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# Kinetic Isotope and Pressure Effects in the Reaction of Leucocrystal Violet with Tetracyanoethylene and Chloranil

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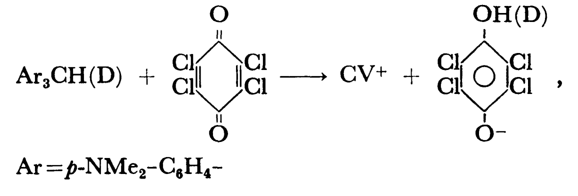
The rates of reaction of Leucocrystal Violet (LCV) with chloranil (CA) and tetracyanoethylene (TCNE) were measured, and the kinetic isotope and pressure effects were examined. In the LCV-CA system, a very large isotope effect ($k_H/k_D \approx 11$) was observed, while in the LCV-TCNE system, it was not so large ($k_H/k_D$= 5—6) suggesting the tunnel effect is not substantial. For both systems, the formation of a CT complex in equilibrium with the reactants was observed at low temperatures ($<-50$ °C). From the rate law, the isotope effect, the electronic and ESR spectra observed during the reaction, and their time dependence, possible reaction processes are proposed.

When hydrogen($H\cdot$, $H^+$, or $H^-$) undergoes transfer in a rate-determining step, it is sometimes observed that the kinetic isotope effects are larger than those expected from differences in the zero-point energy of the isotopic bonds undergoing fission ($k_H/k_D > 7$). This has been regarded as evidence for the occurrence of quantum-mechanical tunneling, a highly mass-dependent property. Besides abnormally large kinetic isotope effects, isotopic dependence of the Arrhenius pre-exponential factor and curved Arrhenius plots are believed to be criteria of tunneling.

In 1977, Isaacs *et al.*[1] found abnormally large isotope effect ($k_H/k_D$=11.2) in the reaction between Leucocrystal Violet (LCV) and chloranil (CA), but it levels off at a value near the maximum normal ratio of about 7.5 when the external pressure is raised to 2 kbar. According to them, the external pressure serves to lower the free energy barrier, thus the relative importance of tunneling diminishes with increasing pressure. They considered that the rate-determining step of the reaction involves a direct hydride ion transfer to produce a Crystal Violet cation and a tetrachlorohydroquinone anion(one-step process):



Ar = $p$-$NMe_2$-$C_6H_4$-

Indeed, reactions of $N$-benzyl-1,4-dihydronicotinamide and related compounds, recognized as models of dihydronicotinamide coenzymes for biological redox reactions, were believed to involve direct hydride transfer.[2,3] However, Steffens and Chipman[4] presumed, based on the kinetic isotope effects, that these reactions involve a two-step process and the intermediate may be a CT complex. Ohno and Kito,[5] and Fukuzumi and Tanaka[6] demonstrated that a CT complex is really formed as an intermediate product in these reactions.

This study has been undertaken to reexamine the direct hydride transfer mechanism in the LCV-CA system in the hope that similar pressure dependence of the kinetic isotope effect might be observed also in the reaction between LCV and tetracyanoethylene (TCNE).

## Experimental

*Reagents.* LCV(H) was prepared as follows: dried Crystal Violet chloride was mortared in dry tetrahydrofuran and then lithium aluminium hydride powder was added slowly until the purple color of the solution diminished. The preparation was carried out under nitrogen in a dry-box. The product was poured into deoxygenated water and the precipitated Leucocrystal Violet was collected and dried. The LCV was recrystallized from benzene-ethanol mixture to give colorless needles. The same method was used with lithium aluminium deuteride to obtain LCV(D). Deuteration was ascertained by NMR. Commercial TCNE was purified by repeated sublimations. Chloroform of the reagent grade which contains *ca.* 1% ethanol for stabilization, was used as received, since no appreciable kinetic effect was observed compared with freshly distilled chloroform. Other solvents were purified as usual.

*Procedures.* A high-pressure reaction vessel, which is made of 17-4PH stainless steel and equipped with a water-circulating jacket and a stop-valve, was used. The vessel consists of two compartments, one for sample solutions and the other for reference solvents, with optical windows.

After a solution containing LCV and TCNE, and the solvent had been charged, same pressure was applied on them by a hand-pump through liquid separation pistons. After reading the pressure by a Heise Bourdon gauge, the stop-valve was closed and the vessel was separated from the pump system, and placed in a cell compartment of a Hitachi 105 double-beam spectrophotometer. The reaction was followed by monitoring the Crystal Violet cation ($CV^+$, $\lambda_{max}$=586 nm), and the absorbance was recorded. Most of the runs were carried out under the conditions that the pseudo first-order plots could be realized. All runs were carried out in air. The kinetic data were checked by duplicate or triplicate runs.

