Charge-transfer complexes of fullerene C_{70} and ternary amines in chlorobenzene. Picosecond dynamics of charge recombination

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The kinetics of charge recombination in radical ion pairs C_{70}^-/Am^+ (Am is *N,N,N'N'*-tetramethyl-*p*-phenylenediamine, *p*-methoxy-*N,N*-dimethylaniline, *p*-methyl-*N,N*-dimethylaniline, *N,N*-diethylaniline, *N,N*-dimethylaniline, and triphenylamine) in chlorobenzene was studied by the picosecond laser photolysis technique. The radical ion states are the products of excitation of charge-transfer complexes between C_{70} and amines and are also formed by quenching of the singlet excited state of C_{70} by the amine. The rate constant of electron transfer in the radical ion pair decreases as the free Gibbs energy (ΔG) of the reaction increases and reflects the Marcus-inverted region of the dependence of the rate constant on ΔG. The C_{70}/Am and C_{60}/Am systems are compared.

Key words: fullerene C_{70}, ternary amines, radical ion pairs; picosecond laser photolysis.

Fullerenes C_{60} and C_{70}, being electron acceptors,[1] can reversibly reduce in ground and excited states.[2—9] Due to their electron-accepting properties, fullerenes form charge-transfer complexes (CTC) with electron donors, for example, with ternary amines.[10—12] Similar complexes are of interest from the viewpoint of nonlinear optical properties;[13] the possibility of using CTC in conducting polymers is also discussed.[12] We have recently studied chlorobenzene solutions of CTC between fullerenes C_{60} and some ternary amines: *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), *p*-methoxy-*N,N*-dimethylaniline (MeODMA), *p*-methyl-*N,N*-dimethylaniline (MeDMA), *N,N*-dimethylaniline (DMA), *N,N*-diethylaniline (DEA), and triphenylamine (TPA).[10] It is shown that the photoexcited state of these complexes can be presented as the contact radical ion pair C_{60}^-/Am^+, where Am is an amine.[10] The dependence of the rate constant of charge recombination in the complexes on the driving force of the reaction (ΔG) can be considered,[10] according to the Marcus theory, as an inverted regime of the dependence of the electron transfer rate constant on ΔG. The substantial peculiarity of this dependence in the series of C_{60}/Am complexes is a sharp decrease in the electron transfer rate constant (k_{CT}) as $|\Delta G|$ increases in chlorobenzene (in the further discussion, ΔG will be considered as the absolute value of the driving force of the electron transfer). In the present work, the photoexcited states and the dynamics of their relaxation in the charge-transfer complexes between fullerene C_{70} and ternary amines in chlorobenzene are considered.

Experimental

Fullerene C_{70} was synthesized by a previously described procedure,[15] and its purity was not less than 98 %. Amines were purified by distillation, sublimation, or recrystallization (in the case of solid amines). Chlorobenzene was purified by the standard procedures.[16]

Experiments on picosecond laser photolysis were carried out on laser kinetic spectrometers controlled by a computer according to an excitation—probing scheme. A spectrometer based on an Nd^{3+}-aluminate laser (duration of the generation pulse of the main harmonic was 20 ps (width at the half-height)) and a spectrometer based on an Nd^{3+}-glass laser (duration of the generation pulse of the main harmonic was 6 ps) were used. The laser spectrometers were described in detail in our recent works[17,18]; the Nd^{3+}-aluminate laser was used for studying the kinetic processes with the characteristic time of transformation >20 ps and for measuring differential spectra of excited samples. In this case, the spectrum of the picosecond continuum excited by the main harmonic in the $H_2O—D_2O$ (1 : 1) mixture was used. The laser on the neodymium glass was used for studying faster processes. The polarization of pump and probe pulses was oriented at the magic angle of 57.4°. In the experiments with a lower time resolution (Nd^{3+}-aluminate laser), a slow time component was more distinct, while in the experiments with an enhanced time resolution (Nd^{3+}-glass laser), a fast component of the decay of the optical density was revealed. Samples were excited by the second harmonic radiation of the lasers. Measurements were carried out in 2-mm cells under anaerobic conditions at ~23 °C. It was established that irreversible photochemical transformations can occur almost for all amines at the density of the excitation energy >1 mJ cm^{-2}. At lower energy densities, these uncontrolled photochemical changes in the system become

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insignificant and do not affect the accuracy of the measurements carried out.

Complex formation between C_{70} and amines was studied by the photometric method using a Specord M-40 spectrophotometer. The resulting spectra were introduced to the computer memory and processed.

Results and Discussion

Equilibrium constants and absorption spectra of charge-transfer complexes. The addition of the ternary amine to a solution of fullerene C_{70} in chlorobenzene results in changes in the absorption spectrum, which are qualitatively similar for all amines studied. For example, the intensity of the absorption decreases in the range of 21500 cm^{-1} (the maximum of the band of C_{70}), and an additional absorption in the range <16000 cm^{-1} appears. The changes in the absorption spectra of the amines with the lowest (TMPD) and highest (TPA) oxidation potentials caused by the formation of CTC between C_{70} and the amine are shown in Figs. 1 and 2. The dependences of the change in the optical density of a solution on the amine concentration were processed by the Benesi—Hildebrandt (B—H) method[19] in the assumption that these complexes have the composition of 1 : 1. The concentration dependence in the B—H coordinates for the C_{70}/TMPD system is presented in Fig. 1, *b*. This dependence agrees with the suggested composition of the complexes (1 : 1). The values of the equilibrium constants for six amines studied range from 0.2 to 0.6 L mol^{-1}. No pronounced correlation between the value of the equilibrium constant and electron-donating properties of the amine was observed. It is likely that steric factors play a substantial role in the complex formation. It is noteworthy that relative changes in the optical density of the solutions of the C_{70}/Am systems are substantially lower than those in the C_{60}/Am systems; therefore, the accuracy in the determination of equilibrium constants and extinction coefficients of the C_{70}/Am complexes is substantially lower than that in the case of C_{60}/Am. The difference is mainly determined by different values of extinction coefficients of these fullerenes in the visible spectral region, which are considerably higher for C_{70} than for C_{60} (see Ref. 20).

