High-pressure Kinetics of Electron Donor–Acceptor Complex Formation and Cycloaddition between Tetracyanoethylene and Enol Ethers

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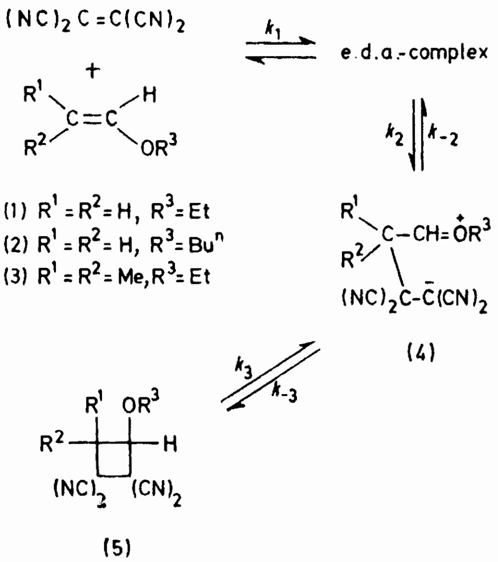
The kinetics of the high-pressure cycloaddition reaction between tetracyanoethylene and enol ethers (n-butyl vinyl ether and ethyl 2-methylpropenyl ether) in chloroform have been studied, by following spectrophotometrically the disappearance of the electron donor–acceptor complex (e.d.a. complex) at 25 °C and up to 1 500 bar. It is concluded that the e.d.a. complex is on the pathway to the zwitterionic intermediate and the final cycloaddition product. The reaction volume ΔV_1 of e.d.a. complex formation is -11.0 ± 1.4 and -5.8 ± 1.0 cm^3 mol^{-1} for n-butyl vinyl ether and ethyl 2-methylpropenyl ether, respectively. The volume of activation $\Delta V_2^\ddagger$ of cycloaddition step from e.d.a. complex to the adduct is -30.8 ± 1.5 and -41.8 ± 1.5 cm^3 mol^{-1} for n-butyl vinyl ether and ethyl 2-methylpropenyl ether, respectively. The variation of ΔV_1 and $\Delta V_2^\ddagger$ is discussed from the viewpoint of the ionization potential and the electron density at the β-carbon atom of the enol ether.

THE cycloaddition of tetracyanoethylene (TCNE) to electron-rich olefins such as enol ethers has attracted much attention as the reaction may proceed through a highly polar transition state or an intermediate. Several observations have supported a stepwise reaction path *via* a zwitterionic state, the incomplete conservation of *cis–trans* stereospecificity,[1,2] the strong dependence of the reaction rate on solvent polarity,[3] and acetal formation in alcoholic solvents.[4] Moreover, evidence for the high polarity of the transition state was also obtained from high-pressure kinetics which gave the volume of activation. The overall values of the volume of activation for such a cycloaddition are largely negative,[5-10] and even the cycloreversion is accompanied by a negative volume of activation.[11]



SCHEME 1

A related topic is the behaviour of a coloured electron donor–acceptor complex (e.d.a. complex).[12,13] In many reactions of TCNE with alkyl vinyl ethers, the coloured species readily fade with the production of cyclobutane adducts.[13] Mechanistic studies so far have not paid much attention to the role of the e.d.a. complex, except for our recent paper [9] and that by Jouanne *et al.*[10] The present study was carried out in order to separate the reaction volume for e.d.a. complex formation and the volume of activation for the cycloaddition step from the e.d.a. complex, as in Scheme 1.[9]

Kinetic studies cannot usually distinguish whether Scheme 1 is correct or the e.d.a. complex is formed in a dead-end equilibrium (Scheme 2, see later). Jouanne *et al.*[10] reached the conclusion that the e.d.a. complex existed in a dead-end by comparing the rate expressions for both processes. However, it is likely that their treatment included the contradiction that an e.d.a. complex is assumed to be in a steady state when a second-order rate constant k_{TCNE} is obtained for the decrease of TCNE, while equilibration is assumed when $k_{\text{e.d.a.}}$ is determined with regard to the decrease of e.d.a. complex. Since e.d.a. complex formation is very rapid the complex is considered to be always in equilibrium regardless of the reaction taking place, no matter whether its quantity is large or small. Thus the observed pseudo-first-order rate constant k_{obs}, defined by either equation (1a or b) should be identical when enol ether is in large excess and the cycloreversion is practically negligible.

