Thermal Dissociation of *N,N*-Dimethylformamide–Tetracyanoethylene and Dimethyl Sulfoxide–Tetracyanoethylene Complexes into Ions

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Ionic dissociation of *N,N*-dimethylformamide (DMF)-tetracyanoethylene (TCNE) and dimethyl sulfoxide (DMSO)–TCNE electron donor-acceptor (EDA) complexes was studied by means of optical absorption and electron spin resonance measurements. Upon dissolving TCNE into DMF or DMSO, essentially all the TCNE became complexed with the electron-donationg solvent; charge-transfer bands with maxima at 310 and 380 nm were found for DMF–TCNE and DMSO–TCNE complexes, respectively. The CT bands were transformed slowly in the dark into the band of $TCNE^-$. This transformation proceeded quantitatively and indicated the dissociation of the EDA complexes into ions. The rate of the ionic dissociation was determined by following a first-order growth of the ESR spectrum of $TCNE^-$ at various temperatures: $k=10^{8.9}\exp(79/RT)$ for the DMF–TCNE complex and $k=10^{6.3}\exp(59/RT)$ for the DMSO–TCNE complex, in units of s and kJ/mol. Dissolved oxygen was found not only to react chemically with the complex to form a new stable species, but also to quench physically the ionic dissociation. Upon evacuating the oxygen, the survival fraction of the complex was found to start dissociation again. It is suggested that the ionic dissociation arises from a long-lived precursor state, probably the triplet state of the complex.

Since the very early work of Kainer and Uberle showing the formation of ions on dissolving *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine–chloranil solid complex in acetonitrile,[1] the role of electron donor–acceptor (EDA) complexes in chemical reactions has been subject of spectroscopic study.[2] The role in photoinduced reactions has been extensively studied mostly by a flash photolysis technique: selective excitation at charge-transfer (CT) band or bands of constituent molecules has facilitated the elucidation of the molecular mechanism in the reactions. The photoinduced formation of ions from donor–acceptor pairs in solution has been shown to occur through an excited state of the EDA complexes and/or through an exciplex.[3] However, ion formation without light has been studied comparatively little, and its molecular mechanism has not been fully elucidated.[4–9]

TCNE, one of the strongest organic acceptors, has been known to form readily its radical anion ($TCNE^-$) when photoilluminated in fluid or rigid etherial solvents such as tetrahydrofuran (THF) which have an electron-donating nature.[7,10–13] Stewart *et al.* further found the formation of $TCNE^-$ in the absence of light upon mixing TCNE in more polar solvents such as dimethyl sulfoxide (DMSO) and *N,N*-dimethylacetamide (DMA).[6,7] The concentration of $TCNE^-$ was found to reach a maximum within a few minutes, before starting the measurements, and then to decay slowly. They proposed, in adopting the mechanism presented by Calvin for the THF-TCNE complex,[12] that the "prompt ESR signal of $TCNE^-$" arises from the thermal population of the CT triplet state, which then decays to give the ground state EDA complex between solvent and TCNE or to give ions. The slow decay was explained by recombination of ions to give the complex. These authors seem to have assumed that the observed $TCNE^-$ is the precusor of the complex rather than its product. Later, Keys and Carper found that in degassed solutions $TCNE^-$ was very stable and its concentration increased slowly after its prompt formation.[8] These observations were again interpreted on the basis of Stewart's view.

Recently, we also studied the formation without light of $TCNE^-$ in DMSO by the ESR method[14] and found a difference in its kinetical features from those reported previously.[6,7] We found no prompt formation of $TCNE^-$. Its concentration increased following a first-order kinetics during the whole period of reaction in the dark. The result suggested, in contrast to Stewart's view, the thermal dissociation of DMSO–TCNE complex into ions which is unexpectedly slow. The previous investigation is extended here and the formation of $TCNE^-$ is studied in either DMSO or *N,N*-dimethylformamide (DMF) by means of not only the ESR technique but also optical absorption measurements.

