigated.

The various states of a charge-transfer complex can be represented diagrammatically as in Figs. 1 and 2, in which D represents the donor, A the acceptor, *I* the ionisation

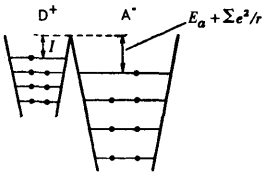


Fig.2.

potential, E_a the electron affinity, and $\Sigma e^2/r$ the coulombic interaction forces. In cases involving unpaired electrons the contribution of the diradical-ion state may actually be less than 100% owing to partial overlapping of the wave functions of D^+ and A^-.

Since in principle the two components of a charge-transfer complex in the radical-ion state, *i.e.* D^+ and A^-, have different g-factors, the spectrum may be expected to show two separate peaks, corresponding to each of the components. This has been found with the complex of p-phenylenediamine with chloranil, and thus the relative weakness of the electronic interaction between the components has been demonstrated[171]. For different ratios of the coefficients a and b in Eqn. (1), it is possible to have charge-transfer complexes which are diamagnetic between wide temperature limits (when $a \gg b$), complexes which can be relatively easily excited to a paramagnetic diradical-ion state (when $a \leqslant b$), and finally those in which the diradical-ion form represents the ground state. Unfortunately, the papers which have been quoted do not always give the precise conditions under which the complexes have been prepared, which makes it difficult to compare the results of the investigations.

Study of the temperature dependence of the electron spin resonance spectra of the ionic complexes of tetracyanoquinodimethane[118] led to the conclusion that their singlet ground state is so easily depopulated thermally that even at -100° about 4% of the substance has passed into the triplet state.

The paramagnetism of several polycyclic aromatic hydrocarbons, as also the form of the electron spin resonance signals which they give, is greatly dependent on the presence or absence of oxygen, and is presumably connected with the formation of a charge-transfer complex between the O_2 molecule as acceptor and the hydrocarbon molecule as donor[172]. The close link between the paramagnetism and the electrical conductivity of such systems suggests the presence of a common mechanism governing both phenomena[173].

In some cases, in particular with the charge-transfer complexes of pyrene and perylene with iodine, the intensity of the electron spin resonance signal shows an exponential dependence on temperature (over the range 77°–350°K), which is very close to that of the conductivity[69]. This suggests that in these cases the unpaired electrons are also the conduction electrons.

3. Investigations of the Electrical Conductivity of Charge-Transfer Complexes

This part of the review deals solely with the electrical conductivity of charge-transfer complexes in the solid state. It has already been suggested[174] that the magnetic, electrophysical, and catalytic properties of such highly ordered structures as nucleic acids, nucleoproteins, and also polymers containing conjugated bonds may be linked with the formation of charge-transfer complexes within these structures. It is assumed that the ordered group in the molecules (or macromolecules), the latter being mostly arranged in piles, *i.e.* packed one on the other, can transmit electrons thus producing a long-range oxidation–reduction process[175]. With charge-transfer complexes an alternating arrangement of D and A is envisaged.

The following mechanism has recently been suggested[176] for conduction in charge-transfer complexes. In the first stage one of the π electrons, having acquired the energy E, passes from a higher filled electronic level to the lowest of the unfilled levels. The ease of excitation determines the "activation energy" of conduction. In the second stage the unpaired electron passes through the intermolecular potential barrier by a tunnel effect. Decrease in intermolecular distances greatly facilitates this process. The ease of transfer determines the mobility of the charge carrier and the magnitude of the preexponential factor σ_0 in Eqn. (4).

The conductivity of polycyclic aromatic hydrocarbons with fused rings is considerably higher than that in saturated systems, and it satisfies the equation

