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The Charge-transfer Complexes of Neutral Donors with Organic Cations as Acceptors

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The principal results of studies on charge-transfer π-complexes (CTC) with an organic cation (carbonium, heteroaromatic, and hetero-onium) as the acceptor are examined and problems of the classification of the CTC on the basis of the structures of the ground and excited states are discussed. The thermodynamic and spectroscopic data for the type of CTC considered are analysed. The results of the determination of the electron affinities of the acceptor cations are examined and surveyed. Ideas concerning the photochemical properties of the CTC or arenediazonium ions, which are of interest as materials for the recording of information, are described.
The bibliography includes 101 references.

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I. INTRODUCTION

The chemistry and physics of charge-transfer complexes (CTC) now constitute in many respects an independent field, which is closely related to a number of other fundamental scientific disciplines as well as practical applications[1]. Despite the fairly large number of reviews and books on this field[2-12], some types of the CTC have been described extremely superficially. These include also the CTC formed by a neutral electron donor and an acceptor cation. Although the specific conductances of crystalline CTC of this type[13-15] are fairly low, one cannot claim that their interaction is of no practical interest. It is known that many acceptor cations are directly involved in important biological processes[4] or exhibit a pronounced biological activity[12,13,16,17]. Charge-transfer complexes with a nitronium cation are considered as intermediates in the nitration of aromatic compounds[18,19] and the CTC of diazonium salts are believed to be a possible means of improving the light sensitivity of photographic materials[20,21]. From this, it follows that the comparatively little investigated type of CTC formed between a neutral π-donor and an acceptor cation is fairly interesting also from the practical point of view.

The aim of the present review is to examine the general characteristics of the formation of the CTC of this type; particular attention has been devoted to the electron affinities of the acceptor cations and the photochemical properties of the CTC of diazonium salts. The complexes between aromatic hydrocarbons and metal cations are not considered

here; the readers interested in this problem are recommended to refer to the interesting monograph of Mulliken and Person[5].

II. THE ENERGY LEVEL SCHEMES AND THE CLASSIFICATION OF THE CHARGE-TRANSFER COMPLEXES

The formation of CTC is usually accompanied by the appearance of one or several new bands in the electronic absorption spectrum. These bands are referred to as the charge-transfer (CT) bands and are due to the intermolecular electronic transition on excitation of the CTC. Despite the fact that the presence of CT bands in the spectrum is not in general proof of the formation of a thermodynamically stable CTC and their absence does not rule out the formation of such a complex, nevertheless CT bands are the most characteristic feature of the absorption spectra of CTC. The charge-transfer energy depends on the ionisation potential of the donor $IP(D)$, the electron affinity of the acceptor $EA(A)$, and the stabilisation energies of the ground and excited states of the CTC.[5] The electronic transitions for different components of the CTC can be represented schematically as follows:

$$D, A \xrightarrow{h\nu_{CT}} D^{+}, A^{-} \qquad (I)$$

$$D, A^{+} \xrightarrow{h\nu_{CT}} D^{+}, A^{\cdot}. \qquad (II)$$

The fundamental differences between the stabilisation energies of the CTC formed by two neutral molecules [reaction (I)] or an ion and a neutral molecule [reaction (II)] follow from this approximate scheme. In the first place the excited state is stabilised by the strong Coulombic interaction of the oppositely charged species, while in the second case this does not occur. The different structures of the ground and excited states of the above CTC make it possible to refer them to two separate types of CTC.[22] The energy levels arising on their formation are presented in Fig.1. Weak CTC, in the formation of which the contribution of the CT forces is insignificant, are considered in both cases.

The CT energies for CTC of both types in the gas phase are expressed by the following equations:

$$h\nu_{CT}(D, A) = IP(D) - EA(A) + (W_0 - E_c) + (R_N + R_E), \qquad (1)$$

$$h\nu_{CT}(D, A^{+}) = IP(D) - EA(A^{+}) + (W_0' - W_1) + (R'_N + R'_E), \qquad (2)$$

where W_0, W'_0, W_1 are the stabilisation energies of the ground and excited states as a consequence of all the types of interaction with the exception of the interaction via the charge-transfer pathway, E_C is the Coulombic interaction energy of the oppositely charged species, and R_N, R_E, R'_N, and R'_E are the energies of stabilisation or destabilisation as a consequence of the interaction of the configurations without charge transfer and with complete charge transfer in the ground (N) and excited (E) states respectively. Assuming that for a weak CTC the sums $R_N + R_E$ and $R'_N + R'_E$ are small and approximately equal, we conclude that the constant terms in Eqns.(1) and (2) are largely determined by the differences $W_0 - E_C$ and $W'_0 - W_1$ respectively. The upper limit to the quantity W_0 is set by the experimental ΔH, which do not exceed 0.5 eV for the CTC of tetracyanoethylene with methylbenzenes and naphthalene in the gas phase[10]. According to theoretical estimates[5], the quantity E_C exceeds somewhat 3 eV. Thus $W_0 - E_C \cong -3$ eV and we obtain from Eqn.(1)

$$h\nu_{CT} \simeq IP(D) - EA(A) - 3 \ \text{(eV)},$$

which agrees fairly well with experiment[23]. When a CTC is formed between an ion and a neutral molecule, one can assume that $W_0 \geq W_1$ and the CT energy in the gas phase is approximately expressed by the equation

$$h\nu_{CT} \simeq IP(D) - EA(A^{+}) + E_{II}, \qquad (3)$$

where $E_{II} \geq 0$. According to the Franck–Condon principle, the energy is higher in solutions (Fig.1).

Thus the $h\nu_{CT}$ in the two cases examined differ greatly, the difference seeming more appreciable than the changes arising as a consequence of the difference between the types of the interacting boundary orbitals of the components (m, σ, π, etc.) for both types of CTC considered. The distinctive features of the CTC having different ground and excited states are also manifested directly in the experiment. For example, it has been established[24] that the CT energy and the formation constants of CTC vary differently with increasing pressure depending on whether the CTC are formed by neutral molecules, a neutral molecule and an ion, or two oppositely charged ions.

Because of the reasons described above, we believe it useful to classify the CTC beginning with the structures of the ground and excited states having specified three main types: (1) CTC between neutral molecules (D, A); (2) CTC between an ion and a neutral molecule (D^{-}, A and D^{+}, A); (3) CTC between oppositely charged ions (D^{-}, A^{+}). Within the limits of these types, further classification can be achieved in conformity with the type of interacting orbitals[5] and, within the limits of the resulting subtypes, also in terms of the classes of the compounds.

III. GENERAL INFORMATION ABOUT THE SPECTROSCOPIC AND THERMODYNAMIC PROPERTIES OF THE CHARGE-TRANSFER COMPLEXES BETWEEN A NEUTRAL π-DONOR AND AN ORGANIC CATION AS AN ACCEPTOR

During the period since the publication of the first studies on the CTC of the type considered[25], a comparatively small amount of experimental data has accumulated. However, the date are sufficient to reach a number of conclusions, which is facilitated by the availability of the results of analysis of extensive experimental data on the CTC between neutral species[1–12].