The absorption spectra presented in Figs. 1 and 2 are determined by the sum of the absorptions of CTC and free C_{70}. To reveal the absorption spectrum of the C_{70}/Am complex itself, the absorption of C_{70} was subtracted from the total spectrum. The procedure of the determination of the absorption spectrum of the complex was the following: (1) the equilibrium constants for each amine were determined from the B—H dependence; (2) the absorption spectrum of CTC was calculated according to Eqs. (1) and (2) determining the CTC concentration and the total optical density of the solution.

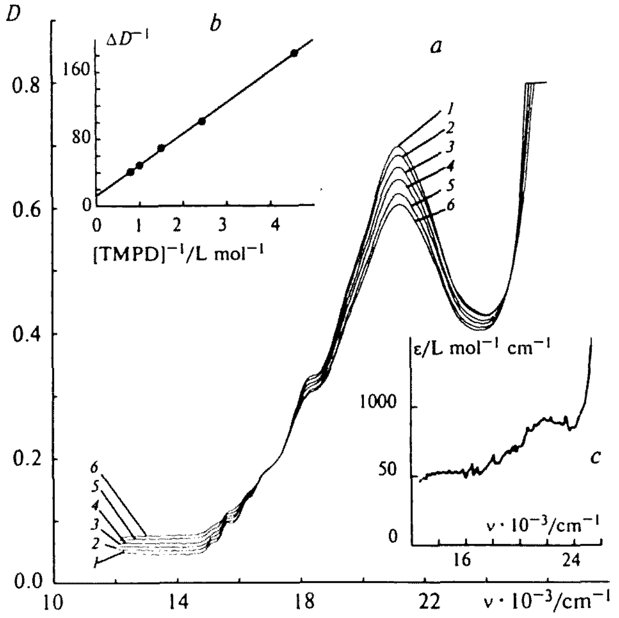


Fig. 1. *a*. Absorption spectrum of a solution of fullerene C_{70} and TMPD in chlorobenzene at $[C_{70}] = 4.54$ mol L^{-1}; [TMPD]/mol L^{-1} = 0 (*1*), 0.22 (*2*), 0.41 (*3*), 0.66 (*4*), 0.99 (*5*), and 1.2 (*6*).
b. Dependence of the value of the increase in the optical density of the solution on the TMPD concentration in the B—H coordinates measured at v = 12000 cm^{-1}.
c. Absorption spectrum of CTC C_{70}/TMPD in chlorobenzene.

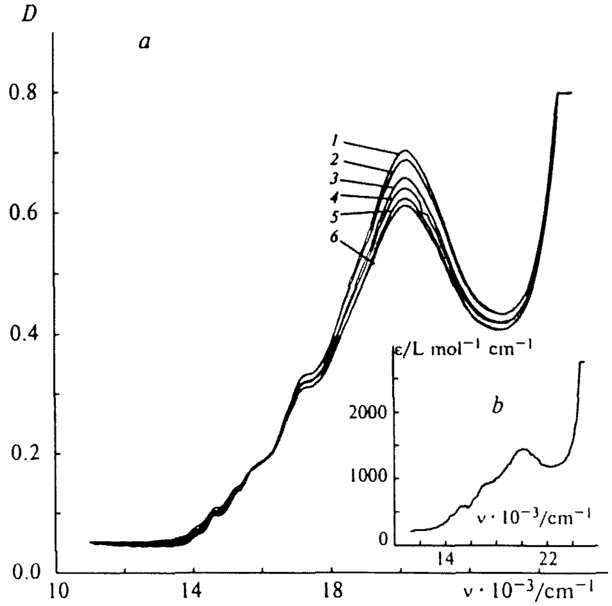


Fig. 2. Absorption spectrum of a solution of fullerene C_{70} and TPA in chlorobenzene at $[C_{70}] = 4.58$ mol L^{-1}; [TPA]/mol L^{-1} = 0 (*1*), 0.236 (*2*), 0.416 (*3*), 0.647 (*4*), 0.799 (*5*), and 1.065 (*6*).
b. Absorption spectrum of CTC C_{70}/TPA in chlorobenzene.

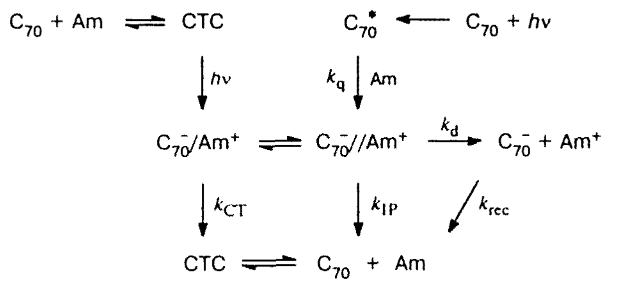
$$[\mathrm{CTC}]/([C_{70}]\cdot[\mathrm{Am}]) = K \quad (1)$$

$$D(\nu) = D_{C_{70}}(\nu) + D_{\mathrm{CTC}}(\nu) \quad (2)$$

The spectra of TMPD and TPA complexes are presented in Figs. 1, *c* and 2, *b*, respectively. When the electron-donating ability decreases in the series of amines from TMPD to TPA, the intensity of the absorption in the long-wave spectral range (12000—16000 cm^{-1}) decreases, and the absorption bands shift to the short-wave range. The same tendency of the general character in homologous series of CTC[21] is observed for the C_{60}/Am systems. The values of the extinction coefficients of CTC of C_{70}/Am are approximately 50 % lower than the similar values for the C_{60}/Am complexes, and are equal to 500—1500 L mol^{-1} cm^{-1} (at the maxima of the charge-transfer band).