Experimental

TCNE of analytical grade was purified by recrystallization from anhydrous methylene dichloride and by sublimation under vacuum several times. DMF of spectroscopic grade was dried under vacuum with calcium hydride and then with barium oxide baked beforehand at *ca.* 650 K overnight, degassed by a freezing-pumping-thawing technique, and kept in the dark. DMSO of spectroscopic grade was dried with calcium hydride, degassed and treated with molecular sieves baked beforehand under vacuum, and kept in the dark.

TCNE was dissolved in DMF or DMSO within a closed glass system with an optical absorption cell or an ESR sample tube through a break seal under vacuum better than 1×10^{-5} Torr, and subjected to measurements. These procedures were carried out cautiously in total darkness. The optical absorption spectrum of the solution was recorded with a conventional recording spectrophotometer (Hitachi, Model EPS-3T) at room temperature (298±1 K) between intermittent warmings at a fixed temperature. Electron spin resonance (ESR) measurements were carried out with a conventional X-band spectrometer (JEOL, Model JES-ME-2X) equipped with a variable temperature accessary (Model JES-VT). The reaction temperature in the ESR resonant cavity was thus controlled within an uncertainty of 0.5 K. Absolute concentrations of $TCNE^-$ formed in the solutions were determined from their ESR spectral intensities, as compared with the intensity of the $TCNE^-$ authentically generated by reducing TCNE with sodium metal in acetonitrile.[15]

Results

Optical Absorption Studies. Immediately after dissolving TCNE into DMF, an optical absorption band with a broad structureless shape was observed at about 310 nm, as shown in Fig. 1, where neither TCNE nor DMF gives an absorption. A similar band was observed at about 380 nm for DMSO solvent, as shown in Fig. 2. The shift of absorption maximum from 310 to 380 nm seems to correspond to the difference in ionization potential and in dielectric constant between DMF and DMSO. These bands are attributed to a charge-transfer transition and indicate the formation of EDA complexes between solvents and TCNE. The CT band of the DMSO–TCNE complex was reported to have an absorption maximum at 372 nm in carbon tetrachloride.[6] The band of the DMF–TCNE complex has not been reported. The 310 nm band in Fig. 1 is very similar to that of the DMA–TCNE complex, which shows an absorption maximum at 298 nm.[7]

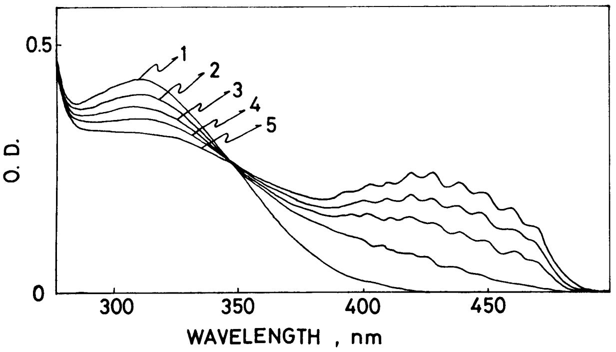

Fig. 1. Optical absorption spectra of DMF-TCNE observed at 298 K (1) immediately after mixing TCNE (3.0×10^{-4} mol dm^{-3}) in DMF under vacuum and after warming at 323 K for (2) 90, (3) 150, (4) 250 (5) 350 min. Optical path: 0.5 cm.

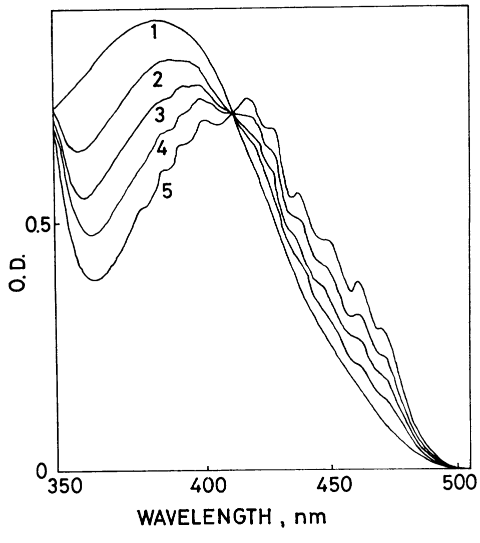

Fig. 2. Optical absorption spectra of DMSO-TCNE observed at 298 K (1) immediately after (2) 15, (3) 50, (4) 110 and (5) 280 min after mixing TCNE (6.0×10^{-4} mol dm^{-3}) in DMSO under vacuum. Optical path: 0.2 cm.