In order to estimate the partial molar volumes of LCV and Crystal Violet chloride, and the molar volume of bulk Crystal Violet chloride, Ostwald-Sprengel and Weld types of pycnometers were used. By measuring the density of their chloroform solutions at various concentrations, the partial molar volumes at infinite dilution were estimated. Liquid paraffin was used for the determination of the molar volume of bulk Crystal Violet chloride.

*Product Analysis.* An equimolar mixture of LCV and TCNE in dichloromethane was allowed to stand at room temperature overnight, and the solution was chromatographed on silica gel(Wakogel C-200). Two kinds of Crystal Violet salts ($F_1$ and $F_2$) were obtained. $F_1$: mp 225—227 °C, golden metallic flakes, $\lambda_{max}$/nm ($\varepsilon$) in $CHCl_3$, 305(30000), 398(22000), 416(21800), 586(140000); IR(Nujol) 2196 $cm^{-1}$ (C≡N str). $F_2$: mp 164—166 °C, dark blue powder, $\lambda_{max}$/nm in $CHCl_3$: 305, 586; IR (Nujol) 2200 $cm^{-1}$ (C≡N str).

## Results

The reaction between LCV and CA in acetonitrile was carried out in a thermostated cell and the spectral change with time in the visible region is shown in Fig. 1. By means of the initial-rate method, the reaction order was confirmed to be first-order with respect to each reactant (Fig. 2). The reaction proceeds, in the initial stage, in accordance with the second-order rate law strictly. Figure 3 shows the Arrhenius plots based on the data of Isaacs *et al.*[1] and ours. The spectral change with time for the reaction between LCV and TCNE in chloroform is shown in Fig. 4. The absorption maxima at 305 and 586 nm are attributed to $CV^+$. These absorption bands increase with time at the expense of the bands due to TCNE ($\lambda_{max}$=266 and 276 nm), the isosbestic point being at 277 nm. Most of the reactions were carried out in excess of TCNE. Under such condition, the plot of $\ln(A_\infty - A_t)$ *versus* time $t$, where $A_\infty$ and $A_t$ are the absorbance at $\lambda$=586 nm at $t=\infty$ and $t$, gave a straight line. The slope of the line was then plotted against the initial concentration of TCNE as shown in Fig. 5, giving a straight line passing the origin. We can therefore conclude that the overall order of reaction is second order. Similar pseudo-first-order plots were made for the reaction under various pressures (Fig. 6). As seen in Fig. 6, the external pressure accelerates the rate remarkably. In Table 1, the second-order rate constants for the reaction between LCV (H and D) and TCNE at various temperatures and under various pressures are listed. On the basis of the data in the table, the Arrhenius parameters were evaluated and they are given in Table 2. In Fig. 7, the rate constants in the logarithmic scale are plotted against

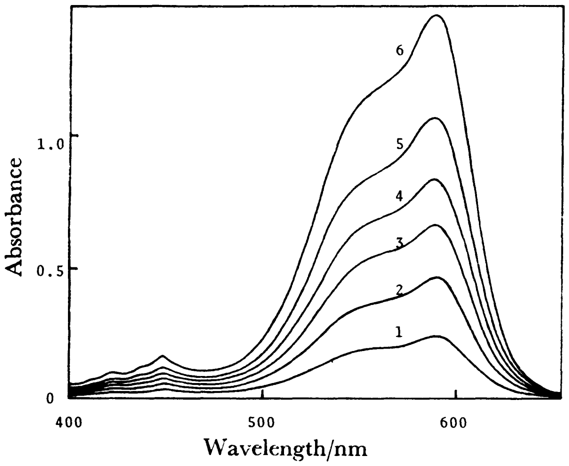


Fig. 1. Spectral change as a function of time for reaction between LCV and CA in acetonitrile at 20 °C. $[LCV(H)]_0 = 5.73\times10^{-4}$ mol $dm^{-3}$; $[CA]_0 = 4.80\times10^{-5}$ mol $dm^{-3}$. Time (min): 1, 5; 2, 10; 3, 15; 4, 20; 5, 30; 6, 60.

