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Reaction of Leucocrystal Violet with Tetracyanoethylene and Chloranil II.[1] Solvent Effects

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The proton/deuteron transfer reaction of Leucocrystal Violet(LCV) with tetracyanoethylene(TCNE) and chloranil(CA) in various solvents has been followed spectrophotometrically. It was found that the reaction proceeds slower in polar solvents such as acetonitrile and acetone than in less polar solvents such as chloroform and 1,2-dichloroethane. The rate is remarkably accelerated by pressure indicating probably a substantial polarity increase in the rate processes. The formation of CT complexes was observed at low temperatures. Their nature is presumed to be similar to that of a complex formed by the reaction of CA with *N,N*-dimethyl-*p*-toluidine(DMT), and the latter is discussed in connection with the reaction rate of the LCV–TCNE and LCV–CA systems. A possible reaction path is proposed.

In a previous paper,[1] the rate of reaction of Leucocrystal Violet(LCV) with tetracyanoethylene(TCNE) and chloranil(CA), and the kinetic pressure and isotope effects were reported. For both reaction systems, it was found that the reaction follows the second-order rate law: first-order with respect to each reactant. In the LCV–CA system, a very large kinetic isotope effect ($k_H/k_D \approx 11$) was observed suggesting that the so-called proton tunneling is involved, while in the LCV–TCNE system, it was not so large ($k_H/k_D \approx 5$). From large kinetic pressure effects, it was suggested that the reaction proceeds *via* very polar transition states for both reactions. At low temperatures, the formation of CT complexes in equilibrium with the reactants was observed. From the above findings, the following alternative reaction schemes have been proposed:

$$\mathrm{LCV} + \mathrm{CA(TCNE)} \rightleftarrows \mathrm{X_1} \rightleftarrows \mathrm{X_2}$$

$$\mathrm{X_1} \text{ or } \mathrm{X_2} \xrightarrow{\text{slow}} \mathrm{CV^+} + \cdots\cdots\cdots\cdots$$

Scheme 1.

$$\begin{tikzcd} \mathrm{LCV} + \mathrm{CA(TCNE)} \arrow[r, shift left] \arrow[d, "\text{slow}"'] & \mathrm{X_1} \arrow[l, shift left] \arrow[r, shift left] & \mathrm{X_2} \arrow[l, shift left] \\ \mathrm{CV^+} + \cdots\cdots\cdots\cdots & & \end{tikzcd}$$

Scheme 2.

where X_1 and X_2 represent outer and inner CT complexes, respectively.

In this paper, the reaction mechanism has been discussed on the basis of solvent effects, together with other factors influencing the reaction rate. The nature of a CT complex (referred to as X_3 hereafter) formed by the reaction between CA and *N,N*-dimethyl-*p*-toluidine(DMT) has been investigated, since this complex may be regarded as a model compound of X_1.

Experimental

Reagents. LCV(H) and LCV(D) were prepared by the procedures described previously. Commercial TCNE was purified by repeated sublimations. Commercial CA was recrystallized from a benzene-ethanol mixture. Reagent grade DMT was used as supplied. Chloroform and dichloromethane which contain a small amount of alcohol (0.5—1.0%) for stabilization were used as received. Other solvents were purified and distilled by usual manner.

Procedures. The rate of reaction was followed by monitoring the absorbance at *ca.* 590 nm due to Crystal Violet cation(CV^+) by means of a Union 401 spectrophotometer. The reaction temperatures were controlled within ±0.1 °C. The reaction under high pressures was carried out in a pressure vessel equipped with an inner cell made of teflon.[2] The equilibrium constant K for the reaction $\mathrm{DMT}+\mathrm{CA} \rightleftharpoons \mathrm{X_3}$ in various solvents was estimated from the Benesi-Hildebrand plot of the CT band. Since the gradual decomposition of the complex occurred in polar solvents, the absorbance extrapolated to $t=0$ was used for the analysis. In the DMT–TCNE system, the produced CT complex was so unstable that the estimation of the equilibrium constant has been unsuccessful. The absorption spectra of the CT complexes in EPA solutions were obtained at 77K by using a plastic cubette immersed in a specially-designed cryostat for the spectrophotometer. The rate constants were checked by duplicate runs.