$$\mathrm{d[TCNE]}/\mathrm{d}t = -k_{\text{obs}}[\mathrm{TCNE}] \qquad (1a)$$

$$\mathrm{d[e.d.a.]}/\mathrm{d}t = -k_{\text{obs}}[\mathrm{e.d.a.}] \qquad (1b)$$

EXPERIMENTAL

Materials.—Commercial TCNE was sublimed three times *in vacuo* at 50—55 °C in the presence of active carbon, m.p. 201 °C. n-Butyl vinyl ether (2) (Nakarai Chemicals Co. Ltd.) was washed several times with slightly alkaline water (pH 8), dried over potassium hydroxide for 30 h, and then distilled three times, b.p. 93.8 °C. Ethyl 2-methylpropenyl ether (3) was prepared, b.p. 94 °C, by decomposing the corresponding acetal in the presence of toluene-*p*-sulphonic acid. Isobutyraldehyde diethyl acetal, b.p. 135—137.5 °C, was synthesized from ethyl alcohol, calcium chloride, and isobutyraldehyde according to the procedure by Adkins *et al.*[14] Chloroform (Spectrograde reagent; Nakarai Chemicals Co. Ltd.), as solvent, was used without further purification. The cycloadduct (5) was prepared from dichloroethane solution for the purpose of identification by n.m.r. and elemental analysis.[13]

Equilibrium and Kinetic Measurements.—The equilibrium constant of e.d.a complex formation and the rate of cycloaddition were determined spectrophotometrically by observing the absorbance of the e.d.a. complex. At 1 bar, a Shimadzu UV-200S spectrophotometer was used in 10 mm quartz cuvettes, equipped with a rapid mixing apparatus (Union Giken MX-7-03). High-pressure experiment was carried out by using the *in situ* mixing technique described elsewhere.[9,15] An inner cell which contained two reaction solutions separately was assembled in a high-pressure bomb equipped with two sapphire windows. The pressure was raised, and after the attainment of thermal equilibrium the two reactant solutions were mixed with the aid of an electrical trigger. Mixing was completed within 5 s. The effective optical path is 8.0 mm, and the transmittance was followed by a Hitachi-139 spectrophotometer. The concentration of enol ether was 0.09—0.5 mol kg^{-1}, and that of TCNE *ca.* 5 mmol kg^{-1} for reaction with (2) and *ca.* 1 mmol kg^{-1} for reaction with (3). The temperature was controlled at 25 ± 0.1 °C by circulating thermostatted fluid around the high-pressure bomb.

RESULTS AND DISCUSSION

TABLE 1

Electronic absorption maxima of e.d.a. complexes between TCNE and enol ethers in chloroform at 25 °C (1 bar), and ionization potentials (I_p) of enol ethers

Enol ether	$\lambda_{e.d.a.}$/nm	I_p/eV [b]
Ethyl vinyl ether (1)	428 [a]	9.07
n-Butyl vinyl ether (2)	435	~8.85
Ethyl 2-methylpropenyl ether (3)	543	8.20

[a] Ref. 9. [b] N. E. Schore and N. J. Turro, *J. Amer. Chem. Soc.*, 1975, **97**, 2482.

Equilibrium of E.d.a. Complex Formation.—The electronic absorption maxima, $\lambda_{e.d.a.}$, of TCNE + enol ethers in chloroform are shown in Table 1. Neither TCNE nor cycloadduct has absorption at wavelengths longer than 300 nm, and the colour can be ascribed solely to the e.d.a. complex.[12,13] The coloured species disappeared in several minutes when the enol ether existed in large excess over TCNE. The decrease in the absorbance at $\lambda_{e.d.a.}$ obeyed the first-order rate equation very well. The absorbance was extrapolated to $t = 0$, and by using the absorbance A_0 at $t = 0$, the equilibrium constant K_1 for e.d.a. complex formation was determined from the Benesi–Hildebrand equation (2). In equation (2) a is the initial concentration of TCNE, d the concentration of the ether, ε the molar absorption coefficient