Figure 1 shows changes in the absorption spectrum when the solution of TCNE in DMF was warmed to 323 K: the CT band of the DMF–TCNE complex decayed slowly, while a new band appeared, extending from 350 to 500 nm. The new band has a vibrational structure which is essentially the same as that previously attributed to TCNE$^-$ which was chemically generated in acetonitrile.[15] The isosbestic point at 350 nm very probably indicates that ionic dissociation of the EDA complex proceeds quantitatively to give negative and positive ions, though no positive ions could be detected. Figure 2 shows similar results observed for the TCNE–DMSO system. An isosbestic point at 410 nm indicates the ionic dissociation of the DMSO–TCNE complex into ions. For this complex, the dissociation was found to be accelerated even by the analyzing light.

The growth of the absorption band of TCNE$^-$ was completely inhibited in the solution prepared in an open cell or in the presence of oxygen in a sealed cell, but an absorption band at about 300 nm was found to grow instead. This is clearly demonstrated in Fig. 3 for a solution of TCNE in DMSO under the pressure controlled to be 1×10^{-3} Torr, higher than that for the usual sample preparation. An isosbestic point at 340 nm indicates the quantitative transformation, in the presence of oxygen, of the EDA complex into another unidentified product. Although this transformation is as slow as the ionic dissociation observed in the absence of oxygen (see Fig. 2), the EDA complex does not dissociate into ions but is transformed exclusively into the unidentified product. Upon evacuating oxygen (or air), a survival fraction of the EDA complexes was found to start the dissociation into ions, but the unidentified product, once formed, was too stable to revert to the original complex.

ESR Studies. The formation of TCNE$^-$ in DMF or DMSO was evidenced also by the ESR method. The signal recorded from the solutions was exclusively due to the ESR spectrum of TCNE$^-$, which was essentially the same as that of TCNE$^-$ generated by reducing TCNE with alkali metal.[16,17] The spectrum

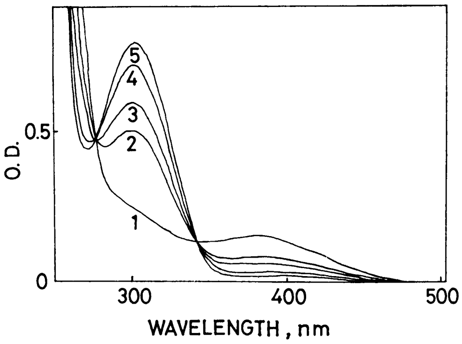

Fig. 3. Optical absorption spectra of unidentified product prepared by mixing TCNE (1.0×10^{-4} mol dm^{-3}) in DMSO under atmospheric pressure of 1×10^{-3} Torr and observed at 298 K (1) 5, (2) 35, (3) 60, (4) 100 and (5) 140 min after the mixing. Optical path: 0.2 cm.

consisted of 11 hyperfine lines equally spaced with a separation of 0.165 mT. Each hyperfine line was very narrow with a width, ΔH_{msl}, of 0.008 mT. The kinetical features of the formation of TCNE$^-$ were followed by observing the intensity of its spectrum at several temperatures. The advantage of ESR studies is that quantitative measurements can be readily made for TCNE$^-$ without any effect from light.