Results and Discussion

Reaction of LCV with CA. Figure 1 shows the second-order plots. It may be seen that even if the molar ratio of the initial concentrations of LCV and CA is varied extremely, the plots agree well with the second-order rate law in the initial stage up to at least 10% conversion. In the later stage, however, the plots deviate from the expected line as shown, suggesting the presence of retardation effects by products. Figure 2 shows the relationship between the absorbance at $\lambda_{max}=448$ nm due to CA semiquinone anion[1] and the absorbance at $\lambda_{max}=590$ nm due to CV^+, at various times. This good linear relationship shows that the 1:1 stoichiometry for these products holds during the initial stage of reaction. The CA anion radicals are so stable even in aerated solutions that it survives for longer than 2 d. Rate constants in various solvents are listed in Table 1. If substantial polarity increase is involved on going from the initial to the transition state, it is expected that the rate would be increased in

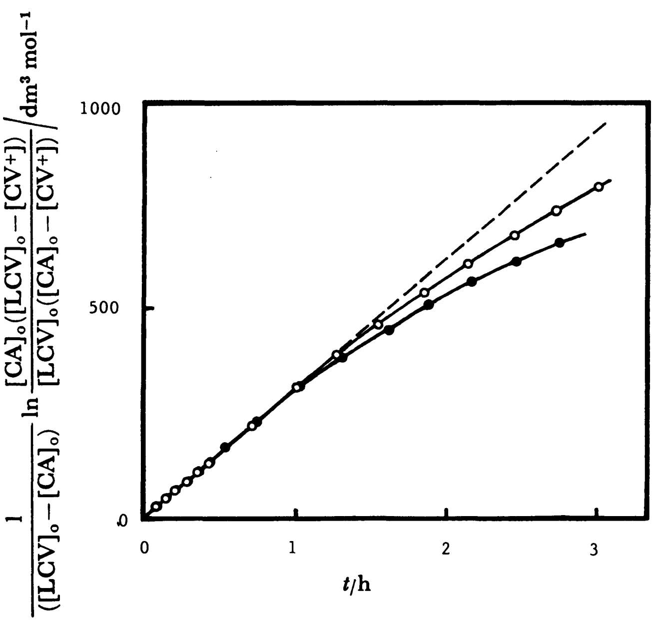


Fig. 1. Second-order plots for the reaction between LCV and CA in acetonitrile at 20 °C. ○: $[LCV]_0 = 2.86 \times 10^{-5}$ mol dm^{-3}, $[CA]_0 = 9.51 \times 10^{-4}$ mol dm^{-3}; ●: $[LCV]_0 = 5.73 \times 10^{-4}$ mol dm^{-3}, $[CA]_0 = 4.80 \times 10^{-5}$ mol dm^{-3}.

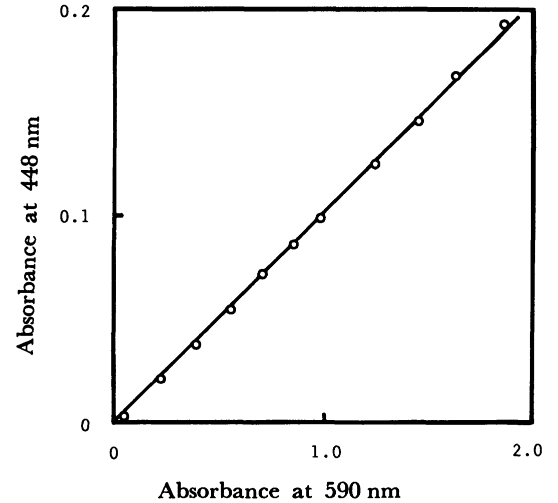


Fig. 2. Relationship between the absorbance at λ_{max} = 448 nm and the absorbance at λ_{max} = 590 nm at various times.

polar solvents. The rate is, however, faster in less polar solvents than in more polar solvents. The second notable point is the solvent dependency of the kinetic isotope effect. According to Isaacs *et al.*[3] and Sugimoto *et al.*,[4] if the atom (H or D) being transferred is strongly coupled with solvent molecules, the probability of tunneling will diminish, because the effective mass of the proton and deuteron should increase. In Scheme 2, a highly polarized transition state was assumed[1] in accordance with the large negative $\Delta V^{\neq}$-values. Substantial solvent effects on the ratio k_H/k_D can be expected in this case. However, the ratios are almost independent of solvent polarity.