Photoexcited states of charge-transfer complexes. Relaxation kinetics. The C_{70}/Am system is more difficult to study by picosecond kinetic spectroscopy than the similar C_{60}/Am system. This is because when the values of binding constants of fullerenes C_{60} and C_{70} with amines are close, the fractions of fullerene molecules bound in CTC differ for different amines, and their values range from 23 to 47 % at the concentrations of 1.5 mol L^{-1}. For the C_{60}/Am system, the extinction coefficient of CTC at the excitation wavelength (540 nm) is approximately threefold higher than that of unbound C_{60}. In the C_{60}/Am system, the absorption of the excitation light is mainly determined by CTC, and the main contribution to the intensity of the signal is made by the photoexcited states of CTC in the experiments using picosecond adsorption spectroscopy. The opposite situation takes place in the case of C_{70}/Am: the extinction coefficient of unbound C_{70} is higher than that for CTC. Therefore, in the C_{70}/Am system, one should expect a considerable contribution to the signal from both excited CTC and excited states of unbound C_{70} and subsequent products of its quenching by the amine. Thus, the excited states and their transformations in the picosecond time scale in the C_{70}/Am system can be presented in the first approximation by Scheme 1.

Scheme 1



Here C_{70}^{-}/Am^{+} is the contact radical ion pair; C_{70}^{-}//Am^{+} is the solvate-separate radical ion pair; C_{70}^{*} is the excited molecule of C_{70}; k_{CT} is the rate constant of charge recombination in the contact radical ion pair; k_{IP} is the rate constant of charge recombination in the solvate-separate radical ion pair; k_q is the rate constant of quenching of the excited fullerene by the amine; k_{rec} is the rate constant of recombination of free radical ions; and k_d is the dissociation constant of solvate-separate radical ion pairs.

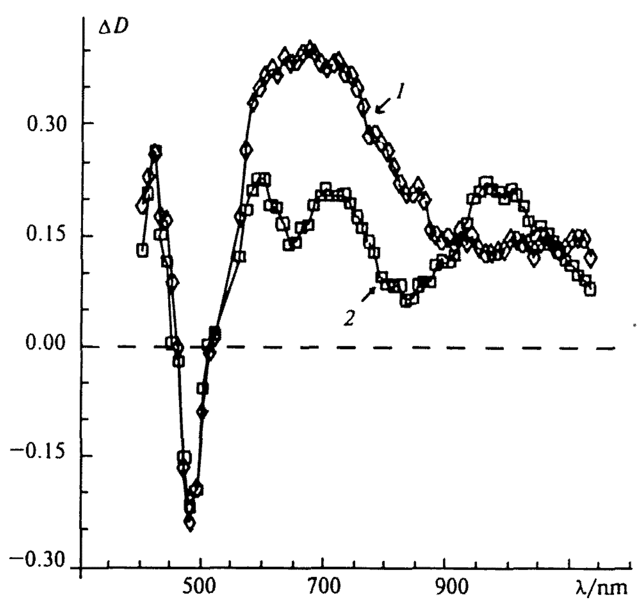


Fig. 3. Differential absorption spectrum of fullerene C_{70} at $[C_{70}]$ = $4\cdot10^{-4}$ mol L^{-1}. Time delay is 30 ps (*1*) and 1200 ps (*2*).

On the whole, the differential absorption spectra of solutions of C_{70} with amines in chlorobenzene and the kinetics of the change in the optical density of the photoexcited C_{70}—C_{70}/Am system in the picosecond time scale confirm Scheme 1. The exception is the C_{70}/TPA system in which the triplet-excited state C_{70} should be additionally considered. The differential absorption spectra appeared upon the excitation of a solution of pure C_{70} without the amine are presented in Fig. 3. The kinetic curves of the change in the optical density of a solution of pure C_{70} at two characteristic wavelengths of absorption maxima of the transitions $S_1 \rightarrow S_x$ (λ = 650 nm) and $T_1 \rightarrow T_x$ (λ = 980 nm) are presented in Fig. 4. The absorption spectra for the C_{70}/TMPD system at the time delays of 5 and 45 ps are presented in Fig. 5, and the corresponding spectra for the C_{70}/TPA system are presented in Fig. 6. The analysis of the absorption spectra for the C_{70}/TMPD (see Fig. 5) and C_{70}/TPA systems (see Fig. 6) at short time delays shows their substantial difference from the spectrum of pure C_{70} (see Fig. 3) and the existence of the amine radical cation TMPD^{+} (the band at ~610 nm, see Fig. 5) and TPA^{+} radical cation (the band at ~650 nm with the pronounced decrease to the long-wave spectral range, see Fig. 6). The similar absorption bands typical of amine radical cations were observed previously[10,14] for the C_{60}/Am systems. The spectra of the C_{70}/Am systems for all six amines studied contain a broad