$$\sigma = \sigma_0 \exp\left(-\frac{E}{kT}\right). \qquad (4)$$

The "activation" energy of conduction E varies linearly with the energy of excitation to the triplet state[177] and falls as rings of quinonoid structure accumulate in the molecule[45]. These relations are shown most clearly in the naturally ordered arrangement of crystals of aromatic hydrocarbons which is obtained on evaporation of the solvent from a solution[45]. It is known that in crystals coplanar molecules of polycyclic hydrocarbons are arranged mainly on top of one another with some lateral displacement[28]. All this cannot but suggest that in these cases a charge-transfer "self-complex" is formed, which results in a relatively high conductivity in these systems. It has even been suggested that ionic conduction may occur in aromatic hydrocarbons, with the formation of Ar^+ and Ar^- ions[178]. Self-complexes of aromatic systems have been often discussed[9,21,22]. The close connection between the activation energy of conduction and the triplet excitation energy indicates that either an excited or (where possible) a ground triplet state is probably responsible for conduction. Polycyclic aromatic systems containing quinonoid rings[45] are not distinguished by an evenness of electron density but contain local active centres[179], which are the most probable regions of charge transfer. Many conductivity measurements on polycyclic aromatic hydrocarbons and related systems have been published and intercompared[180–183]. The values given for the activation energy of conduction [E in Eqn. (4)] vary between 2.0 and 0.2 eV. The excitation energies are about the same. The conduction is of p-type[184–186].

Semiconductor properties have been confirmed in such coplanar aromatic systems as the phthalocyanines[187] and polyphthalocyanines[188], and also chlorophylls contained in the layered particles of chloroplasts[189]. Research on energy transfer processes in aromatic hydrocarbons[190], graphite (which is related to the former in structure)[191], and also in charge-transfer complexes[192] is being actively pursued.

The conduction of organic dyes and their photoelectric properties have recently been reviewed[193], the author paying special attention to the possibility of electron transfer by pairs of oppositely charged ions.

Table 5 gives published data on the electrical resistivity of specially synthesised charge-transfer complexes. The striking variation in the results is partly due to incidental factors. Firstly it may be doubted whether the results ascribed to complexes of *p*-phenylenediamine and diaminopyrenes with chloranil, bromanil, and iodanil, do actually relate to charge-transfer complexes. Amines are known to react readily with halogenated benzoquinones. In particular, diamines yield with such derivatives polymers which both possess increased conductivity and give electron spin resonance spectra[204]. Unfortunately, it was on these complexes that quantitative investigations of the Seebeck effect were made[200].

TABLE 5. Electrical resistivity of charge-transfer complexes.

Acceptor	Donor	Molar ratio A : D	Resistivity at 300 °K, ohm cm	Temp. range, °K	E^*, eV	References
Br_2	perylene	2,2 : 1	7,8	103—253	0.065	194—196
	pyranthrene	1,7 : 1	220	103—253	0.10	194—196
	violanthrene	2,3 : 1	66	103—253	0.10	194—196
	3,4-benzoquinoline	1,19 : 1	10^7		0.45	197
	2,3-benzoquinoline	4,9 : 1	$10^{15,4}$		2.09	
I_2	pyrene	2 : 1	75		0.11;0.068	66, 198
	perylene	3 : 2	8		0.015; 0.019	66, 198
	violanthrene	2 : 1	45	103—253	0.07	194—196
	violanthrene	2 : 1	45	283—388	0.07	194—196
	perylene	—	10			199
	coronene	—	10^9			
	acridine	—	$10^{1\,2}$			
ICl	acridine	—	10^{12}			199
1,3,5-Trinitrobenzene	coronene	—	10^{12}			199
	NN-dimethylaniline	—	10^8,10^{11}			199
Picric acid	coronene	—	10^{12}			199
Trinitrofluorenone	coronene	—	10^{12}			199
Chloranil	pyrene	—	$10^{1\,1}$			199
	perylene	—	10^8			
	hexamethylbenzene	—	10^1			
	NN-dimethylaniline	1-1	$8\cdot10^8$		0.23	176
	p-phenylenediamine	—	10^7			119
	p-phenylenediamine	—	10^6	263—293	0.25	119
	p-phenylenediamine	3 : 5	10^7	250—330	0.57	200
	NN-dimethylaniline	—	10^9,10^{10}		0.22	169, 199
	naphthylene-1,5-diamine	—	10^{11}			199
	naphthylene-1,8-diamine	—	10^{11}			
	p-aminodiphenylamine	—	10^{10}			
	NNN'N'-tetramethyl-*p*-phenylenediamine	—	10^9			
	ditto	1 : 1	$2\cdot10^4$		0.26	176
	3,8-diaminopyrene	—	10^4			199
	3,10-diaminopyrene	—	10^6			199
	p-anisidine	—	10^{11}			199
	acenaphthene	1 : 1	10^{15}		2.9	203
Bromanil	*NN*-dimethylaniline	—	10^9		0.22	169, 199
	ditto	1 : 1	$1.5\cdot10^9$		0.22	176
	p-phenylenediamine		10^{10}			199
	NNN'N'-tetramethyl-*p*-phenylenediamine	1 : 1	$1.3\cdot10^8$		0.28	176
	3,8-diaminopyrene		10^3			199
Iodanil	*NN*-dimethylaniline	—	10^8		0.22	169, 199
	ditto	1 : 1	$1.7\cdot10^8$		0.21	176
	p-phenylenediamine		10^{11}			199
	NNN'N'-tetramethyl-*p*-phenylenediamene	1 : 1	$1.5\cdot10^6$		0.29	176
	3,8-diaminopyrene	—	10^6			199
p-Benzoquinone	quinol	—	10^{11}			199
Tetracyanoethylene	pyrene	—	10^9,10^{10}			199
	perylene	—	10^8,10^{11}			199