Table 1. Rate constants for the reaction between Leucocrystal Violet and chloranil at 25 °C

Solvent	k_H 10^{-2} dm^3 mol^{-1} s^{-1}	k_D 10^{-2} dm^3 mol^{-1} s^{-1}	k_H/k_D
CH_3CN	11.0	1.01	10.9
CH_3COCH_3	5.28	0.502	10.5
CH_2ClCH_2Cl	24.3	2.11	11.5
CH_2Cl_2	25.6	2.31	11.1
$CHCl_3$	31.0	2.67	11.6
CH_3CCl_3	21.5	1.82	11.8

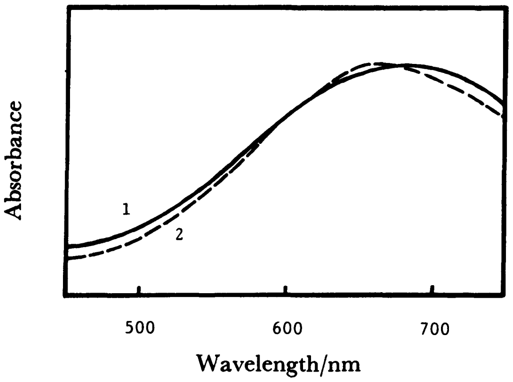


Fig. 3. Absorption spectra of the CT band appeared in the LCV+CA (1) and DMT+CA (2) systems; in EPA, 77K.

These two remarkable points have led us to the question about the single-step hydride ion shift mechanism[3] (Scheme 2). On the other hand, if Scheme 1 is the case, information about X_1 and X_2 is required. As reported previously, the formation of the outer CT complex between LCV and CA was observed at temperatures as low as below −50 °C, as identified by its characteristic spectrum. This made the spectrophotometric measurement of the CT band and hence, the assessment of the equilibrium constant in various solvents difficult. However, the CT band is very similar to that observed in the DMT–CA system (Fig. 3), as can be expected from the structural similarity between LCV and DMT. Hence, X_3 will not be so bad a model for X_1. We expected that informations about X_3 might shed light on the reaction mechanism we are interested in.

Table 2 shows the CT band of X_3 in various solvents. In Fig. 4, $\bar{\nu}_{max}$ is plotted against the E_T-value of the solvents. It appears that the plots can be divided into two groups: Group A containing an electronegative oxygen or nitrogen atom within a molecule, and Group B belonging to the other kind. Since CT complexes are more polar in the excited state than in the ground state, the red shift of the CT band can be expected. For Group A, however, $\bar{\nu}_{max}$ is scarecely sensitive to the solvent polarity parameters such as the E_T-value and Brownstein's *S*-value. Aihara *et al.*[5] investigated Aromatic-TCNE complexes in vari-

TABLE 2. ABSORPTION MAXIMA, λ_{max}/nm OF THE CT BAND FORMED IN THE DMT-CA SYSTEM IN VARIOUS SOLVENTS

	Solvent	λ_{max}/nm		Solvent	λ_{max}/nm
1	Hexane	689	9	CH_2Cl_2	718
2	Cyclohexane	692	10	CH_2ClCH_2Cl	716
3	CCl_4	706	11	Diethyl ether	688
4	Toluene	704	12	THF	686
5	Benzene	709	13	Acetone	687
6	CH_3CCl_3	706	14	DMSO	693
7	Chlorobenzene	716	15	CH_3CN	694
8	$CHCl_3$	720	16	Ethanol	688