It has been observed that organic cations of different classes of compounds are capable of forming CTC with neutral π-donors. The cations include carbonium ions (tropylium, triphenylmethyl, and diphenylmethyl cations), heteroaromatic ions (protonated and alkylated *N*-heterocycles, derivatives of pyrylium and thiopyrylium), and hetero-onium ions (diaryliodonium and arenediazonium ions). So far it is not altogether clear what causes the complex-forming capacity of diaryliodonium ions, since only the formation of their CTC with aromatic amines[26], which are capable of utilising their l orbitals for the interaction, has been reported. For the remaining cations, the CTC with pure π-donors have also been studied.

The complex-formation constants K of CTC in solution are usually low and vary in the range 1–10 litre mol^{-1} depending on the properties of the CTC components and the solvent (Table 1). The individual instances where the constants K are much greater than 10 litre mol^{-1} are either associated with specific conditions promoting complex formation or can be accounted for by experimental difficulties in their correct determination[10].

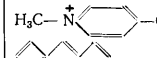
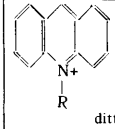
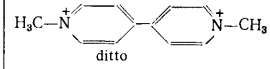
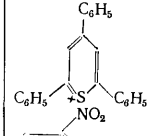
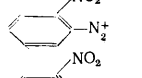
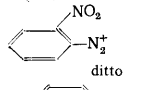
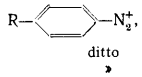
In most cases the constants K for neutral donor–cationic acceptor CTC are similar to those for weak π–π CTC of neutral molecules. As for the latter, there is a tendency towards an increase of K with decrease of the ionisation potential of the donor and with increase of the electron affinity of the acceptor (see Nos.1–4 and 17–25 in Table 1).

However, this tendency does not constitute proof of the predominant contribution of the CT forces[5,10] and there are at present no grounds for the belief that CT forces are the main ones in complex formation. It is most likely that the degree of charge transfer in the ground state is slight and complex formation is determined to a larger extent by the forces of universal intermolecular interactions than by CT forces. Nevertheless the question of the contribution of the CT forces to the formation of CTC of the given type must be regarded as open in view of the inadequacy of the experimental data. The problem of whether CTC of the given type are contact or thermodynamically stable complexes has been studied more widely. The CTC of the given type are thermodynamically stable, since the enthalpies of complex formation ΔH are negative (Table 1). The absolute value of ΔH does not exceed 6 kcal mol^{-1}, which is characteristic of weak $\pi-\pi$ complexes of neutral molecules[5,10]. Like the latter, the CTC between a neutral donor and a cationic acceptor can be obtained in a crystalline state[13-15,27,31,32,35].

In most cases a more or less distinct CT band is observed in the electronic spectrum of the CTC. The CT energy is usually determined from the maximum of the CT band, which in the general does not correspond to the 0–0 transition. Determination of the CT energies for the 0–0 transition has shown[36] that the latter vary approximately in parallel with the CT energies determined from the CT band maxima but are smaller by 0.35–0.4 eV. Therefore the observed dependence of $h\nu_{CT}$ on the characteristics of the components remains unaltered regardless of the way in which the CT energy has been determined.

The study of the CTC formed by identical acceptors with different donors has shown that the CT energy usually varies linearly with IP(D); this is also characteristic of CTC of other types[5,10]. The slope of the $h\nu_{CT}$–IP(D) straight lines is close to unity: for the CTC of aromatic hydrocarbons with the tropylium cation, it is 0.98 in methylene chloride[27] and 1.0 in acetonitrile[37]; it is 0.87 for the CTC of 4-cyano-*N*-methylpyridinium with polyalkylbenzenes in 96% ethanol[29] and 0.96 for the complexes with aromatic hydrocarbons in chloroform containing 8 vol.% of ethanol[38]; for the CTC of aromatic hydrocarbons with benzenediazonium cations in nitromethane, the slope is 0.92.[39,40] Such relations can be regarded as satisfactory evidence that the new absorption bands appearing in the spectrum are indeed CT bands. The slope of the above straight lines depends little on the properties of the solvent, so that the different values obtained in different studies are largely due to the different nature of the donors and their ionisation potentials.

Table 1. Thermodynamic parameters of CTC in solution.

No.	Donor	Acceptor	Solvent	K, litre mol^{-1}	ϵ_{max}, mol^{-1} cm^{-1}	$-\Delta H$, kcal mol^{-1}	T, K	Refs.
1	Anthracene		CH_2Cl_2	1.2	—	2.0	298	[27]
2	Hexamethylbenzene	ditto	CH_2Cl_2	1.1	—	1.5	298	[27]
3	Naphthalene	»	CH_2Cl_2	0.55	—	1.3	298	[27]
4	Mesitylene	»	$C_2H_4Cl_2$	0.67	1850	—	298	[28]
5	1,4-Dimethoxybenzene		C_2H_5OH (96%)	0.35	350	1.46	298	[29]
6	Anthracene		CH_2Cl_2	1.5	1020	—	294	[30]
7	Anthracene	ditto , R=CH_3	CH_2Cl_2	2.7	910	—		[30]
8	Pyrene		CH_3OH	3.4	360	—	298	[31]
9	Hydroquinone	ditto	CH_3OH	5.2	115	5.5	298	[13,31]
10	1-Naphthylamine*	»	CH_3OH	8.7	192	—	298	[31]
11	*N*-Phenyl-2-naphthylamine*	»	CH_3OH	88	42	—	293	[32]
12	*p*-Phenylenediamine*	»	CH_3OH	15.4	95	—	298	[31]
13	Triphenylamine*		CH_2Cl_2	1.1	100		293	[15]
14	Naphthalene		$CH_3COOH:H_2O=4:1$	4.4	—	—	293	[33]
15	1-Methylnaphthalene		$CH_3COOH:H_2O=4:1$	14.4	—	—	293	[33]
16	Naphthalene-1-sulphonic acid	ditto	$CH_3COOH:H_2O=4:1$	30.6	—	—	293	[33]
17	Fluorene		CH_3CN	0.56	—	—	293	[34]
18	Phenanthrene	ditto	CH_3CN	0.61	—	—	293	[34]
19	Hexamethylbenzene	»	CH_3CN	0.65	—	—	293	[34]
20	Pyrene	»	CH_3CN	0.88	—	—	293	[34]
21	Anthracene	»	CH_3CN	0.64	—	—	293	[34]
22	Pyrene	ditto , R=CN	CH_3CN	1.26	—	—	293	[34]
23	Pyrene	» , R=$COOC_2H_5$	CH_3CN	1.13	—	—	293	[34]
24	Pyrene	» , R=CH_3	CH_3CN	0.6	—	—	293	[34]
25	Pyrene	» , R=OCH_3	CH_3CN	0.56	—	—	293	[34]

*The compounds are *l*-donors and coordination involves both the nitrogen atom and the residual π-system.