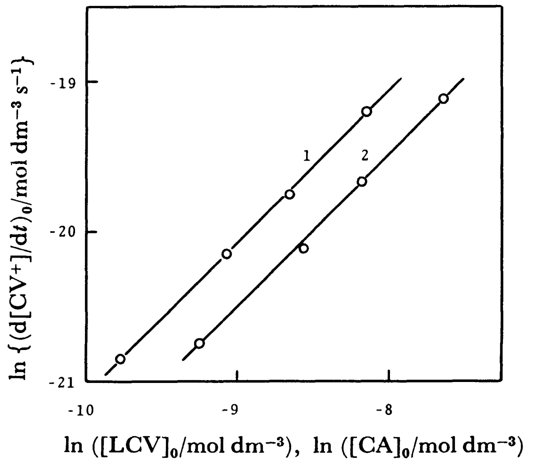


Fig. 2. Determination of the order of reaction by means of the initial-rate method. 1, $[CA]_0 = 1.82\times10^{-4}$ mol $dm^{-3}$; 2, $[LCV]_0 = 1.17\times10^{-4}$ mol $dm^{-3}$; 20 °C in acetonitrile.

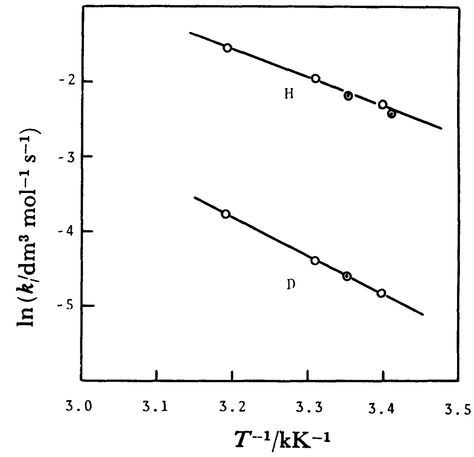


Fig. 3. The Arrhenius plots for the reaction of LCV (H or D) with CA. ⊙: Present results; ○: Isaacs *et al.*

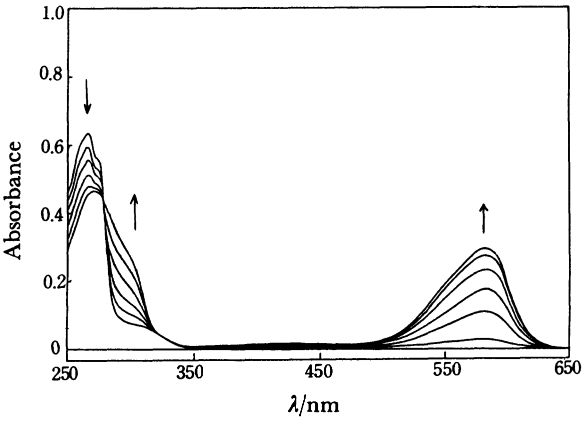


Fig. 4. Spectral change (every 30 min) during the reaction between LCV(H) and TCNE in chloroform at 30 °C. $[LCV]_0 = 6.76\times10^{-6}$ mol $dm^{-3}$; $[TCNE]_0 = 3.65\times10^{-5}$ mol $dm^{-3}$.

the external pressures. The solid lines represent the following quadratic regression equation:

$$\ln k_p = a + bp + cp^2. \tag{1}$$

The activation volumes at the atmospheric pressure were estimated according to the following equation:

$$\left(\frac{\partial \ln k_p}{\partial p}\right)_T = -\frac{\Delta V^{*}}{RT} + \Delta n\kappa_0 \approx b\,, \tag{2}$$

where $\Delta n$ is the difference in the number of species between the activated complex and reactants, and $\kappa_0$ is the isothermal compressibility of the system ($\kappa_0 = 1.54 \times 10^{-9}$ Pa$^{-1}$ for chloroform). In Table 3, the volumes of activation are given. Auxiliary kinetic data in benzene, benzene-toluene and benzene-*p*-xylene binary mixtures are given in Table 4.

## Discussion

*Reacion of LCV with CA.* The maximum absorption at 586 nm (Fig. 1) is assigned to Crystal Violet cations, since the band and its shape agree with

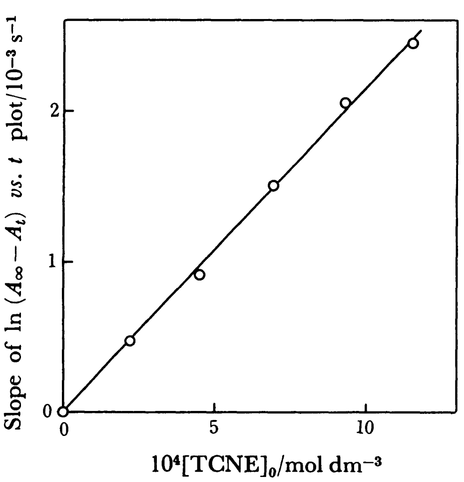


Fig. 5. Determination of the order of reaction with respect to [TCNE] by means of the isolation method. $[\mathrm{LCV}]_0 = 6.90 \times 10^{-6}$ mol dm$^{-3}$; 30 °C.