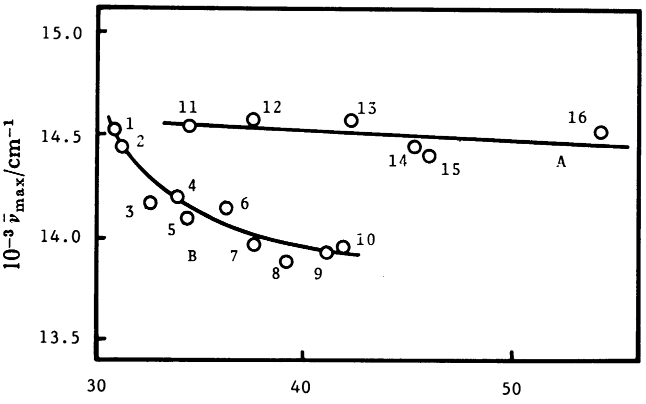


Fig. 4. Plots of $\bar{\nu}_{max}$ of the CT band of X_3 against the E_T-value. Key is shown in Table 2.

ous solvents and interpreted the spectral shift in terms of McRae's formula. They found that a series of solvents except for oxygen-containing solvents behave normally, and suggested that these solvents might change the nature of complexes. Relevant discussion will be made later.

In Fig. 5, ln k_H is plotted, on trial, against $\bar{\nu}_{max}$ in Table 2. It appears that there exists an affirmative correlation in spite of the fact that solvents are classified into two groups. Further, the equilibrium constants for the formation of X_3 in various solvents were estimated by means of the Benesi-Hildebrand plot (Fig. 6), and the results are given in Table 3. In Fig. 7, k_H is plotted against K, giving a fair correlation. In Scheme 1, the reaction proceeds *via* X_1 and therefore, the equilibrium constant must be involved in the numerator of the second-order rate constant expressed in a composite form. If the values of the equilibrium constant for DMT-CA system in the solvents we used are related to those for LCV-CA system, this may be responsible for the above finding. On the other hand, the existence of the equilibria in Scheme 2 must scarcely affect the rate, since the equilibrium constant for the LCV-CA system must be small at the vicinity of room temperature(*vide supra*). Although the situation has not been clarified sufficiently, the above observations and considerations support the involvement of X_1 in the reaction process.

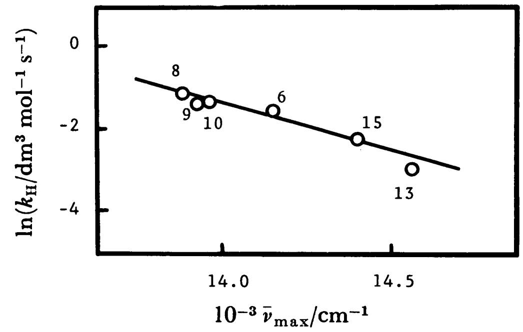


Fig. 5. Relationship between ln k_H and $\bar{\nu}_{max}$ of X_3. Key is shown in Table 2.

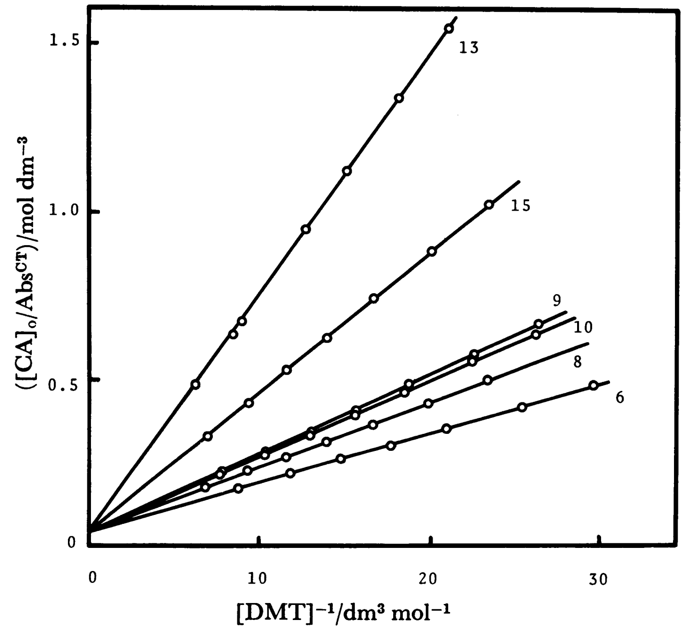


Fig. 6. Benesi-Hildebrand plots in various solvents. Key is shown in Table 2.