The influence of the solvent on the CT energy has been studied in a number of investigations[28,29,36,41,42]. According to the energy level scheme in Fig.1, the CT energy in the gas phase is expressed by Eqn.(2), while in solution a more complex relation obtains:

$$h\nu_{CT}(D, A^+)_{solv} = IP(D) - EA(A^+) + \\ + (W_0' - W_1) + (R_N' + R_E') + [E_{solv}(D, A^+) - E_{solv}(D^+, A^-)] + E_{FC} \quad (4)$$

Since it can be assumed with adequate approximation that the solvation energy $E_{solv}(D, A^+) \cong E_{solv}(D^+, A^-)$, the frequency shift on transition from the gas phase to the solution and also when the solvent is altered should be determined mainly by the quantity E_{FC}, i.e. $\Delta h\nu_{CT}(D, A^+) \cong \Delta E_{FC}$. In this case a comparatively slight hypsochromic shift is to be expected on passing from the gas phase to the solution as well as a comparatively weak solvatochromism in different solvents. The latter hypothesis has been confirmed experimentally (Table 2). Nevertheless there is no reason to believe that the solvent virtually does not influence the CT energy[36]. The shift of the CT band in a series of 14 solvents presented in Table 2 is approximately 2000 cm^{-1} for the majority of CTC. This quantity is small compared with the corresponding shift of the CT band for the CTC formed by oppositely charged ions (approximately 7000 cm^{-1}), but is too large to neglect the influence of the solvent. The influence of the properties of the solvent on the CT energy is confirmed also by experimental data on the solvatochromism of substances with an analogous intramolecular transition[44,45].

Table 2. The influence of the solvent on the position of the CT band maximum ($10^{-3}\nu$, cm^{-1}).

Solvent	E_T (Ref.43)	Charge-transfer complex					
		Hexamethylbenzene.tropylium fluoroborate (Ref.41)	Anthracene.tropylium fluoroborate (Ref.41)	Pyrene.tropylium fluoroborate (Ref.41)	Anthracene.N-methylacridinium fluoborate (Ref.41)	Dimethylaniline.4-cyano-N-(n-decyl)pyridinium fluoroborate (Ref.29)	Phenothiazine.tropylium fluoroborate (Ref.42)
Methanol	55.5	—	—	—	20.1	21.37	—
Ethanol	51.9	—	—	—	—	21.14	—
Acetic acid	51.2	24.6	20.4	20.3	—	—	16.9
1-Propanol	50.7	—	—	—	—	21.19	—
Nitromethane	46.3	24.0	20.2	—	19.9	—	—
Acetonitrile	46.0	24.2	20.6	20.5	19.9	21.62	17.0
Dimethyl sulphoxide	45.0	—	21.3	21.3* (i)	—	22.52	14.7
Acetic anhydride	43.9	24.2	20.6	20.5	20.3	—	17.0
Dimethylformamide	43.8	24.5	21.7	22.2 (i)	21.5 (i)	22.47	15.5
Acetone	42.2	24.3	20.8	20.8	20.2	22.2	17.1
Nitrobenzene	42.0	22.2	19.4 (i)	19.3	19.5	—	15.9
Dichloroethane	41.9	22.6	18.6	18.7	19.0	—	14.9
Methylene chloride	22.9	18.7	—	19.1	20.83	—	—
Chloroform	39.1	—	—	—	19.7	21.03	—

*Here i = inflection.

There is a satisfactory linear relation between the energy shifts of the CT bands for all six CTC in Table 2. Consequently, apart from the individual instances of the specific interaction of the components or of the CTC itself with the solvent, these data contain information about the influence of

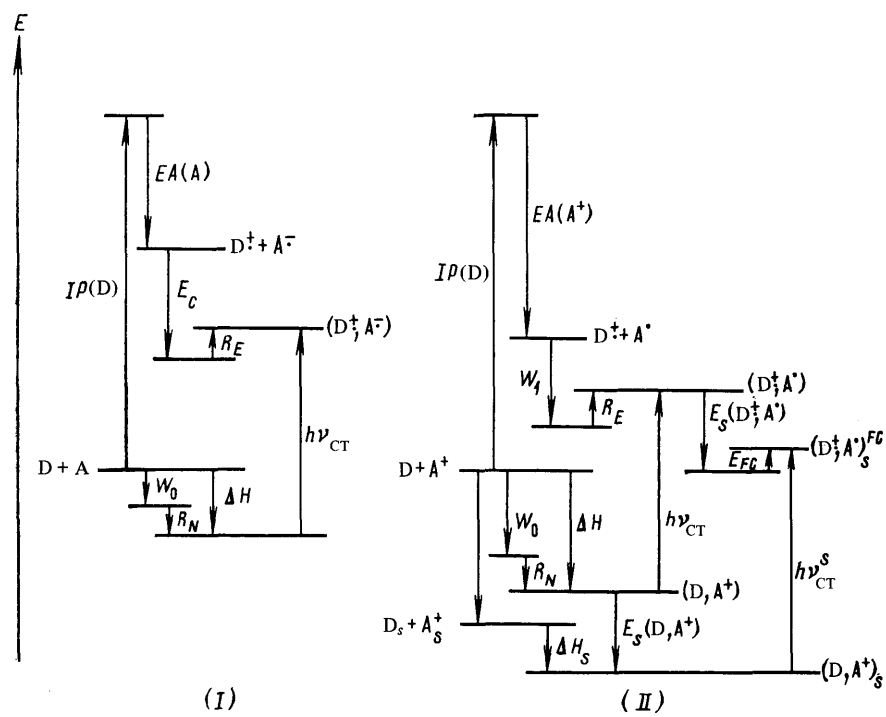


Figure 1. Schematic arrangement of the energy levels for CTC between neutral molecules (I) and a neutral molecule and an ion (II); E_C = Coulombic interaction energy; R_N, R_E = stabilisation or destabilisation energies as a consequence of the interaction of the configurations without and with complete charge transfer in the ground and excited states respectively; W_0, W_1 = stabilisation energies of the ground and excited states as a consequence of all types of interactions with the exception of CT forces; ΔH, ΔH_S = enthalpies of complex formation in the gas phase and in solution; $h\nu_{CT}$ = CT energy; $E_S(X)$ = solvation energy of the corresponding structure X; E_{FC} = destabilisation energy of the non-equilibrium excited state relative to the equilibrium state (the Franck–Condon state).

the solvent on the CTC of this class as a whole. The changes in the CT energies when the solvent is altered are not correlated with empirical parameters of the solvent such as the values of Z and E_T.[29,41,42] Nor does one observe their dependence on the polarisability of the solvent expressed in the form $(n^2 - 1)/(2n^2 + 2)$, where n is the refractive index. A quantitative description of the dependence of the CT energy on the properties of the solvent is probably possible in this case only with the aid of a multiparameter equation[43]. In broad outline, the state of the problem is very similar to that in the case of neutral $\pi-\pi$ complexes[45,46,47], although there is no correlation between the frequency shifts for the CTC of the two types. The structure of the so-called cybotactic region probably plays the most important role in both cases[4].