Figure 4 shows the formation of TCNE$^-$ in DMF. The TCNE$^-$ concentration increased slowly at a temperature-dependent rate and then tended to an asymptotic value, which was identical with the concentration of TCNE added in the solution. The observed time-concentration curves agreed well with a first order reaction, and the rate constant was independent of the concentration of TCNE. TCNE$^-$ was very stable in the dark and no decay was observed during a few weeks. Nor was any decay found even when the solution was exposed to air. The observed first order rate constant, k, is shown as a function of reciprocal temperature in Fig. 5, which gives a good Arrhenius relation with an activation energy of 79 kJ/mol and frequency factor of $10^{8.9}\,\text{s}^{-1}$.

The time-concentration curves for the formation of TCNE$^-$ in DMSO were already reported.[14] The observed kinetical features were essentially the same as those in DMF, except that the rate of the anion formation was larger in DMSO. The dashed curve in Fig. 6 shows the formation at 303 K under white light from a tungsten lamp, which is much quicker than that in the dark at the same temperature, as shown by a solid curve. It was found that even room light gives a large amount of TCNE$^-$ during the procedure of dissolving TCNE into DMSO. The activation energy and the frequency factor in DMSO in the dark were previously reported to be 59 kJ/mol and $10^{6.3}\,\text{s}^{-1}$,

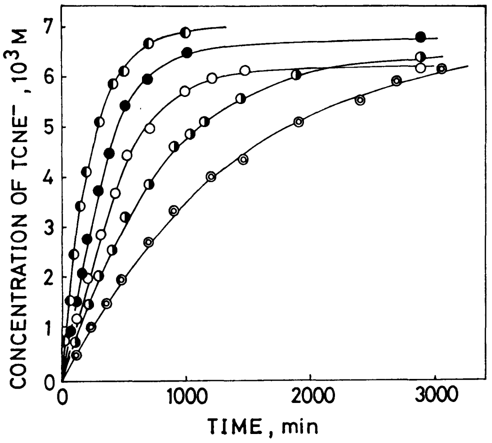

Fig. 4. Increase of the concentration at various temperatures of TCNE$^-$ formed from TCNE (7.0×10^{-3} mol dm^{-3}) mixed in DMF under vacuum determined by ESR. ◑, 318 K; ●, 313 K; ○, 308 K; ◑, 308 K; ◑, 303 K; ◎, 298 K.

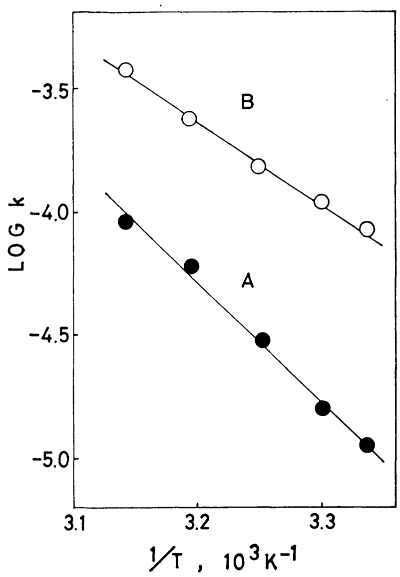

Fig. 5. Arrhenius plot of the first-order rate constant, k, for the formation of TCNE$^-$ (A) in DMF-TCNE, and (B) DMSO-TCNE systems in the dark determined by ESR.

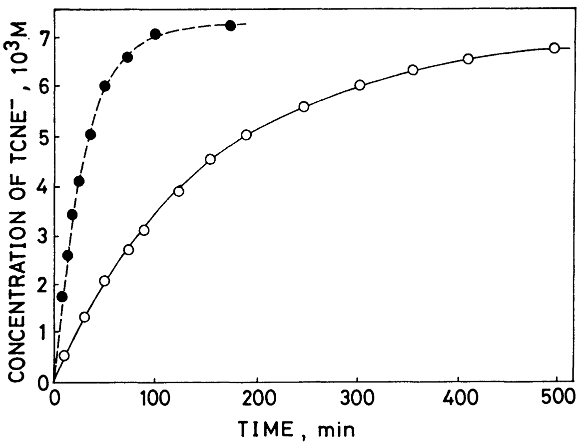

Fig. 6. Growth of the concentration of TCNE$^-$ formed from TCNE (7.0×10^{-3} mol dm^{-3}) in DMSO (solid line) in the dark and (dashed line) under light from an incandescent lamp both at 303 K determined by ESR.