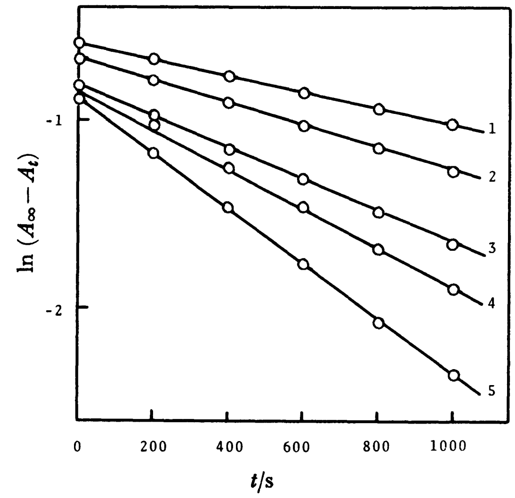


Fig. 6. Pressure dependence of the pseudo-first-order plot for the reaction between LCV(H) and TCNE in chloroform at 25 °C. $[\mathrm{LCV}]_0 = 6.76 \times 10^{-6}$ mol dm$^{-3}$, $[\mathrm{TCNE}]_0 = 2.43 \times 10^{-4}$ mol dm$^{-3}$; pressure ($10^5$ Pa): 1, 1; 2, 300; 3, 600; 4, 900; 5, 1200.

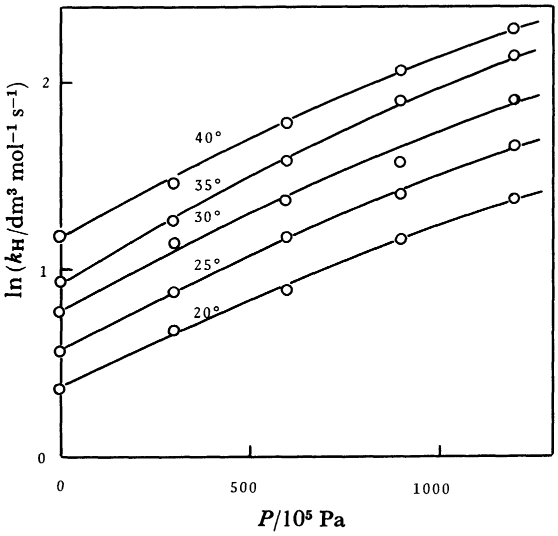
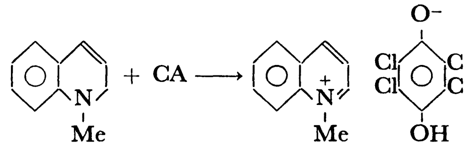


Fig. 7. Pressure dependence of $k_H$.

Table 1. Rate constants for the reaction between Leucocrystal Violet and tetracyanoethylene in chloroform

| | $\frac{P}{10^5\ \mathrm{Pa}}$ | $\frac{k}{\mathrm{dm^3\ mol^{-1}\ s^{-1}}}$ 20 °C | 25 °C | 30 °C | 35 °C | 40 °C |
|---|---|---|---|---|---|---|
| H | 1 | 1.44±0.20 | 1.73±0.08 | 2.13±0.10 | 2.50±0.11 | 3.20±0.18 |
| | 300 | 1.95 | 2.36 | 3.09 | 3.43 | 4.19 |
| | 600 | 2.39 | 3.18 | 3.88 | 4.75 | 5.89 |
| | 900 | 3.13 | 4.01 | 4.74 | 6.67 | 7.79 |
| | 1200 | 3.95 | 5.27 | 6.64 | 8.44 | 9.78 |
| D | 1 | 0.237±0.019 | 0.295±0.012 | 0.383±0.025 | 0.460±0.031 | 0.580±0.022 |
| | 300 | 0.328 | 0.396 | 0.535 | 0.680 | 0.792 |
| | 600 | 0.437 | 0.571 | 0.672 | 0.912 | 1.16 |
| | 900 | 0.564 | 0.745 | 0.846 | 1.16 | 1.32 |
| | 1200 | 0.694 | 0.863 | 1.08 | 1.46 | 1.80 |

those of an authentic sample. As for the assignment of the band system in the region 400—500 nm with maxima at 448 and 20 nm in acetonitile, there has been a confusion. Braude *et al.*[7] reported that the reaction of 1,2-dihydro-1-methylquinoline with CA can occur only by removal of a hydride ion from the position next to the nitrogen atom, followed by quaternization,