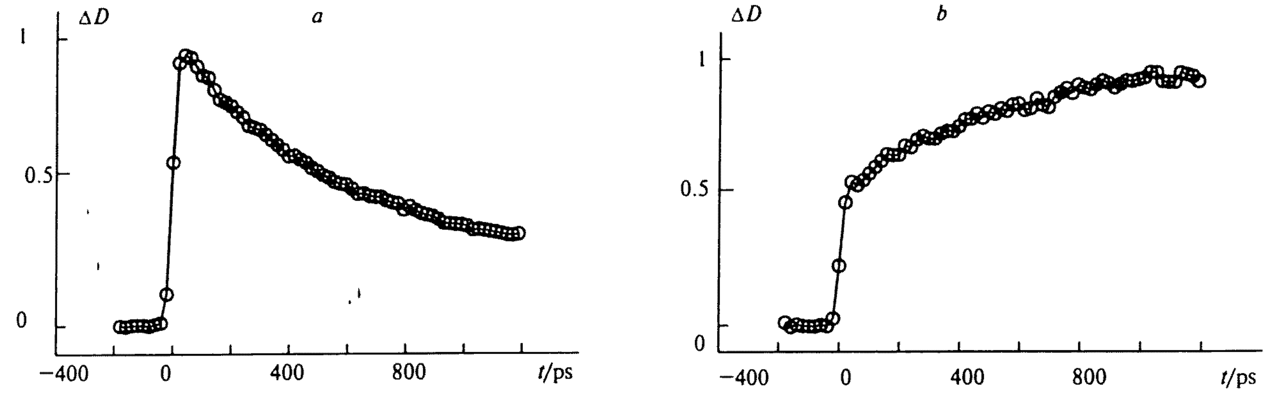


Fig. 4. Kinetics in the change in the optical density of a solution of fullerene C_{70} in chlorobenzene at $[C_{70}] = 5.8 \cdot 10^{-5}$ mol L^{-1}; λ = 650 nm (*a*) and 980 nm (*b*).

band in the range of 700—1100 nm with a small minimum at ~880 nm. This band can be assigned to the radical anion C_{70}^- (see Ref. 6). Since the absorption of the transition $S_1 \rightarrow S_x$ in C_{70} is manifested as a sufficiently broad band (see Fig. 3), the possibility of the presence of this band in the spectra presented in Figs. 5 and 6 cannot be completely excluded. The specific feature of the C_{70}/TPA system is the fact that at long time delays (about 1000 ps) the absorption band of the triplet-excited C_{70} with a maximum at ~980 nm (*cf.* Figs. 3 and 6) is observed, while it is not manifested in the spectra of the other five more easily oxidized amines.

Additional information on the rate of transitions and the nature of excited states can be obtained on the basis of the data on the kinetics of the change in the optical density. For example, the kinetic curves of the decrease in the optical density with different values of time resolution for the TMPD, MeODMA, and MeDMA systems are presented in Figs. 7, 8, and 9. For easily oxidizable TMPD, MeODMA, and MeDMA, its decrease is characterized by at least two exponents. For the amines with a lower electron-donating ability (DMA, DEA, and TPA), the kinetics of the decrease in the optical density does not have a pronounced biexponential character. The changes in the optical density for the C_{70}/TPA system at the maximum of the absorption band of the radical cation TPA^+ (λ = 630 nm) and at the absorption maximum of the transition $T_1 \rightarrow T_x$ in C_{70} (λ = 980 nm) are presented

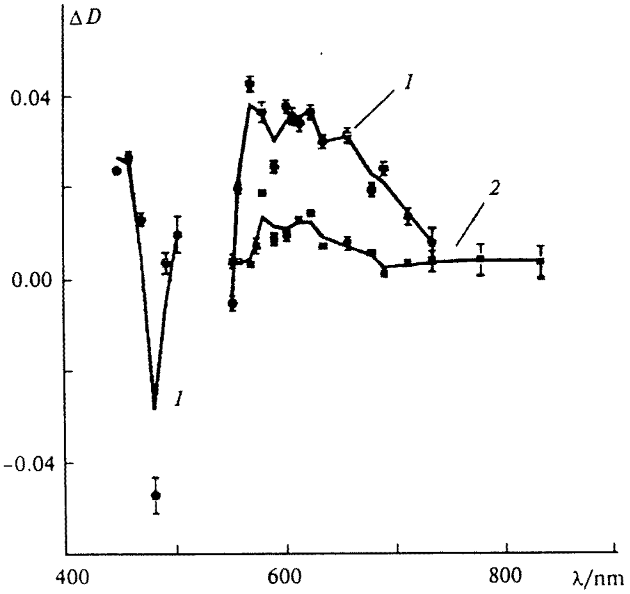


Fig. 5. Differential absorption spectrum of a solution of fullerene C_{70} and TMPD in chlorobenzene at $[C_{70}] = 4.1 \cdot 10^{-4}$ mol L^{-1} and [TMPD] = 1.6 mol L^{-1}. Time delay is 5 ps (*1*) and 45 ps (*2*).