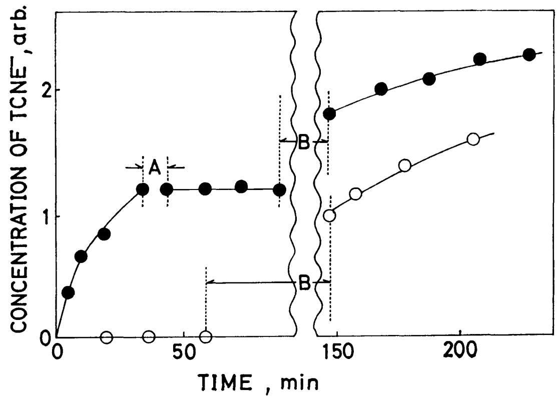

Fig. 7. Growth of the concentration of TCNE$^-$ ● in DMSO-TCNE prepared under vacuum and ○ in DMSO-TCNE prepared under 760 Torr of oxygen both at 303 K determined by ESR. A indicates the period of introducing 760 Torr of oxygen into the solution and B indicates the period of evacuating oxygen from the solution. The concentration of added TCNE was 7.0×10^{-3} mol dm^{-3}.

respectively.[14)]

Figure 7 shows the effect of oxygen studied by ESR. When oxygen was introduced into the solution during ESR measurements, the formation of TCNE$^-$ became inhibited, as shown by closed circles. On re-evacuating the oxygen, the formation started again, but the formation rate was smaller than before. The solution prepared under 1 atm of oxygen gave no TCNE$^-$, but it was found to form when the dissolved oxygen was removed by evacuation, as shown by the open circles. These results indicate the physical quenching of the TCNE$^-$ formation and the chemical elimination of the precursor of the radical anion by the oxygen dissolved in the solution.

Discussion

Formation of EDA Complexes. CT bands have been studied for the EDA complexes between several electron donors and TCNE.[6,7,18,19)] The molar extinction coefficient at the absorption maximum at 372 nm and the equilibrium constant were reported for the complex formation for the DMSO–TCNE system in carbon tetrachloride to be 973 mol^{-1} dm^3 cm^{-1} and 95.4 dm^3 mol^{-1}, respectively, at 298 K. The CT band of the DMSO–TCNE complex was found in the present investigation to develop before starting the measurements of the absorption spectrum (see Fig. 2). Its absorption maximum lay at a slightly longer wavelength, 380 nm. The shift in wavelength is attributed to a larger dielectric constant for the present donor-solvent, DMSO, compared with that of carbon tetrachloride. Adopting the reported equilibrium constant, the uncomplexed fraction of TCNE is estimated to be as small as 7.5×10^{-4}. Thus, it is concluded that essentially all the TCNE becomes complexed with DMSO immediately after mixing the former into the latter. It should be noted that the present results, shown in Fig. 2, indicate an extinction coefficient of 7500 mol^{-1}· dm^3 cm^{-1} for the DMSO–TCNE complex (in DMSO solution), much larger than that reported previously. This large extinction coefficient is substantiated by the isosbestic point at 410 nm and the reported extinction coefficient of 6200 mol^{-1} dm^3 cm^{-1} at 407 nm for TCNE$^-$.[6)] Nevertheless, the conclusion of complete complex formation is tenable, even if the equilibrium constant is presumed to be one-tenth as small as that reported. As a matter of fact the equilibrium constant was reported to be 83.5 dm^3 mol^{-1} for the DMA–TCNE complex,[7)] which seems to be very similar in nature to the DMSO–TCNE complex.