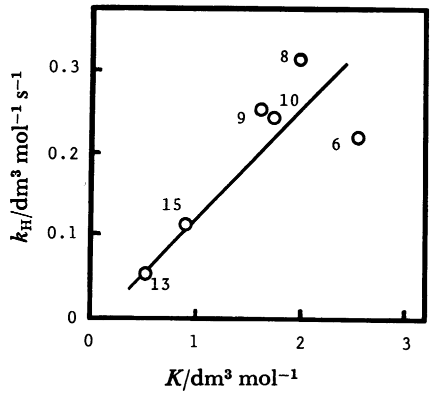


Fig. 7 Relationship between k_H and the equilibrium constant for the formation of X_3.

LCV-TCNE System. In the preceding paper, we reported the pressure dependence of the rate constant for this system. In order to examine the pressure effects in polar solvents, acetonitrile was chosen as representative, and the rate was followed under high pressures. The results are given in Table 4. The rate was also followed in various solvents under atmospheric pressure, and the results are given in Table 5, together with the activation parameters. By inspection of these data, we notice some points. (1) The application of external pressure remarkably accelerates the rate in acetonitrile as well as in chloroform. It is generally accepted that a large polarity increase of reacting species gives rise to a large volume shrinkage of surrounding solvent molecules as exemplified by the pressure effect on the rate. It appears that during the course of reaction from the initial to the transition state, there exists a step in which a large polarity increase is involved. When we remember that the products in our systems are ionic ones, this presumption may be accepted. (2) The kinetic isotope effect(k_H/k_D) in acetonitrile is a little smaller than that in chloroform. This might be ascribed to the solvent-coupled proton transfer as stated above. The isotope effect is far smaller than that in the LCV–CA system. Therefore, the proton tunneling would, if any, be very small. (3) Much more remarkable kinetic solvent effects are observed in this system than in the LCV–CA system, *i.e.*, in polar solvents the rate is reduced greatly and the activation energy increased. This is apparently inconsistent with the fact stated in (1) by the reason explained in the previous section.

TABLE 3. EQUILIBRIUM CONSTANTS FOR THE REACTION $CA+DMT \rightleftharpoons X_3$ AT 25 °C IN VARIOUS SOLVENTS

Solvent	$K\varepsilon$/dm³ mol⁻¹	K*/dm³ mol⁻¹
CH_3CN	2394	0.921
CH_3COCH_3	1398	0.538
CH_2ClCH_2Cl	4401	1.69
CH_2Cl_2	4225	1.63
$CHCl_3$	5174	1.99
CH_3CCl_3	6982	2.69

* Calculated as $\varepsilon=2600$.

TABLE 4. PRESSURE DEPENDENCE OF THE RATE CONSTANT FOR THE REACTION BETWEEN LCV AND TCNE IN ACETONITRILE AT 35 °C

$P/10^5$ Pa	$10^2\,k$/dm³ mol⁻¹ s⁻¹			
	1	300	600	900
H	6.41	8.91	11.4	14.9
D	1.25	1.67	2.21	2.93