IV. THE ELECTRON AFFINITY OF ACCEPTOR CATIONS

The electron affinity EA is defined as the energy evolved (+) or absorbed (−) when a given species (atom, molecule, ion, radical, or radical-ion) captures an electron in the gas phase. If the species is a positive ion, then the vertical and adiabatic electron capture processes can be illustrated by the following equations:

$$A^+(r_{A^+}) + e \xrightarrow{EA_v(A^+)} A^{\cdot}(r_{A^+}), \quad (5)$$

$$A^+(r_{A^+}) + e \xrightarrow{EA_{ad}(A^+)} A^{\cdot}(r_{A^{\cdot}}), \quad (6)$$

where $EA_v(A^+)$ and $EA_{ad}(A^+)$ are the vertical and adiabatic electron affinities of the cation A^+ and r_{A^+} and $r_{A^{\cdot}}$ denote the equilibrium geometries of the ion and radical respectively.

The majority of methods used to determine the EA for neutral species[48] are inapplicable to the determination of the EA for positive ions and the only way in which the latter can be found directly involves the study of the energy characteristics of the reverse process—the ionisation of the conjugate radicals:

$$A^{\cdot}(r_{A^{\cdot}}) \xrightarrow{IP_v(A^{\cdot})} A^+(r_{A^{\cdot}}) + e, \quad (7)$$

$$A^{\cdot}(r_{A^{\cdot}}) \xrightarrow{IP_{ad}(A^{\cdot})} A^+(r_{A^+}) + e, \quad (8)$$

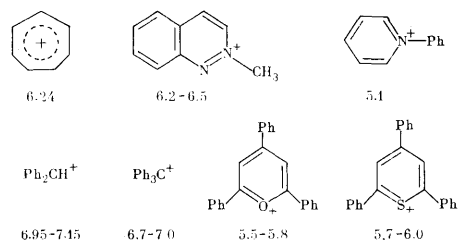
where $IP_v(A^{\cdot})$ and $IP_{ad}(A^{\cdot})$ are the vertical and adiabatic ionisation potentials of the conjugate radical $A^{\cdot}$.

Since only Eqns.(6) and (8) reflect the transition between identical energy levels, the determination of $IP_{ad}(A^{\cdot})$ makes it possible to determine simultaneously also $EA_{ad}(A^+)$, while the $IP_v(A^{\cdot})$ will in general differ from both $EA_v(A^+)$ and $EA_{ad}(A^+)$.

In view of the purely experimental difficulties in the determination of $IP(A^{\cdot})$, only a few ionisation potentials of radicals whose ionisation leads to cations forming stable CTC are at present known. One of these is the tropylium radical, whose $IP(A^{\cdot})$ is 6.24 eV [49,50] (obtained from Rydberg spectra). The electron impact method leads to a higher value (6.6 eV).[51] These differences can be largely caused by the method of measurement itself, since it is known that, without special modification of the measuring apparatus, the latter method yields unduly high results[52]. For benzene, whose values of IP_{ad} and IP_v are equal, the ionisation potential obtained by Tajima and Tsuchiya[52] is higher by 0.3 eV than the value of IP obtained from photoelectron spectroscopy. One must therefore assume that the true adiabatic ionisation potential of the tropylium radical is close to 6.24 eV. The ionisation potential of the N-methylcinnolinyl radical, amounting to 6.5 eV [53] (electron impact method), is also known. In the light of the foregoing, it is to be expected that the true ionisation potential of this radical is in the range 6.2–6.5 eV.

The photoelectron spectroscopic data mentioned by Kosower et al.[54], according to which the values of IP_v and IP_{ad} for the 1-ethyl-4-methoxycarbonylpyridyl radical are 7.2 and 6.8 eV respectively, must be regarded as erroneous. In all probability these ionisation potentials do not correspond to the ionisation of the pyridyl radical. The ionisation potential of the 1-phenylpyridyl radical, determined by the mass-spectrometric method and estimated from the IP of the corresponding 1,4-dihydropyridine, is 5.1 eV.[55] The IP for the triphenylmethyl radical can also be estimated approximately. According to the results of a study of the CTC of the diphenylmethyl and triphenylmethyl radicals with neutral π-acceptors[56], the value of IP for the latter is lower by ~0.2 eV. Assuming that the transition from the benzyl to the diphenylmethyl radical is associated with the same change in IP and using the value of IP_{ad} for the benzyl radical, which is 7.2–7.3 eV,[57,58] we find that IP_{ad} for the triphenylmethyl radical should be in the range 6.7–7.0 eV. Using mass-spectrometric data for pyrylium salts[59], one can estimate the IP also for the 2,4,6-triphenylpyrylium and 2,4,6-triphenylthiopyrylium radicals. Their values are most probably 5.5–5.8 and 5.7–6.0 eV respectively.

All the results described above make possible a direct estimate of the $EA(A^+)$ for acceptors which are listed below together with their structural formulae:



The results of quantum-chemical calculations also permit, in principle, the estimation of the EA for acceptor cations. The approximate nature of the versions of the calculations which are simplest in practice nevertheless makes it necessary to treat with caution the absolute values obtained, while the relative changes in the EA in individual series of compounds can be obtained with a fairly high accuracy.

At least three approaches can be used to calculate the EA. These involve the calculation of the $IP(A^{\cdot})$ and $EA(A^+)$ as the orbital energies in terms of the approximation of Koopmans theorem and the calculation of $EA(A^+)$ as the difference between the total energies of the radical and the ion. Calculation of the $IP(A^{\cdot})$ for tropyl, 1-methylpyridyl, 3-cyano-1-methylpyridyl, and 2-methoxycarbonyl-1-methylpyridyl radicals led to the following values: 8.85; 7.83; 7.96; and 8.73 eV respectively[60]. Despite the fact that all the results are much too high, the difference between the IP for tropyl and 1-methylpyridyl radicals agrees fairly well with experiment, which gives rise to hope for progress in this field when computational methods have been improved[61,62].

Calculations have been made in a number of studies for acceptor cations[63–67]. The most satisfactory agreement with the above experimental data has been obtained taking into account all the valence electrons. As an example, we shall present data obtained in the calculation for the N-methylpyridinium cation. According to the CNDO/2 method, the energy of the lowest vacant molecular orbital is 4.74 eV,[64] while a non-empirical calculation yielded[67] 5.23 eV.