**1** **2**

and the salt (**1**+**2**) in an acidic solution has one of its absorption maxima at 452 nm. Hajdu and Sigman[8] followed the rate of reaction between CA and a series of dihydronicotinamides by monitoring the absorption maximum at 448 nm in acetonitrile. They considered that tetrachlorohydroquinone anion **2** is responsible for the band. Very recently, Fukuzumi and Tanaka[6] also reported that in the same system a 1 : 1 CT complex is formed at first as an intermediate product, followed by a hydride transfer to afford **2** which is characterized by the absorption spectrum ($\lambda_{max}$=448 nm in acetonitrile).

Table 2. Activation parameters for the reaction between LCV and TCNE in chloroform

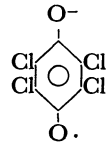
| | $P$ / $10^5$ Pa | $E_a$ / kJ mol$^{-1}$ | $\Delta S^{\neq}$ / J K$^{-1}$ mol$^{-1}$ | $r$[a)] |
|---|---|---|---|---|
| H | 1 | 30.0±0.8 | −148±3 | 0.997 |
| | 300 | 29.1±1.3 | −148±4 | 0.994 |
| | 600 | 33.6±0.8 | −131±3 | 0.998 |
| | 900 | 35.6±1.5 | −123±5 | 0.994 |
| | 1200 | 34.5±1.2 | −123±4 | 0.996 |
| D | 1 | 34.1±0.6 | −149±4 | 0.999 |
| | 300 | 35.2±1.3 | −143±5 | 0.996 |
| | 600 | 36.9±1.3 | −134±5 | 0.996 |
| | 900 | 32.8±1.6 | −146±4 | 0.992 |
| | 1200 | 37.1±1.1 | −130±4 | 0.997 |

a) Correlation coefficient for the plot of ln $k$ *versus* $1/T$.

Table 3. Volumes of activation($\Delta V^{\neq}$/cm$^3$ mol$^{-1}$) for the reaction between LCV and TCNE in chloroform

| Temp / °C | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|
| H | −25.4 | −29.6 | −28.6 | −33.7 | −32.0 |
| D | −31.4 | −35.7 | −29.2 | −37.0 | −34.1 |

On the other hand, Kainar and Überle[9] demonstrated that a mixture of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) and CA acetonitrile solutions exhibits spectrum similar to that of CA-Na system in the range 400—500 nm. They considered that the complete transfer of an electron from TMPD to CA takes place to produce radical ions as ascertained by magnetic susceptibility measurements. Foster and Thomson[10] reported the visible absorption spectra for systems of TMPD-halobenzoquinones and considered that the band in question is due to CA semiquinone anion (**3**)



**3**

Iida[11] and Tsubomura *et al.*[12] also reported that the band can be assigned to **3**. The g-value of **3** is reported as 2.0058[13] and 2.0056±0.0002.[14]

When a mixture of LCV and CA acetonitrile solutions was subjected to ESR spectroscopy at room temperature, signals shown in Fig. 8 were recorded. The signal centered at 3337 G† has the *g*-value of 2.0058 in agreement with the reported one. From the above discussion and findings, the band system in the range 400—500 nm can unequivocally be assigned to **3**. The time dependence of the radical concentration is shown in Fig. 9. The radical concentration increases in parallel with the concentration of CV$^+$ at first, reaches a maximum and then decreases gradually. Therefore we regard **3** as the main product of the reaction.

Table 4. Rate constants for the reaction between Leucocryatal Violet and tetracyanoethylene in benzene and in binary mixtures

| Solvent | Temp / °C | $k_H$ / $10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_D$ / $10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_H/k_D$ |
|---|---|---|---|---|
| Benzene | 25 | 5.63±0.05 | 1.01±0.05 | 5.57 |
| Benzene | 30 | 7.46±0.14 | 1.40±0.03 | 5.43 |
| Benzene | 35 | 9.77±0.03 | 1.86±0.04 | 5.25 |
| Benzene | 40 | 12.60±0.05 | 2.56±0.02 | 4.92 |
| Benzene-Toluene (6:4 v/v) | 30 | 4.98±0.01 | 0.95±0.03 | 5.25 |
| Benzene-Toluene (2:8 v/v) | 30 | 3.35±0.05 | — | — |
| Benzene-*p*-Xylene (6:4 v/v) | 30 | 1.11±0.02 | 0.24±0.01 | 4.70 |

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† 1 G=$10^{-4}$ T.