In this respect, we considered that the kinetic study in binary mixtures might afford useful informations about the solvent effect. Kondo *et al.*[6] have developed a theory of bimolecular reactions in binary mixed solvents 1 and 4. If one of the reactants is solvated by, say, 4, to form a kind of addition product, the simplified rate equation can be given by

$$\ln k_{\rm mix} = x_1 \ln k_1 + x_4 \ln k_4 + x_4 \ln(K_x+1) - \ln(x_4 K_x + 1)$$

where K_x denotes the association constant expressed in terms of mole fractions for the formation of the addition product; x_1 and x_4 are the mole fractions of 1 and 4, respectively. This equation predicts that the ln $k_{\rm mix}$ *versus* x_1 plot should deviate downward from a straight line expected for ideal binary mixed solvents, the extent of the deviation depending on the value of K_x. On the other hand, according to the theory, if none of the reactants are solvated, but the activated complex is solvated, with one of the solvents, the upward deviation can be expected. In Table 6, the rate constants in chloroform–acetonitrile mixtures are given. By using these data, ln $k_{\rm mix}$ is plotted against the mole fraction of chloroform as shown in Fig. 8. It is seen that the plots constitute a curve shifted downward from the ideal line. Previously,[7] we reported that this type of curve was realized in the reaction of 2,2-diphenyl-1-picrylhydrazyl with phenols in dioxane–2,2,4-trimethylpentane, and cyclohexane–acetone mixed solvents. In that case, a special interaction through hydrogen bonding between phenols and the oxygen-containing solvents was assumed. Marrifield and Philipps reported[8] that the equilibrium constant for the π-complex formation between TCNE and various kinds of aromatic compounds is remarkably affected by variation of the solvent. According to them, this effect is due to the formation of a complex between TCNE and the solvent, as exemplified by a new weak band at 335 nm when TCNE is dissolved in diethyl ether. Although, owing to the experimental difficulties, conclusive evidence for the formation of

TABLE 5. RATE CONSTANTS FOR THE REACTION BETWEEN LCV AND TCNE AT 25 °C AND ACTIVATION PARAMETERS

	Solvent	$10^2\,k_H$ dm³ mol⁻¹ s⁻¹	E_a[b] kJ mol⁻¹	ΔS^{*} [b] JK⁻¹ mol⁻¹	ΔV^{*} cm³ mol⁻¹
H	Acetonitrile	3.78	43.1	−135	−29.9
	Acetone	4.66			
	1,2-Dichloroethane	52.2			
	Chloroform[a]	173	30.0	−148	−28.6
D	Acetonitrile	0.78	46.8	−137	−26.9
	Chloroform[a]	29.5	34.1	−149	−29.2

a) Cited from Ref. 1. b) Estimated from the k_H-values at 25—45 °C.

TABLE 6. RATE CONSTANTS FOR THE REACTION BETWEEN LCV AND TCNE IN ACETONITRILE-CHLOROFORM MIXTURES AT 30 °C

Mole fraction of $CHCl_3$	$\frac{10^2 k_{mix}}{dm^3\,mol^{-1}\,s^{-1}}$
0	5.20
0.304	7.70
0.495	11.9
0.724	32.2
0.880	84.4
1.00	213