The spectroscopy of the CTC and electrochemical reduction are indirect methods for the determination of the EA. According to Eqns.(3) and (4), the CT energy in both the

gas phase and in solution can be approximately expressed by the following relation:

$$h\nu_{CT} = IP(D) - EA(A^+) + E, \quad (9)$$

where E is a quantity which varies somewhat as a function of the conditions of the investigation. For known values of $h\nu_{CT}$, $IP(D)$, and $EA(A^+)$, it is possible to determine E and to estimate $EA(A^+)$ for other acceptor cations. This approach was first used by Feldman and Winstein[37], who established, on the basis of the results of a study of the CTC of the tropylium cation [$EA(A^+) = 6.24$ eV] that E in solution is close to 1.2 eV. This value agrees well with the expectation based on the analysis of the energy levels of the CTC of the given type, but differs markedly from that for the CTC between a neutral π-donor and a π-acceptor.

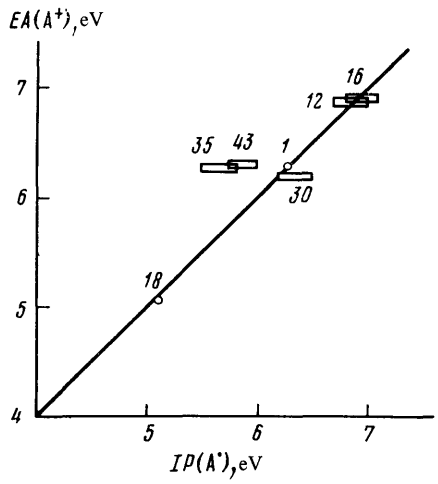


Figure 2. Dependence of the electron affinities of acceptor cations, determined by the method involving the study of CTC, on the ionisation potentials of the conjugate radicals. The points are numberd as in Table 3. In the case of the acceptor No.18 the value of $IP(A^·)$ for the N-phenylpyridyl radical was used; it is assumed that $IP(A^·)$ for acceptor No.16 is lower than $IP(A^·)$ for the diphenylmethyl radical (the difference may be 0.1–0.3 eV).

There is no reason to doubt that, in the study of different CTC under identical conditions, the value of E can be regarded as a constant to a satisfactory approximation under identical conditions in the vast majority of cases. The changes in E following the alteration of the solvent can be taken into account by studying a standard system (the CTC of the tropylium cation) in different solvents (Table 3).

It is noteworthy that certain complications arise because the CT band is associated with the vertical transition and the CT energy depends on $IP_v(D)$ and $EA_v(A^+)$. In this respect the parametrisation of Eqn.(5) relative to the EA_{ad} for the tropylium cation is justified only when $EA_v(A^+) = EA_{ad}(A^+)$ for this cation. Unfortunately measurements of the absolute values of these quantities have not been made for any acceptor cations and the increase in the complexity of the parametrisation produced by introducing any assumptions is at present unjustified. The satisfactory agreement between the values of $IP(A^·)$ and $EA(A^+)$ obtained by the method involving the study of the CTC (Fig.2) suggests that an equation of type (5) can be used to estimate $EA(A^+)$. Nevertheless one must bear in mind that the values of $EA(A^+)$ obtained in this way should vary in proportion to $EA_v(A^+)$ and can therefore differ from the values of $EA_{ad}(A^+)$ obtained by other methods. The difference should be particularly marked in the study of cations A^+ whose equilibrium geometry differs strongly from that of A (for example, arenediazonium salts).

Polarography is a second indirect method which is used fairly frequently to estimate EA.[48,76] It is most likely that the electrochemical reduction process carries information about the adiabatic addition of an electron and hence about the $EA_{ad}(A^+)$.

The half-wave potential for the reversible one electron reduction ($E_{1/2}$) can be expressed by the following equation with a satisfactory degree of approximation[77]:

$$E_{1/2} = EA + \Delta E_{solv} + Z, \quad (10)$$

where E_{solv} is the difference between the solvation energies of the reduced and oxidised forms and Z is a constant characterising the free energy of the electron in the standard electrode relative to that *in vacuo*.

The quantity ΔE_{solv} is virtually determined by the solvation energy of the charged species, since the solvation energies of neutral species are insignificant. The solvation energies of organic ions with a markedly delocalised charge in a series of polar solvents are ~2.0 eV [78] and vary comparatively little (by ±0.2 eV) when their structure is altered. The quantity Z for the saturated calomel electrode (s.c.e.) in acetonitrile solution is 4.38 eV.[78] When cations are reduced, the highly solvated species is the oxidised form and not the reduced form as happed in the reduction of neutral species. ΔE_{solv} therefore enters into Eqn.(10) with the opposite sign and $E_{1/2}$ in acetonitrile relative to the s.c.e. is expressed by the equation

$$E_{1/2}(V) = EA(A^+) - 6.38 \pm 0.2 \text{ (eV)}. \quad (11)$$

Using the literature data for the electrochemical reduction of acceptor cations[15,53,64,68,71,79–83], it is possible to test the validity of Eqn.(11). It follows from Eqn.(3) that in most cases there is an entirely satisfactory agreement between the $E_{1/2}$ and $EA(A^+)$. This agreement can actually be regarded as satisfactory, since the values of $E_{1/2}$ have been obtained in different solvents using different supporting electrolytes, which, together with the possible adsorption on the surface of mercury, can appreciably alter $E_{1/2}$.[84,85]

The data for acceptors Nos.41, 44–46, and 49 deviate from the overall relation (Fig.3). Whereas in the case of dibenzopyrylium (No.41) this can be associated with inaccurate experimental data, for benzenediazonium acceptor cations[40] the problem can be complicated by the appreciable difference between $EA_v(A^+)$ and $EA_{ad}(A^+)$. In this case one can assume that the experimental $EA(A^+$, CTC) are insufficiently high for Eqn.(11) to be observed and that the deviations of the experimental points vary with the substituent. Since this does actually occur, presumably the difference between $EA_{ad}(A^+)$ and $EA_v(A^+)$ for benzenediazonium ions reaches ~1 eV. For heteroaromatic and also carbonium ions, there is no reason to believe that the difference between the adiabatic and vertical electron affinities exceeds 0.2–0.3 eV. It should also be assumed that the parametrisation of Eqn.(5) has been carried out correctly and that the data in Table 3 reflect the true vertical values of EA for acceptor cations, which, with the exception of hetero-onium ions, are close to the adiabatic values.

Table 3. The CT energies and the values of $EA(A^+)$ obtained on their basis.