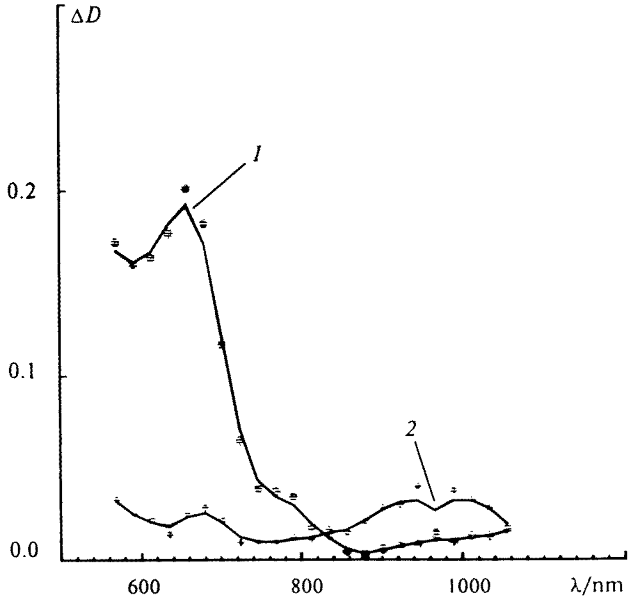


Fig. 6. Differential absorption spectrum of a solution of fullerene C_{70} and TPA in chlorobenzene at $[C_{70}] = 4.2 \cdot 10^{-4}$ mol L^{-1} and [TPA] = 1.7 mol L^{-1}. Time delay is 5 ps (*1*) and 1000 ps (*2*).

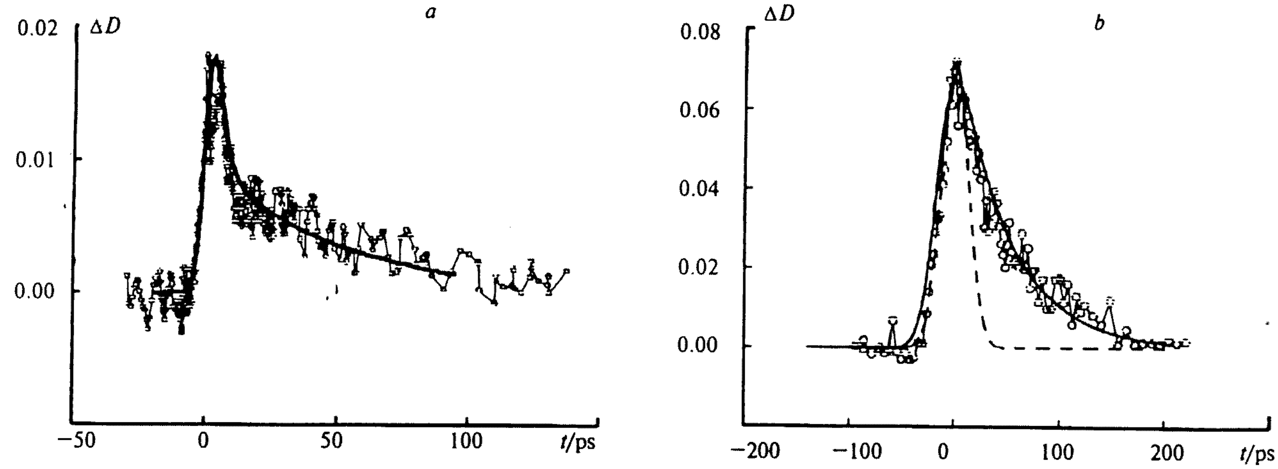


Fig. 7. Kinetics of the change in the optical density of a solution of fullerene C_{70} and TMPD in chlorobenzene at $[C_{70}] = 3 \cdot 10^{-4}$ mol L^{-1} and [TMPD] = 1.8 mol L^{-1}. The dotted line shows the convolution of the apparatus function, $A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$.
a. Nd^{3+}-glass laser, λ_{exc} = 528 nm. The coherent ejection is observed near the zero delay; τ_1 = 3 ps, τ_2 = 50 ps.
b. Nd^{3+}-aluminate laser, λ_{exc} = 540 nm, λ = 615 nm; τ_1 = 3 ps, τ_2 = 70 ps.

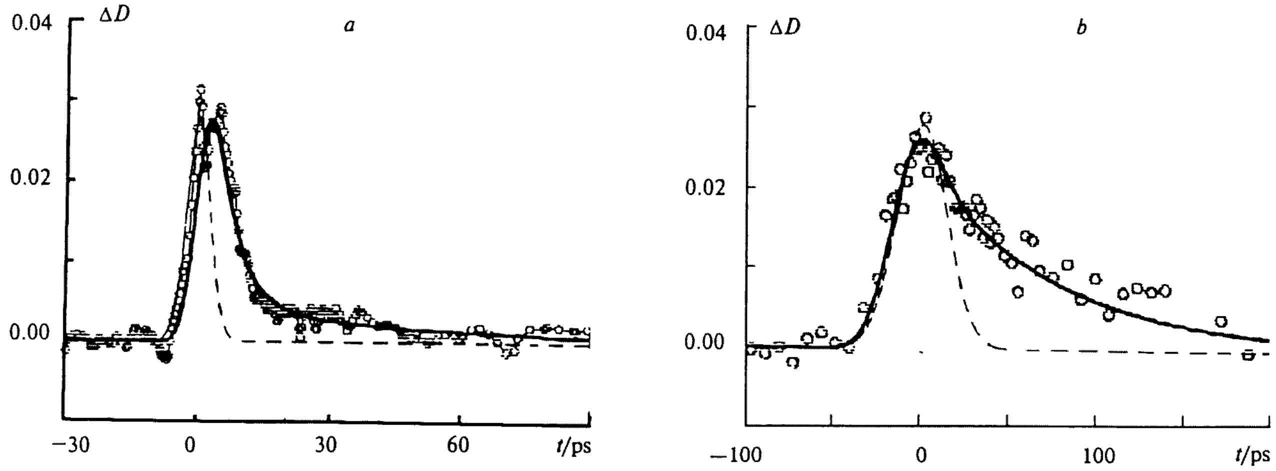


Fig. 8. Change in the optical density of a solution of fullerene C_{70} and MeODMA in chlorobenzene at $[C_{70}] = 2.7 \cdot 10^{-4}$ mol L^{-1} and [MeODMA] = 2.1 mol L^{-1}. The dotted line shows the convolution of the apparatus function, $A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$.
a. Nd^{3+}-glass laser, λ_{exc} = 528 nm. The coherent ejection is observed near the zero delay; τ_1 = 5 ps, τ_2 = 60 ps.
b. Nd^{3+}-aluminate laser, λ_{exc} = 540 nm, λ = 630 nm; τ_1 = 5 ps, τ_2 = 75 ps.