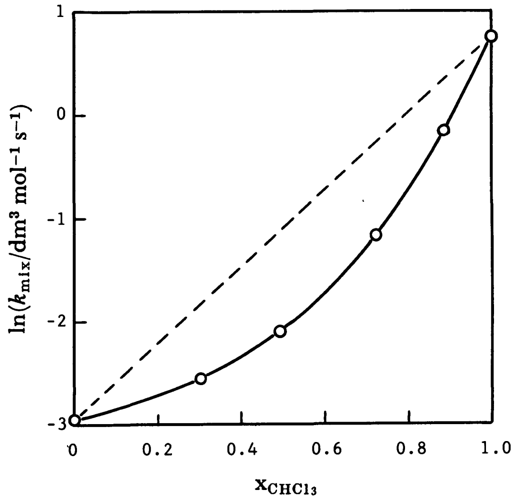
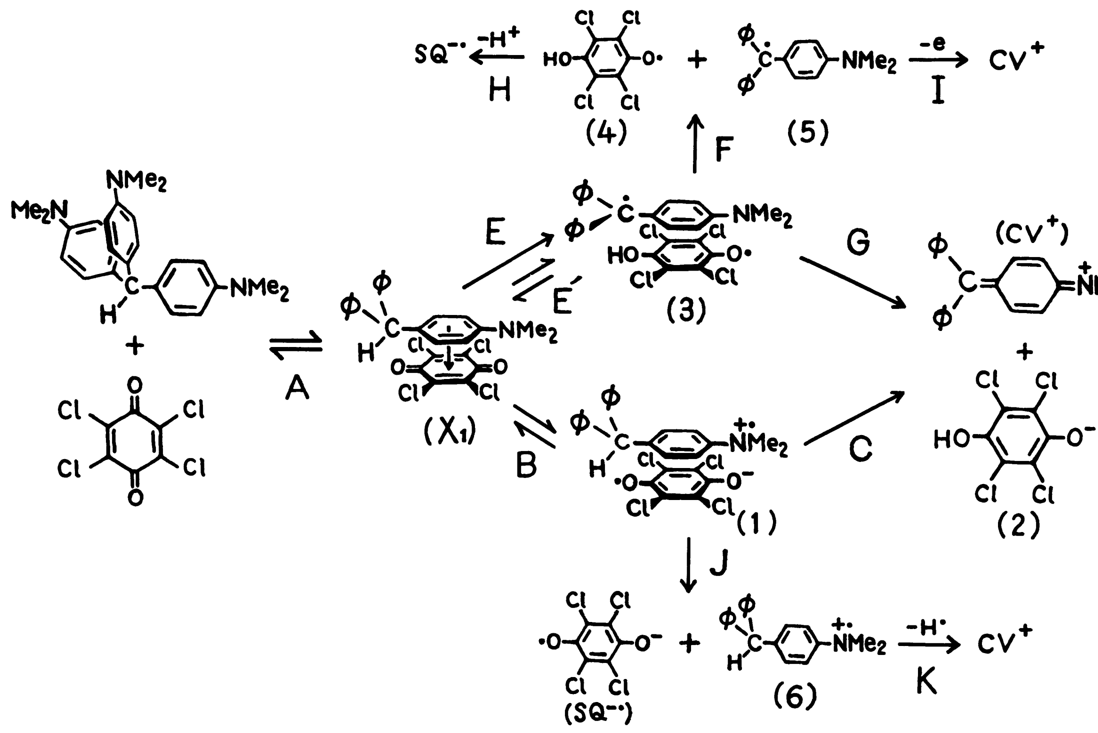


Fig. 8. Relationship between $\ln k_{mix}$ and the mole fraction of $CHCl_3$ in $CHCl_3$-CH_3CN binary mixtures.

such TCNE/solvent complexes has not been obtained yet in the solvent we used, a special interaction between TCNE(CA) and the solvents belonging to Group A may be assumed to exist. The interaction with the TCNE as a reactant must be the greatest, intermediate with the TCNE in the ground CT complex, and the smallest with the TCNE in the excited CT complex, since the interaction between TCNE and LCV must increase in this order. If this is the case, the reactivity of "solvated" TCNE will diminish and this may be responsible for the decreased rate of reaction, the enhanced activation energy, the blue shift of the CT band of X_3 in acetonitrile and acetone, and the kinetic behavior in the binary mixtures.

Reaction Mechanism From the point of view of the kinetic solvent effects, and the correlation of the rate of reaction with the nature of X_3 chosen as a model of X_1, it may be concluded that the reaction proceeds probably *via* X_1. Although the processes thereafter have not necessarily been fully elucidated, we could presume probable reaction routes on the basis of the informations obtained so far: The second-order kinetics and simultaneous formation of CV^+ and semiquinone anion radicals and available informations on reactions which proceed through inner and outer CT complexes.[9–13] The following chart for the LCV–CA system may be proposed:



In accordance with this chart, the possible reaction routes are summarized as follows:

$$1)\quad \mathrm{LCV} + \mathrm{CA} \underset{\mathrm{A}}{\overset{\text{fast}}{\rightleftarrows}} \mathrm{X}_1 \underset{\mathrm{B}}{\overset{\text{fast}}{\rightleftarrows}} \mathbf{1} \xrightarrow[\mathrm{C}]{\text{slow}} \mathrm{CV}^+ + \mathbf{2} \xrightarrow[\mathrm{D}]{\text{fast}} \mathrm{SQ}^{-\cdot}$$

$$\begin{aligned} 2)\quad \mathrm{LCV} + \mathrm{CA} \underset{\mathrm{A}}{\overset{\text{fast}}{\rightleftarrows}} \mathrm{X}_1 \xrightarrow[\mathrm{E}]{\text{slow}} \mathbf{3} &\xrightarrow[\mathrm{F}]{\text{fast}} \mathbf{4} + \mathbf{5} \xrightarrow[\mathrm{H,\,I}]{\text{fast}} \mathrm{CV}^+ + \mathrm{SQ}^{-\cdot} \\ &\xrightarrow[\mathrm{G}]{\text{fast}} \mathrm{CV}^+ + \mathbf{2} \xrightarrow[\mathrm{D}]{\text{fast}} \mathrm{SQ}^{-\cdot} \end{aligned}$$

$$3)\quad \mathrm{LCV} + \mathrm{CA} \underset{\mathrm{A}}{\overset{\text{fast}}{\rightleftarrows}} \mathrm{X}_1 \underset{\mathrm{B}}{\overset{\text{fast}}{\rightleftarrows}} \mathbf{1} \xrightarrow[\mathrm{J}]{\text{slow}} \mathrm{SQ}^{-\cdot} + \mathbf{6} \xrightarrow[\mathrm{K}]{\text{fast}} \mathrm{CV}^+$$

$$\begin{aligned} 4)\quad \mathrm{LCV} + \mathrm{CA} \underset{\mathrm{A}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{X}_1 \underset{\mathrm{E'}}{\overset{\text{fast}}{\rightleftharpoons}} \mathbf{3} &\xrightarrow[\mathrm{F}]{\text{slow}} \mathbf{4} + \mathbf{5} \xrightarrow[\mathrm{I,\,H}]{\text{fast}} \mathrm{CV}^+ + \mathrm{SQ}^{-\cdot} \\ &\xrightarrow[\mathrm{G}]{\text{slow}} \mathrm{CV}^+ + \mathbf{2} \xrightarrow[\mathrm{D}]{\text{fast}} \mathrm{SQ}^{-\cdot} \end{aligned}$$

Of these reaction paths, the kinetic isotope effect precludes the possibility of 3) and 4), since proton transfer is not involved in the rate-determining steps. The volume change in Step A may be 0—−14 cm^3/mol observed for most cases for the formation of CT complexes.[14] The volume change in step E in which hydrogen atom transfer is involved, will be no more than few cm^3. Hence, the large negative value of $\Delta V^{\neq}$ obtained for our systems could eliminate the possibility of 2). We have noticed that X_3 decomposes gradually to produce $SQ^{-\cdot}$ in polar solvents, suggesting the existence of **1** instead of **3**. In the remaining possibility 1), Step C is assumed to be the rate-determining one. Proton transfer is involved in this step and this is in accord with the observed large isotope effect. A remarkable volume change can be expected in Step B where electron transfer is involved, and this is responsible for the large kinetic pressure effect. We have observed the correlation between ln k_H and $\bar{\nu}_{max}$. It could be assumed that $\bar{\nu}_{max}$ is proportional to the energy difference between **1** and X_1. As for the kinetic isotope effect, we consider as follows. Owing to the bulkiness of CA skeleton, the hydrogen atom being transferred is blocked from the surrounding solvent molecules. The effective mass of the hydrogen (and deuteron) is then not affected substantially by solvent polarity, thus accounting for the constant k_H/k_D-value in various solvents. This is in accord with the appreciable tunneling effect, too. In the LCV–TCNE system, the ratio is considerably smaller, and the tunneling effect, if any, so small. We tentatively consider that the difference would arise from the difference in the ability of protecting the hydrogen atom from the surrounding solvent molecules during its transfer. We conclude that the reactions of LCV–CA and LCV–TCNE systems probably proceed *via* Route 1).

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