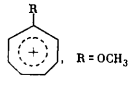
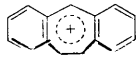
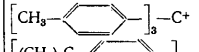
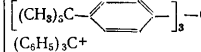
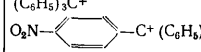
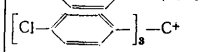
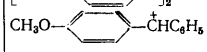
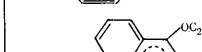
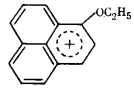
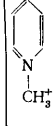
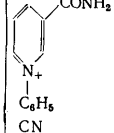
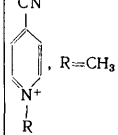
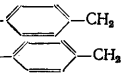
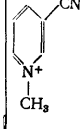
No.	Acceptor	Donor*	Solvent	λ_{max}, nm	$h\nu$, eV	Refs.	IP(D), eV	E_{11}, eV	$EA(A^+)$, eV
1		perylene	CH_2Cl_2	611	2.03	[27]	7.12	1.15	6.24
	ditto	anthracene	CH_2Cl_2	535	2.32	[27,41]	7.4	1.16	—
	»	pyrene	CH_2Cl_2	535	2.32	[41,42,68]	7.53	1.03	—
	»	HMB	CH_2Cl_2	437	2.87	[27,41]	7.95	1.16	—
	»	phenanthrene	CH_2Cl_2	428	2.90	[27]	8.03	1.11	—
	»	anthracene	CH_3CN	488	2.54	[37]	7.4	1.35	—
	»	pyrene	CH_3CN	488	2.54	[42]	7.54	1.25	—
	»	HMB	CH_3CN	417	2.98	[24,37]	7.95	1.27	—
	»	naphthalene	CH_3CN	398	3.11	[37]	8.12	1.23	—
	»	NDMA	$CH_2Cl_2 : CH_3CN = 1 : 1$	571	2.17	[69]	7.45	0.96	—
2		pyrene	CH_2Cl_2	480	2.59	[68]	7.53	1.05**	6.0
3	ditto , R=OH	pyrene	CH_2Cl_2	450	2.76	[68]	7.53	1.05	5.8
4	» , $R=C(CH_3)_3$	pyrene	CH_2Cl_2	503	2.47	[68]	7.53	1.05	6.1
5	» , R=Br	pyrene	CH_2Cl_2	585	2.12	[68]	7.53	1.05	6.5
6	» , R=Cl	pyrene	CH_2Cl_2	605	2.05	[68]	7.53	1.05	6.55
7	» , R=CN	pyrene	CH_2Cl_2	680	1.83	[68]	7.53	1.05	6.75
8		durene	CH_2Cl_2	447	2.78	[37]	8.3	1.18	6.7
	ditto	HMB	CH_2Cl_2	522	2.38	[37]	7.95	1.13	—
	»	pyrene	CH_2Cl_2	667	1.86	[37]	7.53	1.05	—
9		pyrene	CH_2Cl_2	575	2.26	[68]	7.53	1.05	6.4
10		pyrene	CH_2Cl_2	640	1.94	[68]	7.53	1.05	6.65
11		pyrene	CH_2Cl_2	705	1.76	[68]	7.53	1.05	6.8
12		pyrene	CH_2Cl_2	710	1.75	[68]	7.53	1.05	6.85
13		pyrene	CH_2Cl_2	790	1.57	[68]	7.53	1.05	7.0
14		pyrene	CH_2Cl_2	820	1.51	[68]	7.53	1.05	7.05
15		pyrene	CH_2Cl_2	675	1.84	[68]	7.53	1.05	6.75
16		pyrene	CH_2Cl_2	725	1.71	[68]	7.53	1.05	6.85
17		pyrene	CH_2Cl_2	674	1.84	[37]	7.53	1.05	6.75
	ditto	anthracene	CH_2Cl_2	713	1.74	[37]	7.40	1.05	—
18		TMPD	$CHCl_3$+5% C_2H_5OH	430	2.88	[23]	6.75	1.2	5.05
19		anthracene	dioxan : water = 6 : 4	391	3.17	[70]	7.40	1.25	5.5
20	 , R=CH_3	NDMA	C_2H_5OH (96%)	433	2.86	[29]	7.45	1.25	5.85
	ditto , R=CH_3	TMOB	C_2H_5OH (96%)	473	2.62	[29]	7.20	1.25	—
	» , R=CH_3	pyrene	$CHCl_3$+5% C_2H_5OH	434	2.86	[38]	7.20	1.25	5.85
21	» , R=n-C_4H_9	TMOB	C_2H_5OH (96%)	473	2.62	[29]	7.20	1.25	5.85
22	» , R=O_2N--CH_2	TMOB	C_2H_5OH (96%)	486	2.55	[29]	7.20	1.25	5.9
23	» , R=CHO_2--CH_2	TMOB	C_2H_5OH (96%)	482	2.57	[29]	7.20	1.25	5.9
24		NDMA	C_2H_5OH (96%)	430	2.89	[29]	7.45	1.25	5.8

Table 3 (contd.).

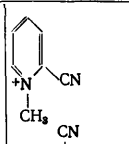
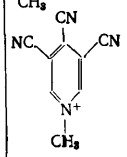
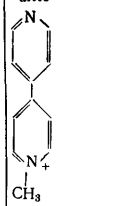
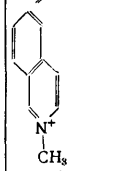
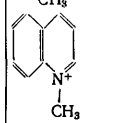
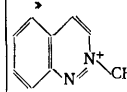
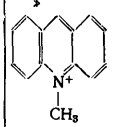
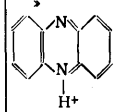
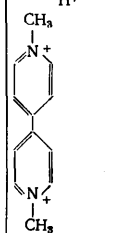
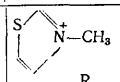
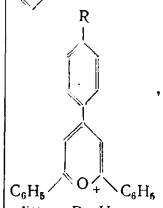
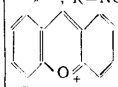
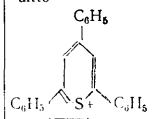
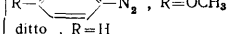
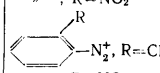
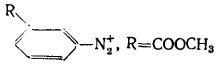
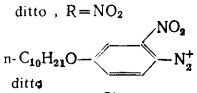
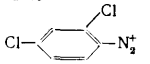
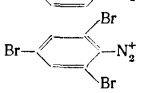
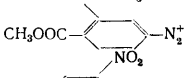
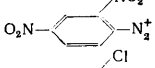
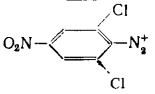
No.	Acceptor	Donor*	Solvent	λ_{max}, nm	$h\nu$, eV	Refs.	$IP(D)$, eV	E_{11}, eV	$EA(A^+)$, eV
25		NDMA	C_2H_5OH (96%)	478	2.59	[71]	7.45	1.25	6.1
26		HMB	CH_2Cl_2	507	2.45	[37]	7.95	1.1	6.6
	ditto	pyrene	CH_2Cl_2	620	2.0	[37]	7.53	1.05	—
27		naphthalene	$CHCl_3$+10% C_2H_5OH	338	3.67	[38]	8.12	1.2	5.65
	ditto	pyrene	$CHCl_3$+10% C_2H_5OH	400	3.1	[38]	7.53	—	—
	»	anthracene	$CHCl_3$+10% C_2H_5OH	416	2.98	[38]	7.40	—	—
28		TMDP	$CHCl_3$+5% C_2H_5OH	500	2.48	[23]	6.75	1.2	5.45
29		NDMA	$C_2H_4Cl_2$	430	2.88	[72]	7.45	1.05	5.6
	ditto	anthracene	$CHCl_3$+5% C_2H_5OH	415	2.72	[22]	7.12	1.2	—
	»	perylene	$CHCl_3$+5% C_2H_5OH	456	2.72	[22]	7.12	1.2	—
	»	pyrene	$CHCl_3$+5% C_2H_5OH	420	2.95	[73]	7.53	1.2	—
30		naphthalene	$CHCl_3$+5% C_2H_5OH	403	3.08	[38]	8.12	1.2	6.2
	ditto	pyrene	$CHCl_3$+5% C_2H_5OH	496	2.5	[38]	7.53	1.2	—
	ditto	anthracene	$CHCl_3$+5% C_2H_5OH	508	2.44	[38]	7.4	1.2	—
	»	perylene	$CHCl_3$+5% C_2H_5OH	564	2.20	[38]	7.12	1.2	—
31		pyrene	CH_2Cl_2	505	2.46	[42]	7.53	1.05	6.15
	ditto	anthracene	CH_2Cl_2	517—525	2.36—2.40	[30,37]	7.40	1.05	—
	»	perylene	CH_2Cl_2	595	2.09	[30,37]	7.12	1.15	—
	»	anthracene	$CHCl_3$	508	2.44	[41]	7.4	1.20	—
	»	NDMA	CH_2Cl_2	538	2.3	[69]	7.45	1.05	—
	»	NDMA	$C_2H_4Cl_2$	560	2.21	[72]	7.45	1.05	—
32		pyrene	CH_3CN	620	2.0	[74]	7.53	1.25	6.8
33		pyrene	CH_3OH	468	2.65	[31]	7.53	1.25	6.15
	ditto	perylene	CH_3OH	531	2.34	[31]	7.12	1.25	—
	»	naphthalene	CH_3OH	383	3.24	[31]	8.12	1.25	—