in Fig. 10. At time delays >100 ps, the decrease in the optical density at λ = 630 nm is accompanied by the parallel growth of the optical density at λ = 980 nm. At time delays <100 ps, the minimum at λ = 980 nm that is not related to the manifestation of laser artefacts is observed on the kinetic curve of the change in the optical density. This minimum was not observed for the kinetics of the growth of the triplet absorption of C_{70} in the absence of TPA. In this work, the reasons for this effect are not considered; the detailed analysis of possible transitions in the C_{70}/TPA and C_{60}/TPA systems will be presented elsewhere.

Thus, the following generalizations can be made on the basis of the data: (1) radical ion states predominate upon the excitation of the C_{70}/Am system; (2) radical ion pairs of two types are observed: contact and solvate-separate pairs, which is indicated by the biexponential character of the decrease in the optical density of easily oxidizable amines. It is noteworthy that the experiments are performed at an amine concentration >1.5 mol L^{-1}. According to the statistics, not less than one amine molecule is present in the first solvate shell. Therefore, the quenching of the excited state C_{70}* by the amine in Scheme 1 can reasonably be considered to be quenching in the statistic pair rather than the dynamic quenching occurring due to diffusion encounters with a quencher. Contact radical ion pairs are mainly the products of the excitation of CTC, while solvate-separate pairs are the products of quenching in the statistic pair.

The data on the lifetimes of radical ion pairs are presented in Table 1. It is reasonable to suppose that short lifetimes are related to contact pairs, because the param-

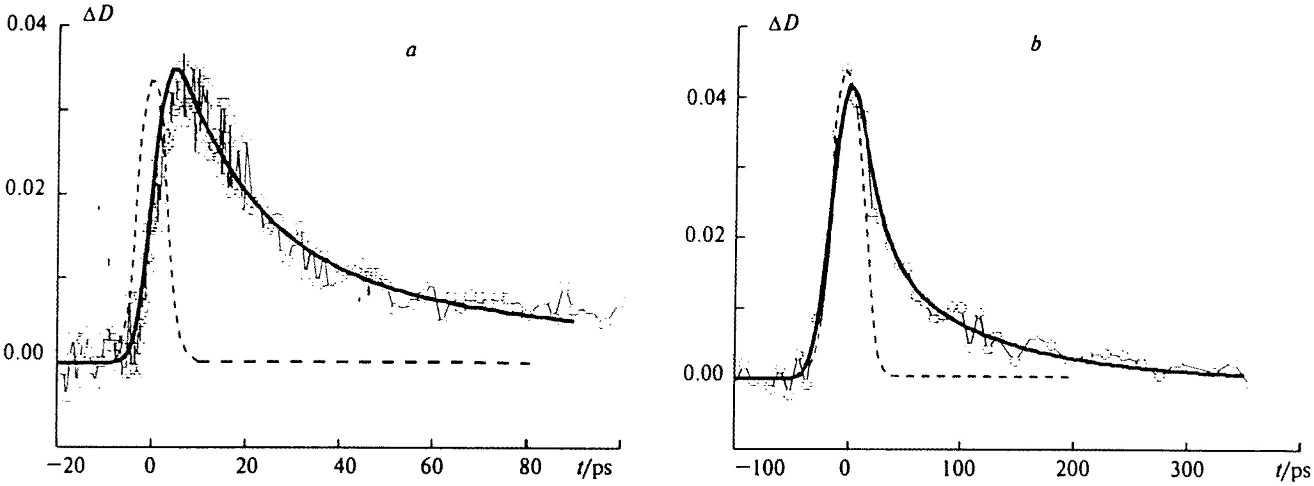


Fig. 9. Change in the optical density of a solution of fullerene C_{70} and MeDMA in chlorobenzene at $[C_{70}] = 3.3 \cdot 10^{-4}$ mol L^{-1} and [MeDMA] = 1.8 mol L^{-1}. The dotted line shows the convolution of the apparatus function, $A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$.
a. Nd^{3+}-glass laser, λ_{exc} = 528 nm. The coherent ejection is observed near the zero delay; τ_1 = 17 ps, τ_2 = 100 ps.
b. Nd^{3+}-aluminate laser, λ_{exc} = 540 nm, λ = 700 nm; τ_1 = 17 ps, τ_2 = 100 ps.

eter of the electron-electron interaction (V) between the C_{70}^{-}...Am^{+} and C_{70}...Am states for the contact pair is considerably higher that for the solvate-separate one. In this case, the value that is inversely proportional to the lifetime τ_1 is the rate constant of charge recombination (k_{CT}). Since additional transitions between the excited states occur in the C_{70}/TPA system along with the charge recombination, the value that is inversely proportional to the lifetime τ_1 is the upper boundary of k_{CT} at Am = TPA.