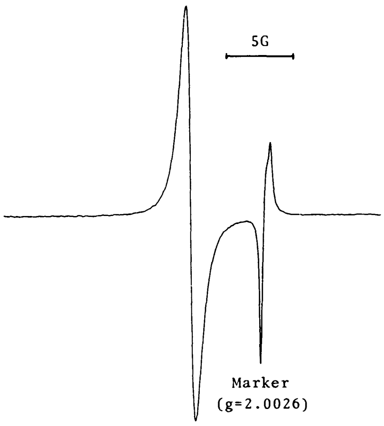


Fig. 8. ESR spectrum of CA anion radical in acetonitrile.

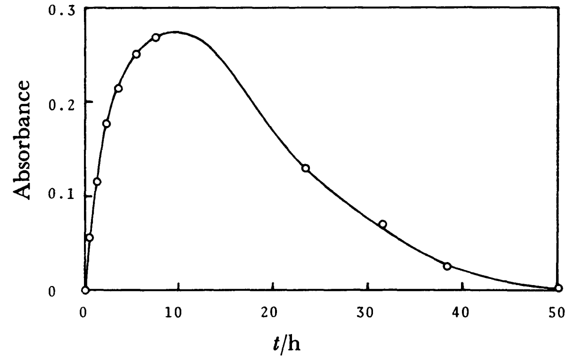


Fig. 9. Time dependence of CA anion radical concentration. $[\mathrm{LCV}]_0=5.73\times10^{-4}$ mol dm$^{-3}$, $[\mathrm{CA}]_0=4.80\times10^{-5}$ mol dm$^{-3}$, 20 °C in acetonitrile.

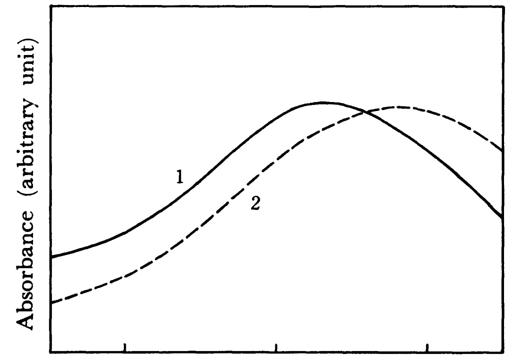


Fig. 10. Absorption spectra appeared when the mixture of LCV and TCNE (1) and LCV and CA (2) in EPA are cooled to $\approx$77 K.

There is a number of reports on the formation of CT complexes between CA and TCNE as electron acceptors, and bases. Since LCV may be regarded as a base, we expected the formation of CT complexes in our reaction systems. At room temperatures, there was no indication of the formation. However, when the reaction mixtures were cooled to below −50 °C, the solution turned deep blue. The color faded when warmed, and appeared again when cooled. The absorption spectra at $\approx$77 K are shown in Fig. 10. Judging from the position and the shape these absorption bands could be assigned to outer CT complexes in equilibrium with their components.

Nagakura *et al.*[15] found that an outer complex which is characterized by the absorption band at $\lambda_{\max}=560$ nm ($\varepsilon=1250$) exists as a stable species in equilibrium with component CA and aniline below 200 K. On the basis of the time delay between the decay of the outer complex and the formation of a product, they further postulated the existence of an inner complex which is a precursor of the product.

Taking these situations into account, together with the substantial isotope effect and the kinetic law, the following alternative reaction schemes may be proposed.

$$\mathrm{LCV} + \mathrm{CA} \rightleftharpoons \mathrm{X}_1 \rightleftharpoons \mathrm{X}_2$$

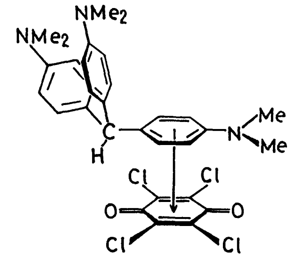
$$\mathrm{X}_1 \text{ or } \mathrm{X}_2 \xrightarrow{\text{slow}} \mathrm{CV}^+ + \mathbf{2}$$

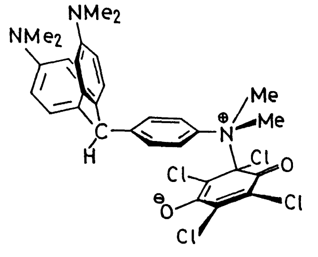
Scheme 1.

$$\begin{tikzcd}
\mathrm{LCV} + \mathrm{CA} \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{X}_1 \arrow[r, phantom, "\rightleftharpoons"] \arrow[dr, "\text{slow}"'] & \mathrm{X}_2 \\
& & \mathrm{CV}^+ + \mathbf{2}
\end{tikzcd}$$

Scheme 2.

where X1 and X2 represent outer and inner complexes, respectively and their structures may be as follows:

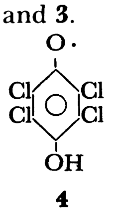

$\mathrm{X}_1$


$\mathrm{X}_2$

We have not ascertained the existence of X2 yet.