TABLE 5 (contd.)

Acceptor	Donor	Molar ratio A : D	Resistivity at 300 °K, ohm cm	Temp. range, °K	E^*, eV	References
Tetracyanoethylene	hexamethylbenzene	—	10^{11}			199
	dimethoxybenzene	—	10^{11}			
	naphthalene	1 : 1	$3.2\cdot10^{15}$		1.24	115
	phenanthrene	1 : 1	$2.2\cdot10^{12}$		0.76	
	pyrene	1 : 1	$4.5\cdot10^{15}$		0.85	
	perylene	1 : 1	$2.4\cdot10^{12}$		0.72	
	anthanthrene	1 : 1	$1.1\cdot10^{10}$		0.57	
	violanthrene	1 : 1	$5.2\cdot10^8$		0.18	
	pentamethylbenzene	1 : 1	$4.4\cdot10^{13}$		0.56	
	hexamethylbenzene	1 : 1	$4.1\cdot10^{13}$		0.58	
	acenaphthene	1 : 1	$5.3\cdot10^{12}$		1.02	
	azulene	1 : 1	$4.7\cdot10^{10}$		0.38	
Tetracyanoquinodimethane	quinolinium	2 : 1	10^{-2}		<0.01	117
	trimethylammonium	2 : 1	0,25		0.14	
	K	2 : 2	$5\cdot10^3$		0.34	
Anthracene	Li	1 : 1.16	10^{11}	300—350	1.36	201
	Na	1 : 1.08	10^8	300—350	1.20	201, 202
	K	1 : 1.18	10^{11}	300—350	1.13	201
3,4-Benzoquinoline	Na	1 : 1.11	10^{21}		2.34	202
		1 : 1.49	10^{10}		0.35	

* From the equation $\rho = \rho_0 \exp(E/kT)$.

Secondly, some of the complexes[176,199] were obtained by crystallisation from solution, while several others were obtained directly by interaction between the components. Such a difference in methods of preparation can lead to marked differences in conductivity.

In spite, however, of these reservations, it is clear that the charge-transfer complexes of aromatic hydrocarbons with halogens have outstandingly high conductivity. This may be linked with their structure, *i.e.* with the alternation of hydrocarbon planes, both atoms of the halogen molecule being located between the planes on the same axis of symmetry as the latter[33,34].

Complexes of chloranil, bromanil, and iodanil with *NN*-dimethylaniline and with *NNN'N'*-tetramethyl-*p*-phenylenediamine[205], which are also distinguished by relatively high conductivity, have a similar structure, with alternating donor and acceptor molecules, of the type ADAD... In the purely organic complexes steric and other factors may prevent donor and acceptor from coming sufficiently close together, but the highest conductivity is in fact shown by ionic organic complexes of 7,7,8,8-tetracyanoquinodimethane. Discussion continues on the relation between the crystal structure of charge-transfer complexes and their conductivity.

Existing data do not permit the conductivity parameters to be directly linked with the ionisation potential of the donor. One cause of this is undoubtedly that the conductivity measurements were usually made on tablets pressed out of microcrystalline preparations. With this mode of preparation of the specimens, the measurements cannot reveal the anisotropy of conductivity which is undoubtedly characteristic of the charge-transfer complexes, and yield a mean result which is too low.