It seems reasonable to analyze the dependence of the lifetime τ of the corresponding radical ion pair on the driving force of the electron transfer upon the charge recombination in this pair. The ΔG value can be estimated by the standard procedure[21] from the redox potentials of C_{70} and the corresponding amine according to the expression

$$-\Delta G = E_{1/2}(\mathrm{Am/Am^+}) - E_{1/2}(C_{70}^{-}/C_{70}) + \Delta, \qquad (3)$$

where Δ/eV is the correction determined by the equation

$$\Delta = 0.38 - 0.75\left[2\frac{\varepsilon_s - 1}{2\varepsilon_s + 1} - \frac{\varepsilon_0 - 1}{2\varepsilon_0 + 1}\right]. \qquad (4)$$

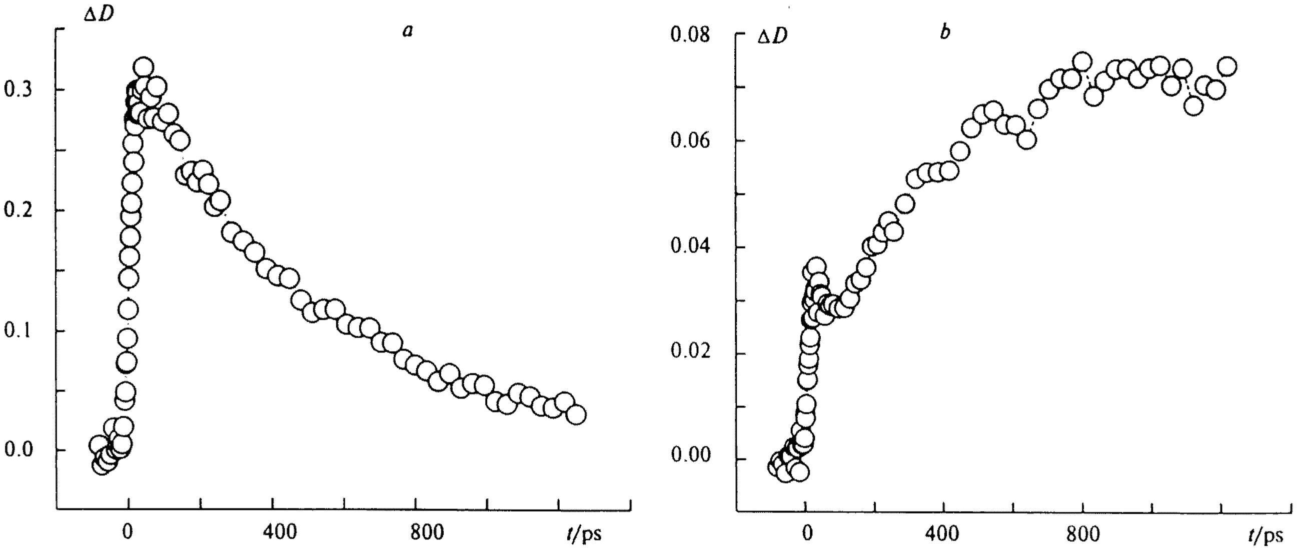


Fig. 10. Change in the optical density of a solution of fullerene C_{70} and TPA in chlorobenzene at $[C_{70}] = 2.8 \cdot 10^{-4}$ mol L^{-1} and [TPA] = 1.49 mol L^{-1}; Nd^{3+}-aluminate laser, λ = 630 nm (*a*) and 980 nm (*b*).

Table 1. Oxidation potentials of amines [E(Am/Am$^+$)], electron transfer driving force (ΔG) upon charge recombination in the ion pair, and lifetime (τ) of the radical ion pair

Am	E(Am/Am$^+$)/V*	$-\Delta G$/eV	τ_1/ps	τ_2/ps
TMPD	0.12	0.70	3±2	50±20
MeODMA	0.55	1.13	6±2	60±20
MeDMA	0.71	1.29	19±3	90±20
DEA	0.76	1.34	85±10	—
DMA	0.81	1.39	66±10	—
TPA	1.12	1.70	500±50	—

* In acetonitrile relative to SCE.[22]

Then $E_{1/2}(C_{70}{}^-/C_{70}) = -0.41$ V and $E_{1/2}(C_{60}{}^-/C_{60}) = -0.44$ V (relative to SCE) in benzonitrile[12]; ε_s is the static dielectric constant of the medium, and ε_0 is the optical dielectric constant of the medium. We used the previously obtained estimation of ΔG for the C_{60}/Am system in chlorobenzene with account for the difference in the redox potentials of C_{60} and C_{70}. The data are presented in Table 1.

The dependences of k_{CT} on ΔG for the C_{70}/Am and C_{60}/Am systems are presented in Fig. 11. These two dependences are similar, and their essential peculiarity is a very sharp decrease in k_{CT} as ΔG increases. If it is assumed that the transition from the photoexcited state of CTC to the ground state is equivalent to the electron transfer in the contact radical ion pair, the dependence of k_{CT} on ΔG can be described in terms of the electron transfer theory, for example, in the form of Eq. (5).[23]

$$k_{CT} = A_n \sum e^{-S} \frac{S^n}{n!} \exp\left[-\frac{(\hbar\omega + \Delta G + \lambda_s)^2}{4\lambda_s k_B T}\right](1 + H_n)^{-1}, \quad (5)$$

$$A_n = \frac{2\pi V^2}{\hbar\sqrt{4\pi\lambda_s k_B T}},$$

$$H_n = \frac{4\pi V^2 \tau_L}{\hbar\lambda_s}\left(\frac{S^n}{n!}\right)\exp(-S),$$

$$S = \lambda_{in}/h\omega,$$

where λ_s is the external energy of the medium reorganization; λ_{in} is the internal reorganization energy; ω is the frequency of internal vibrations associated with the electron transfer; τ_L is the longitudinal relaxation time of a dielectric that is equal to 5.7 ps for chlorobenzene; H_n is the nonadiabatic factor; k_B is the Boltzmann constant; V is the parameter of the electron-electron interaction; and S is the parameter of the electron-vibration interaction.