If X1 or X2 is a precursor of CV$^+$, the transfer of an electron from the LCV-moiety to the CA-moiety, followed by the hydrogen atom transfer, is more likely than the direct hydride transfer. In Scheme 2, a highly polarized partial bond formation of the type $\equiv\mathrm{C}^{\delta+}\cdots\mathrm{H}\cdots{}^{\delta-}\mathrm{O}=$ in the transition state may be involved. The remarkable kinetic pressure effect[1] could better be accounted for by this scheme rather than Scheme 1. In any way, the preference and detailed discussion for the reaction mechanism are open to future investigations. Steady-state assumption for **2** could explain the simultaneous formation of CV$^+$ and **3**.

$\mathbf{2} + \mathrm{CA} \xrightarrow{\text{fast}} \mathbf{3} +$



**4**

$\mathbf{4} \longrightarrow$ dimerization, disproportionation

*Reaction of LCV with TCNE.* As seen in Fig. 4, a very weak band appears in the region $\lambda=350$—500 nm.

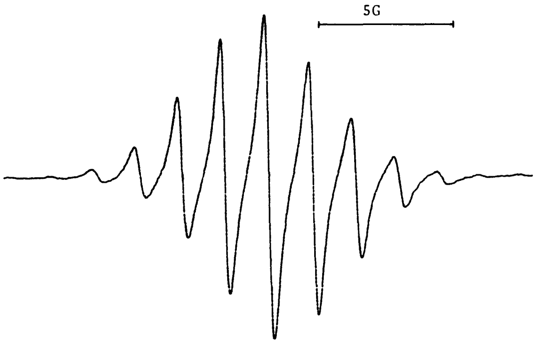


Fig. 11. ESR spectrum of TCNE anion radical.

The band spectrum becomes well-characterized in acetonitrile, and is assigned to TCNE anion radical, since the spectrum coincides with the reported one.[16] This is supported by the appearance of ESR signals when a mixture of LCV and TCNE solutions was subjected to ESR spectroscopy at room temperature (Fig. 11). The spectrum consists of nine lines (and two $^{13}C$ satellites) with a spacing of 1.6 G, and is assigned to TCNE anion radical, since the spectrum and the splitting constant agree with those reported.[17,18]

As seen in Table 3, the pressure effect on the rate of reaction is remarkable, suggesting also a large polarity change on going from the initial to the transition state in this system.

However, the ratios $k_H/k_D$ in the LCV-TCNE system under various pressures are considerably smaller than those in the LCV-CA system,[1] and no systematic change in the ratio with increasing pressure was observed. The Arrhenius plots are not curved and the isotopic dependences of $\Delta S^{\neq}$ and $\Delta V^{\neq}$ (Tables 2 and 3) are not substantial. Therefore, we can conclude that the isotopic tunnel effect is, if any, immaterial in this system. As far as we inspected our data and those of Isaacs *et al.*, the reason why the tunnel effect is observed in the LCV-CA system alone has not been clarified.

When the reaction was carried out in benzene, the rate decreased a great deal (Table 4), while the isotope effect is similar to that in $CHCl_3$. The formation of CT complexes involving TCNE and various aromatic compounds are well known. Therefore, the very small rate constants in benzene compared with those in $CHCl_3$ may be attributed to the complex formation rather than the kinetic solvent effects. This is supported by the fact that the rate further decreased in the binary benzene-toluene and benzene-xylene systems in which more stable complexes are formed.[19]

The final electronic spectrum in the visible region for both the LCV-CA and LCV-TCNE systems agreed with the spectrum of authentic Crystal Violet in the case of kinetic runs. Under much more concentrated conditions, two kinds of salts ($F_1$ and $F_2$) were obtained (see Experimental section). The spectrum of $F_1$ involves extra maxima at 398 and 416 nm. Middleton *et al.*[20] reported that 1,1,2,3,3-pentacyano-2-propenide anion (PCP) in aqueous solutions is characterized by the absorption maxima at 393 nm ($\varepsilon$=22600) and 412 nm ($\varepsilon$=22100). Since our data for $F_1$ coincide with these values, the counter anion of the Crystal Violet cation may be PCP. The structure of $F_2$ has not been clarified yet.