Although the spectroscopic data have not been reported for the DMF–TCNE pair, DMF is a rather strong electron donor.[22)] Therefore, all the TCNE may safely be assumed to form initially the complex with DMF. Assuming a complete complex formation, the molar extinction coefficient is estimated from spectral curve 1 in Fig. 1 for the DMF–TCNE complex to be 2900 mol^{-1} dm^3 cm^{-1} at 310 nm.

Ionic Dissociation of EDA Complex. The present optical absorption studies reveal the growth of an absorption band at 350—500 nm due to TCNE$^-$ simultaneously with the decay of the CT band due to the EDA complexes (see Figs. 1 and 2). The ESR observation (Figs. 4 and 6) also indicates the slow formation of TCNE$^-$. It is concluded that the DMF–TCNE and DMSO–TCNE complexes dissociate into ions in the dark. It should be emphasized that the formation of TCNE$^-$ occurs after the completion of complex formation between TCNE and solvent. The observation of an isosbestic point appeared in the optical absorption studies and the asymptotic value of the TCNE$^-$ concentration indicate that the complexes dissociate quantitatively into ions.

The radical cation of DMSO and also that of DMF should be formed simultaneously with the TCNE$^-$ formation, but no cationic species could be detected either by the optical absorption measurements or by the ESR technique, as reported previously.[6–8,10–14)] Absence of an ESR spectrum due to DMSO$^+$ has been interpreted as due to a rapid spin exchange between DMSO$^+$ and the remaining DMSO.[6)] However, such an interpretation seems highly inconceivable, because it turns out that such a rapid exchanging spin (positive hole) has a lifetime as long as that of TCNE$^-$, which was found to be more than several weeks in the present investigation. DMSO$^+$ might be transformed readily into a stable diamagnetic cation, which no longer reacts with TCNE$^-$ and causes the stability of TCNE$^-$, as suggested by Achiba and Kimura for 2-methyltetrahydrofuran–TCNE system.[20)] Both acceptor radical anion and donor radical cation were observed by ESR for 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and *p*-phenylendiamine and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine in acetonitrile.[21)]

The formation of TCNE$^-$ in DMSO and DMA in the dark was studied previously by ESR, but the observed kinetical features differ from those in the present investigation. Stewart *et al.* reported that the formation is completed promptly before starting the measurements (within a few minutes).[6,7)] Keys and Carper observed that, in addition to the prompt development of the ESR spectrum of TCNE$^-$, its intensity still increases slowly to an asymptotic value, though they gave no interpretation for the difference between these two modes of the formation of TCNE$^-$.[8)] The present investigation indicates no prompt formation of TCNE$^-$. Taking account of the striking effect of light in accelerating the TCNE$^-$ formation (see Fig. 6), the prompt formation reported previously seems to result from this light effect.

On the basis of the observed total participation of TCNE in the EDA complexes and the subsequent exponential growth of the concentration of TCNE$^-$, the formation of TCNE$^-$ is attributed simply to dissociation of the complexes into ions. The apparent activation energy was found to be as large as 0.82 eV (79 kJ/mol) and 0.61 eV (59 kJ/mol) for the dissociation of the DMF–TCNE and the DMSO–TCNE complexes, respectively. As far as we know, this is the first example where the thermal ionic dissociation of EDA complex has been evidenced and its rate constant determined. Recently, Farrell and Ngô studied the spontaneous formation of TCNE$^-$ in *N*,*N*-dimethylaniline–TCNE system and found it apparently slow.[23)]

However, they interpreted this slow formation by assuming the competition between an essentially fast formation of $TCNE^-$ and its fast disappearance. The ionic dissociation of EDA complex in the dark is really a slow process, at least in the DMF–TCNE and DMSO–TCNE systems.

Effect of Dissolved Oxygen. Stewart *et al.* observed the slow decay of the ESR signal of $TCNE^-$ by a second-order process and explained it by a recombination of ions.[6,7] Later, Keys and Carper found that careful exclusion of oxygen affects the ESR signal and that it persists for a period as long as a month in the dark. They also observed that introduction of oxygen kills the signal.[8] However, the present observations indicate that $TCNE^-$ is stable either in the absence or in the presence of oxygen, if it is once generated. The reason is not known for the difference in the observed stability of $TCNE^-$ when oxygen is introduced.