When the C_{70}/Am complexes are considered as a series according to the increase in their redox potentials, the dependence of the observed k_{CT} on ΔG should reflect the dependence of the electron transfer rate constant on the value of the driving force.[24–29] This assumes that the parameters V, λ_{in}, λ_s, and ω are equal for all CTC. Despite the nonrigid character of this assumption, it is acceptable for the semiquantitative analysis based on Eq. (5).[10,14,24–29] This dependence has been previously analyzed[10,14] in detail for the C_{60}/Am system. Since the spectral parameters of the charge-transfer band turned out to be close for the C_{70}/Am and C_{60}/Am systems and the distances in the radical ion pairs are also comparable for C_{70} and C_{60}, it is clear without the detailed analysis followed by the justification of the choice of the values of internal and external reorganization energies and electron-electron interaction for the C_{70}/Am system that the application of Eq. (5) for the description of the dependence of k_{CT} on ΔG in this system is conjectural as in the case of C_{60}/Am. This is related to the fact that the experimental dependence of the electron transfer rate constant on ΔG for the systems with fullerenes (see Fig. 11) exhibits a very drastic decrease compared to the similar dependence in radical ion pairs involving planar aromatic hydrocarbons.[24–29] This decrease can be described by Eq. (5), assuming either a very low value of the frequency ω close to 500 cm^{-1} or a low internal reorganization energy λ_{in} (<0.1 eV). In the first case, we are out of the commonly accepted assumption that the transition is determined by the frequencies close to 1500 cm^{-1}, *i.e.*, the frequencies of the vibrations of the C=C bond.[24–29] Numerous data on the charge recombination in radical ion pairs involving planar conjugated systems favor the choice of ω = 1500 cm^{-1}. In the second case,

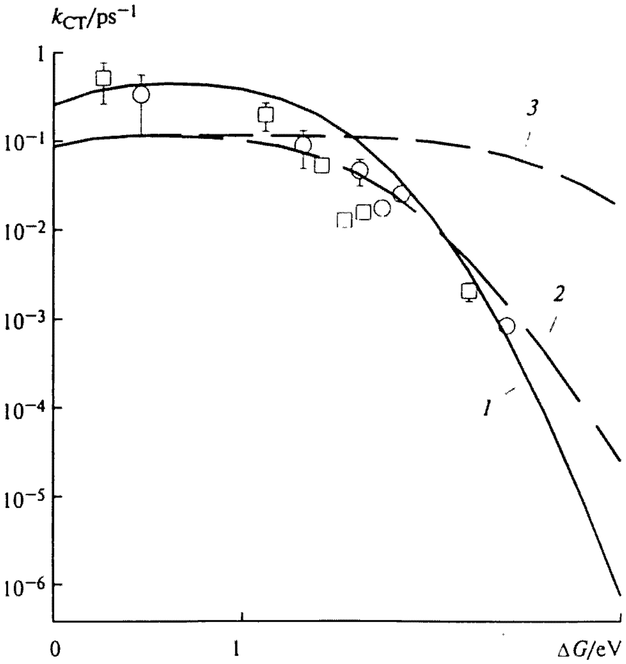


Fig. 11. Dependence of the charge reconbination rate constant (k_{CT}) in the contact ion pair on the electron transfer driving force (ΔG). Experimental points indicate C_{60}/Am (circles) and C_{70}/Am systems (squares). Curves indicate the theoretical dependences calculated by Eq. (5): *1*, λ_{in} = 0.25 eV, λ_s = 0.5 eV, V = 700 cm^{-1}, ω = 470 cm^{-1}; *2*, λ_{in} = 0.07 eV, λ_s = 0.5 eV, V = 700 cm^{-1}, ω = 1500 cm^{-1}; *3*, λ_{in} = 0.25 eV, λ_s = 0.5 eV, V = 700 cm^{-1}, ω = 1500 cm^{-1}.

the λ_{in} value turns out to be substantially lower than 0.4 eV (reorganization energy in amines upon the electron transfer[29]). Thus, if the use of the commonly accepted Eq. (5)[24–29] is valid, it should be assumed that in the fullerene system the frequency of internal vibrations determining the Franck—Condon factor in the electron transfer is the frequency of framework vibrations of the ball of the fullerene molecule, which is close to 500 cm^{-1} (see Ref. 30). It is likely that the experiments using resonance Raman excitation to the regions of the charge-transfer band can answer this question more exactly.

* * *

The following conclusions can be drawn from the aforesaid.

1. Fullerene C_{70} forms CTC with amines. The values of equilibrium constants of formation of these complexes in chlorobenzene are close to the corresponding constants for CTC of C_{60} with amines.

2. The absorption spectra with the picosecond time resolution obtained by the excitation of solutions of C_{70} with amines exhibit the absorption bands of the amine radical cation and radical anion $C_{70}^{\cdot -}$. The formation of the radical ion pair in the picosecond time scale is observed in terms of Scheme 1. Unlike the C_{60}/Am system, the C_{70}/Am system manifests the more pronounced biexponential kinetics of the radical ion pair decay, which is likely related to the charge recombination in contact and solvate-separate radical ion pairs.

3. The dependence of the inverse lifetime of the contact radical ion pair of C_{70} with the amine on the driving force of the electron transfer ΔG can be considered as the Marcus-inverted regime for the electron transfer rate constant.

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