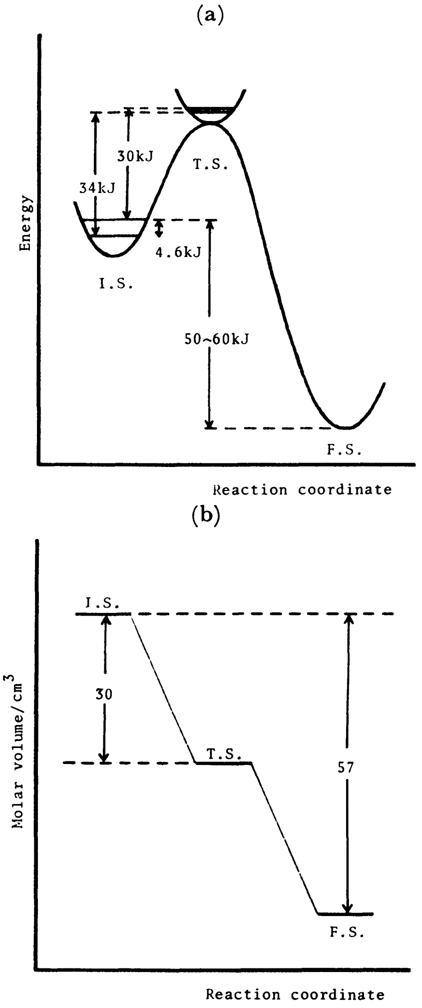


Fig. 12. (a) Energy profile. (b) Volume profile.

*Potential and Volume Profiles.* We finally wish to draw approximate potential and volume profiles. The zero point energy difference between C-H and C-D stretching vibrations of LCV was estimated to be *ca.* 4.6 kJ on the basis of the data for $CHCl_3$ ($\nu_{C\text{-}H}$=3019 cm$^{-1}$, $\nu_{C\text{-}D}$=2256 cm$^{-1}$). This might be responsible for the difference in the activation energy between the isotopic species (Table 2). Blanch *et al.*[22] studied the proton transfer reaction of 4-nitrophenylnitromethane with pentamethylguanidine to give an ion pair. According to them, the heat of reaction is −59.8 kJ mol$^{-1}$ in acetonitrile and −54.0 kJ mol$^{-1}$ in toluene. From the difference in the activation energy for the forward and backward reactions of *N*-ethyl-*N*-methylaniline with methyl iodide in nitrobenzene, Stewart and Weale[22] estimated the heat of forward reaction as −64.0 kJ mol$^{-1}$. If the overall heat of reaction in LCV-TCNE system is similar to those observed in perfect charge transfer reactions, it would be −50—−60 kJ mol$^{-1}$. In Fig. 12 (a), the potential profile for the reaction of LCV with TCNE is shown.

On the other hand, the partial molar volumes of LCV and $CV^+$ $Cl^-$ in chloroform were estimated to be 349±6 and 320±10 cm$^3$ mol$^{-1}$, respectively. These values may be compared with the molar volume of bulk Crystal

Violet, 344.9 $cm^3$ $mol^{-1}$. The van der Waals volume of $Cl_2$ was estimated as 25.7 $cm^3$ $mol^{-1}$. The molar volume of $Cl_2$ may be twice as large as its van der Waals volume.[23] From the density data,[24] the partial molar volume of HCl in 40% aqueous solution was estimated as 23 $cm^3$ $mol^{-1}$. If we tentatively use these values, the volume change for the following reaction can be estimated as $\Delta V = -57$ $cm^3$.

$$\mathrm{LCV} + \mathrm{Cl_2} \xrightarrow{\Delta \bar{V}} \mathrm{CV^+Cl^-} + \mathrm{HCl}$$

It is noted that the estimated volume change is similar to those observed in Menschutkin reactions (50—60 $cm^3$).[25] The volume of activation for the LCV-TCNE reaction are about −30 $cm^3$ $mol^{-1}$ for both isotopic species (Table 3), indicating that the transition state is considerably polar. It was reported that in the LCV(H or D)-CA system, the volumes of activation in acetonitrile are −25(H) and −35(D) $cm^3$ $mol^{-1}$, respectively, the difference having been ascribed to the tunnel effect.[1] By using the above values, we can draw the volume profile for a reaction involving the nominal transfer of a hydride ion from LCV to a base, as shown in Fig. 12(b).

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