An important finding here is the reversible inhibition of the ionic dissociation of the complexes by the introduction of oxygen. Figure 3 indicates that the DMSO–TCNE complex is transformed by a trace of oxygen into another species giving an absorption band at about 300 nm, which is not identified but presumed to be a ternary complex of DMSO, TCNE, and oxygen. Although this unidentified species develops as slowly as the $TCNE^-$ formation in the absence of oxygen, the latter does not proceed at all in the presence of oxygen. This indicates that dissolved oxygen not only chemically reacts with the DMSO–TCNE complex but also physically quenches the precursor of $TCNE^-$. The formation of $TCNE^-$ on re-evacuation, shown in Fig. 7, also indicates the quenching of the precursor by oxygen in the closed cell.

Assuming that oxygen at low pressure (10^{-3} Torr) is totally dissolved in the solution, the concentration of oxygen is roughly estimated to be 10^{-6} mol dm^{-3}. If one further assumes that the quenching is a diffusion-controlled process with a rate constant of 10^{10} mol$^{-1}\cdot$dm^3 s^{-1}, the lifetime of the precursor is estimated to be as long as 10^{-4} s or more. The efficient quenching by a trace of oxygen supports the view that the thermal ionic dissociation of the complexes occurs through their lowest triplet state. It would be inconceivable that there exists any long-lived transient intermediate other than the triplet state complex, which is thermally accessible, is quenched by oxygen, and acts as a precursor of $TCNE^-$.

Based on the kinetic features of formation and decay of $TCNE^-$, Ilten and Calvin proposed a molecular mechanism for the photoinduced ionic dissociation of the THF–TCNE complex, where $TCNE^-$ results from a long-lived triplet state of the complex populated by intersystem crossing from a photoexcited singlet state.[12] Later, the involvement of the triplet state has been reported for the photoinduced ionic dissociation of other EDA complexes as well.[13,24–26] Stewart *et al.* proposed a similar triplet state mechanism for the formation of $TCNE^-$ in the dark from DMSO–TCNE and DMA–TCNE pairs, on the basis of experimental observations different from those in the present investigation.[6–8] They assumed that the high enthalpy of complex formation leads to an appreciably populated triplet state of the complexes, during complex formation, from which the ionic dissociation occurs. In contrast, the present investigation reveals that the triplet state is populated by a slow thermal process long after the complex formation.

In conclusion, we can formulate the simplified reaction scheme for the thermal ionic dissociation of the DMF–TCNE and DMSO–TCNE complexes as

$$\mathrm{D.\,A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^3(\mathrm{D.\,A})^* \xrightarrow{k_2} \mathrm{D}^+ + \mathrm{A}^-, \qquad (1)$$

on the basis of the present observation, where D and A denote the electron donor (DMF or DMSO) and the acceptor (TCNE), respectively. Naturally k_1 is much smaller than k_{-1}. If $k_{-1} \ll k_2$, the observed first-order rate constant, k, for the formation of acceptor anion is given by k_1 and the thermal activation to $^3(\mathrm{D.\,A})^*$ is the rate-determinant step of the anion formation. The observed activation energy (see Fig. 5) corresponds to the energy separation between $^3(\mathrm{D.\,A})^*$ and D. A. If $k_{-1} \gg k_2$ on the other hand, k is given by k_1k_2/k_{-1}, and the rate-determinant step is the dissociation of $^3(\mathrm{D.\,A})^*$. In this case, the activation energy seems to give the upper limit of the energy separation. The most crucial question which might arise about the triplet state of the EDA complexes is whether it lies so low as to be populated thermally. Unfortunately, there appear to be no results, either experimental or theoretical, in the literature which could answer this question, and there is an obvious need for data (in particular energy and lifetime) on $^3(\mathrm{D.\,A})^*$ to substantiate the above reaction scheme.

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