Table 3 (contd.).

No.	Acceptor	Donor*	Solvent	λ_{max}, nm	$h\nu$, eV	Refs.	$IP(D)$, eV	E_{II}, eV	$EA(A^+)$, eV
34		2,6-dimethylnaphthalene	CH_3CN	280	4.43	[23]	7.82	1.25	4.6
35	 , R=H	DMPD	CH_3CN	360	3.45	—	6.75	1.25	—
	ditto , R=H	anthracene	CH_2Cl_2	570	2.18	[15]	7.4	1.05	6.3
36	» , R=OCH_3	anthracene	CH_2Cl_2	540	2.27	[15]	7.4	1.05	6.2
37	» , R=Cl	anthracene	CH_2Cl_2	580	2.14	[15]	7.4	1.05	6.3
38	» , R=$COOCH_3$	anthracene	CH_2Cl_2	600	2.01	[15]	7.4	1.05	6.4
39	» , R=CN	anthracene	CH_2Cl_2	610	2.03	[15]	7.4	1.05	6.4
40	» , R=NO_2	anthracene	CH_2Cl_2	610	2.03	[15]	7.4	1.05	6.4
41		pyrene	CH_2Cl_2	660	1.88	[68]	7.53	1.05	6.7
42		isobutene	CH_3CN	400	3.1	[75]	9.35	1.25	7.5
	ditto	cyclohexene	CH_3CN	434	2.86	[75]	9.12	—	—
43		anthracene	CH_2Cl_2	580	2.14	[15]	7.40	1.05	6.3
44	 , R=OCH_3	pyrene	CH_3NO_2	365	3.4	[40]	7.53	1.25	5.4
45	ditto , R=H	pyrene	CH_3NO_2	420	2.95	[40]	7.53	1.25	5.85
	» , R=H	2,6-dimethylnaphthalene	CH_3NO_2	385	3.22	[40]	7.82	1.25	—
46	» , R=Br	pyrene	CH_3NO_2	450	2.76	[40]	7.53	1.25	6.0
47	» , R=Cl	pyrene	CH_3NO_2	445	2.79	[40]	7.53	1.25	5.95
48	» , R=$COOC_2H_5$	pyrene	CH_3NO_2	485	2.56	[40]	7.53	1.25	6.2
49	» , R=NO_2	pyrene	CH_3NO_2	540	2.30	[40]	7.53	1.25	6.5
50	 , R=Cl	pyrene	CH_3NO_2	490	2.53	[40]	7.53	1.25	6.25
51	ditto , R=NO_2	pyrene	CH_3NO_2	572	2.17	[40]	7.53	1.25	6.6
52		pyrene	CH_3NO_2	485	2.56	[39,40]	7.53	1.25	6.15
53	ditto , R=NO_2	pyrene	CH_3NO_2	510	2.43	[39,40]	7.53	1.25	6.4
54		pyrene	$CHCl_3$	544	2.28	[34]	7.53	1.10	6.3
	ditto	anthracene	$CHCl_3$	554	2.24	[34]	7.40	—	—
55		pyrene	CH_3NO_2	500	2.48	[39]	7.53	1.25	6.3
56		pyrene	CH_3NO_2	520	2.38	[39]	7.53	1.25	6.4
57		pyrene	CH_3NO_2	520	2.38	[39]	7.53	1.25	6.4
58		anthracene	CH_3NO_2	753	1.65	[39]	7.40	1.25	7.0
59		pyrene	CH_3NO_2	695	1,78	[39]	7,40	1,25	7,0

*Notation: HMB = hexamethylbenzene; NDMA = *N*,*N*-dimethylaniline; TMPD = *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine; TMOB = 1,2,3,5-tetramethoxybenzene.

**Here and henceforth the values of E_{II} have been adopted on the basis of the results for the CTC of the tropylium cation and the average value of $EA(A^+)$ has been rounded off to 0.05 eV.

Despite the limited number of studies whose results permit a direct estimation of the absolute values of $EA(A^+)$ in the gas phase, there is no doubt that the latter greatly exceed the values for neutral electron acceptors[48]. For example, *EA* for one of the weakest acceptor cations (*N*-methylpyridinium) is ~5.05 eV, while *EA* for one of the strongest neutral electron acceptors (tetracyanoquinodimethane) is ~2.8 eV. On the other hand, if one considers the entire set of possible acceptors, one may conclude that the CTC with clearly detectable CT bands are formed by neutral acceptors whose *EA* are in the range 0.5–3.0 eV and acceptor cations for which the *EA* are 4.5–7.0 eV. In fact these limits of the *EA* lie in both cases in an intermediate region between the values reflecting a weak CTC type interaction and those characteristic of one-electron transfer. Therefore another conclusion is also valid, namely in a condensed phase a neutral acceptor and an acceptor cation manifest approximately the same electron-accepting properties, provided that the *EA* (in the gas phase) for the latter exceeds ~4 eV. This difference is due to the effects of solvation or polarisation of the medium, which are clearly shown on comparing the photoelectron spectra of solutions and gases comprising neutral substances and ions[85–87]. The external ionisation potential for solutions of neutral molecules is lower by 1–2 eV and for solutions of ions is higher by 2–3 eV than the corresponding characteristics in the gas phase[88]. On this basis, we arrive at the analogous conclusion that a neutral molecule and an ion have approximately the same electron-donating or electron-accepting properties in solution, provided that their values of *IP* and *EA* in the gas phase differ on average by 4 eV.