The conductivity of tetracyanoquinodimethane complexes and of graphite and its lamellar compounds, in particular those with potassium, $(C_8K)_n$, and with bromine, $(C_8Br)_m$,

exhibits a marked anisotropy (it can differ by a factor of 10^4); there is also an increase in the conductivity of graphite when either a donor or an acceptor is introduced into it[208]. Graphite itself, in which the ionisation potential, 4.39 eV, is equal to the electron affinity, can act either an an acceptor or as a donor, depending on the properties of the second component. The Hall effect could not be observed with any of the charge-transfer complexes: *i.e.* the mobility of the current carriers is low. Measurements of the thermoelectric power have been made on the tetracyanoquinodimethane complexes[117]. The few data available on the magnitude of the preexponential factor σ_0 and the activation energy of conduction E do not, in most cases, permit the steepness of the conductivity–temperature curve for charge-transfer complexes to be assessed. Now, however, it is already clear that the conductivity of such complexes is always greater than that of their organic components, and also that charge-transfer complexes can be obtained having either low or high values of σ_0 and E. These two important facts open up wide theoretical possibilities for the utilisation of such complexes as organic semiconductors having various specified properties. In the solid state charge-transfer complexes are, of course, polymeric complexes. If the hypothesis[174] should prove correct that the conductivity and the magnetic properties of polymers having conjugated bonds, many of which have been described[182,207-210], result from the formation of charge-transfer complexes, such an approach will enable us to speed up the production not only of synthetic polymeric semiconductors but also of synthetic polymeric catalysts[211-213], including those which simulate biological catalytic systems[214].

Several charge-transfer complexes[169], in particular those of *NN*-dimethylaniline with chloranil, catalyse the ortho–para conversion of hydrogen. Sometimes, however, this catalytic activity did not appear. Its presence or absence is probably associated with differences in the method of preparing the complexes[176].

The synthesis of polymeric donor and polymeric acceptor systems should be of considerable interest from the point of view of conductivity and magnetic and catalytic properties. The charge-transfer complexes formed by such systems should be characterised by stability, high conductivity, and stable paramagnetism. The effects may be expected to be especially marked when both donor and acceptor are polymers having an extensive system of conjugated bonds.

V. CHARGE-TRANSFER COMPLEXES AND THE MECHANISM OF CHEMICAL REACTIONS

Starting from the idea that the first stage in many organic reactions is a sudden shift in electron density from one reactant to another, whereas movement of the nuclei to new fixed positions corresponding to the reaction products is a secondary process, we readily conclude that the first reaction complex is actually a charge-transfer complex. Consideration of the effect of the polarity and polarisability of the reactants on the reaction mechanism leads to the same conclusion[215,216].

Table 6 shows clearly that the rate of halogenation of various aromatic hydrocarbons[217] and the stability of the charge-transfer complexes formed by these hydrocarbons with such acceptors as Br_2 [218] and HF [41] can be correlated. In these cases the tendency of the hydrocarbon to form a charge-transfer complex and the stability of the complex are probably the factors governing the rate of halogenation. Such complexes of aromatic hydrocarbons with bromine are unstable, forming brominated derivatives on storage.

TABLE 6. Relative stabilities of charge-transfer complexes and rates of halogenation of aromatic hydrocarbons (benzene = 1).

Hydrocarbon	Stability of charge-transfer complex with		Rate of halogenation
	Br_2	HF	
Benzene	1.00	1.00	1
Toluene	1.43	7	$3 \cdot 10^2$
o-Xylene	2.4	12.2	$4 \cdot 10^2$
m-Xylene	2.08	290	$4 \cdot 10^5$
p-Xylene	2.16	12.2	$2 \cdot 10^2$
1,2,4-Trimethylbenzene		700	$6 \cdot 10^5$
1,2,3-Trimethylbenzene		770	$8 \cdot 10^5$
1,3,5-Trimethylbenzene		145000	$1.6 \cdot 10^8$
1,2,4,5-Tetramethylbenzene		1560	$3 \cdot 10^6$
1,2,3,4-Tetramethylbenzene		4450	$4 \cdot 10^6$
1,2,3,5-Tetramethylbenzene		178000	$5 \cdot 10^8$
Pentamethylbenzene		320000	$7 \cdot 10^8$

The formation of charge-transfer complexes has also been suggested[85] in reactions of diene synthesis between maleic anhydride and other acceptors — between dienophiles on the one hand and donors (dienes) on the other.

The view that charge-transfer complexes are important intermediates in many reactions has been used to systematise a large number of facts[219]. The formation of unstable charge-transfer complexes in chemical reactions could be confirmed experimentally in actual cases by investigation of the reaction mechanism using such modern physical methods as conductimetric measurements and radiofrequency spectroscopy.

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Institute of Chemical Physics,
USSR Academy of Sciences