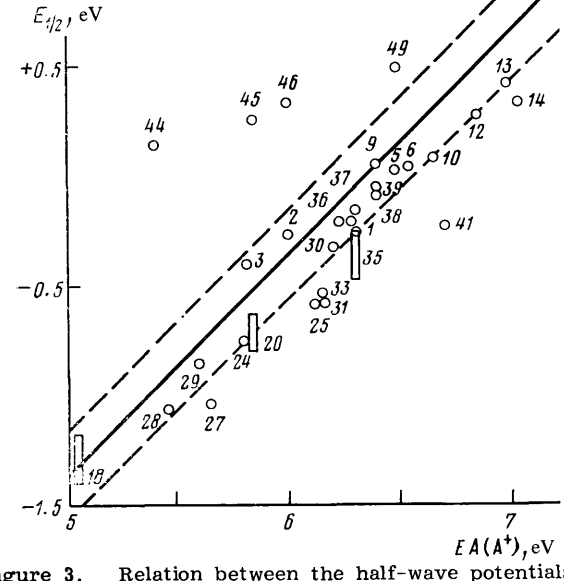


Figure 3. Relation between the half-wave potentials of the polarographic reduction of A^+ and $EA(A^+)$ obtained from the study of CTC. The acceptors are numbered as in Table 3. The straight lines have been drawn on the basis of Eqn.(11).

V. THE PHOTOCHEMICAL PROPERTIES OF THE CHARGE-TRANSFER COMPLEXES OF ARENEDIAZONIUM IONS

The ability of arenediazonium ions to decompose under the influence of light constitutes the basis of many non-silver photographic materials and photoresistors[20,21,89–93]. Many of these contain a substituted benzenediazonium cation as the light-sensitive substance. As a rule, a disadvantage of these materials is a comparatively low overall and not especially favourable spectral sensitivity. On formation of CTC with neutral π-donors, new absorption bands appear, which in principle can lead to the expansion of the spectral sensitivity and an increase of the overall light sensitivity of such materials[20,21,94]. Indeed, depending on the donor and arenediazonium salt employed, CT bands can occur up to 750 nm (see Table 3) which, in the case of photodecomposition on irradiation with light corresponding to the given band, should naturally lead to an appreciable expansion of spectral sensitivity. The photodecomposition on irradiation with light corresponding to the CT band can be regarded as a special case of the familiar radical mechanism of photodecomposition[20,21,95]. In the general case benzenediazonium salts can decompose via both ionic and radical mechanisms[20,21,94], which in isolated instances can be complicated by other processes[96]:

$$\mathrm{ArN_2^+} \begin{cases} \longrightarrow \mathrm{N_2 + Ar^+} \xrightarrow{\mathrm{R^1OH}} \mathrm{ArOR^1} \\ \longrightarrow \mathrm{ArN_2^{\cdot}} \rightarrow \mathrm{Ar^{\cdot} + N_2} \xrightarrow{\mathrm{R^2R^3CHOH}} \end{cases}$$

$$\rightarrow \mathrm{ArH} + \mathrm{R^2R^3\dot{C}{-}OH} \xrightarrow{\mathrm{ArN_2^+}} \text{chain propagation.}$$

Photodecomposition via an ionic mechanism can be regarded as a consequence of intramolecular electron transfer to the diazonium group and leads to nucleophilic substitution products. This pathway cannot be achieved with a quantum yield ϕ exceeding unity. Photodecomposition via a radical mechanism can be regarded as a consequence of intermolecular electron transfer and leads to reduction products. Despite the fact that in the given instance the primary photoprocess cannot be achieved with $\phi > 1$, the overall quantum yield can exceed unity owing to the occurrence of chain reactions with participation of the solvent or the polymer matrix[21,34,97–100]. For example, in alcoholic solutions chain propagation can proceed via the following mechanism:

$$\mathrm{ArN_2^+} + \mathrm{R_2\dot{C}{-}OH} \rightarrow \mathrm{ArN_2^{\cdot}} + \mathrm{R_2C{=}O} + \mathrm{H^+},$$

$$\mathrm{ArN_2^{\cdot}} \rightarrow \mathrm{Ar^{\cdot}} + \mathrm{N_2}\ .$$

The solvent, the corresponding anion, or a neutral electron donor can serve as a source of the external electron necessary for the first stage[21,34]. This process is limited thermodynamically by the energy necessary for electron transfer and the free energy of activation is expressed by the following equation[21,34]:

$$\Delta G^{\neq} = E_{1/2}^{oxy}(\mathrm{D}) - h\nu_{00} - E_{1/2}^{red}(\mathrm{A^+}),$$

where $E_{1/2}^{oxy}(\mathrm{D})$ is the half-wave potential for the anodic oxidation of the donor and $h\nu_{00}$ is the energy of the 0–0 transition on excitation of the donor, acceptor, or the CTC (for a thermal process, $h\nu_{00} = 0$).

Simple ideas about orbital symmetry in photochemical reactions confirm the occurrence of the adiabatic transition from the excited CT state to the aryldiazo-radical[101] and the experimental results for solutions[21,34,94,100,101] demonstrate the validity of the ideas described above. Irradiation with

light corresponding to the CT band leads to the decomposition of the arenediazonium ion[34] and the photolysis of the CTC of the *p*-chlorobenzenediazonium ion with pyrene results in 100% formation of chlorobenzene. An analogous increase of the amount of the products of the photodecomposition via the radical mechanism has been observed also in other instances[34, 100,101]. The operation of the radical mechanism is also indicated by the influence of various inhibitors of similar reactions on the process[34,100,101].

The quantum yield of the photodecomposition by light corresponding to the CT band depends on a number of factors[34]. It increase on enhancement of the electron-donating, properties of the donor D and the electron-accepting properties of the acceptor A^+ and with increase of the concentration of the H-donor solvent and diminishes in the presence of oxygen and other radical traps and also with increase of the donor concentration. When the CTC of pyrene with the 4-chlorobenzenediazonium ion was irradiated with light at $\lambda = 405$ nm in an atmosphere of nitrogen in a mixed solvent (dioxan : acetonitrile = 4 : 1), the yield ϕ exceeded 10 for certain concentration ratios[34]. In an atmosphere of oxygen the quantum yield of the photodecomposition was ~0.1.

Consequently, despite the fact that the use of CTC of arenediazonium ions with neutral electron donors does in principle make it possible to eliminate the significant disadvantages of the photographic materials based on diazonium salts used nowadays, their practical application constitutes an extremely complex problem. In a polymer matrix it is complicated still further by the restriction of diffusion which prevents the release of the primary radical pair from the cage.

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