$$a/A_0 = 1/\varepsilon l + (1/K_1\varepsilon l)\cdot(1/d) \qquad (2)$$

of the e.d.a. complex, and l the optical path length. Figure 1 shows a plot of equation (2) for TCNE + (2) at 1 and 1 000 bar. A similar plot was obtained for TCNE + (3). It has often been observed that ε increases with pressure,[16] but no appreciable change could be found in the present systems. Thus we used the value of ε/kg mol^{-1} cm^{-1} at 1 bar, which was 1 500 for TCNE + (2) and 1 600 for TCNE + (3), even at high pressure. The results thus obtained are summarized in Table 2, with the previous results for TCNE + (1).[9]

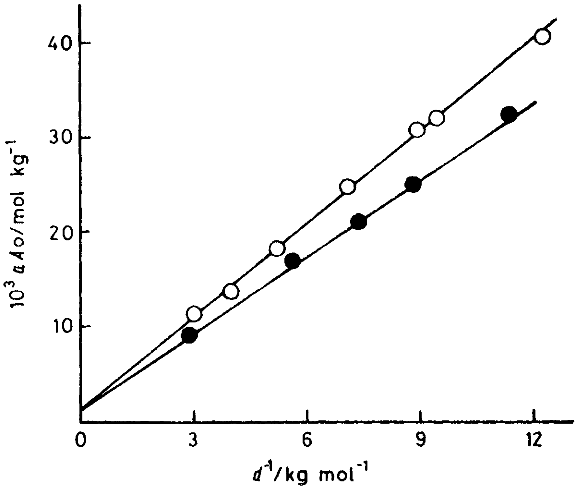


FIGURE 1 Benesi–Hildebrand plot for TCNE + (2) in chloroform at 25 °C: ○, 1 bar; ●, 1 000 bar

The electronic properties of the e.d.a. complex depends on the ionization potential I_p of the donor. The values of $\lambda_{e.d.a.}$ for (1) and (2) are close with each other, in accord with the small difference in I_p (Table 1), but $\lambda_{e.d.a.}$ and I_p for (3) differ from those for (1) and (2). The equilibrium constant at 1 bar in Table 2 is in line with the investigation by Nakayama [16] of the stability of the e.d.a. complex. For a series of weak complexes in which the entropy changes remain almost invariant, he derived the approximate relation that the stabilization energy increases with increasing wavelength of the absorption

TABLE 2

Equilibrium constants K_1 and reaction volumes ΔV_1 for e.d.a. complex formation of TCNE with enol ethers at 25 °C

		p/bar				
	Ether	1	250	500	1 000	1 500
K_1/kg mol^{-1}	(1) [a]	0.37 ± 0.01	0.42 ± 0.02	0.49 ± 0.02	0.56 ± 0.02	0.63 ± 0.03
	(2)	0.24 ± 0.01	0.27 ± 0.01	0.29 ± 0.02	0.31 ± 0.02	0.32 ± 0.02
	(3)	1.60 ± 0.03	1.67 ± 0.03	1.81 ± 0.03	2.02 ± 0.04	
ΔV_1/cm^3 mol^{-1}	(1) [a]	−10.3 ± 1.4				
	(2)	−11.0 ± 1.4				
	(3)	−5.8 ± 1.0				

[a] Ref. 9.

maximum. Thus, the equilibrium constant is enhanced with increasing charge transfer interaction.

The reaction volume ΔV_1 for the e.d.a. complex was calculated from equation (3) where R denotes the gas

$$-RT(\partial \ln K_1/\partial p)_T = \Delta V_1 \qquad (3)$$

constant, T the absolute temperature, and p the pressure. A correction for the compression of the reaction solution is unnecessary since the molality unit is adopted. As seen in Figure 2, equation (3) gives an almost linear plot for TCNE + (3) but a slightly curved one for TCNE + (2), to which a quadratic function for the pressure was used and ΔV_1 at 1 bar was calculated from the differential coefficient. The value of ΔV_1 (Table 2) usually reflects both contraction of the van der Waals distance between TCNE and the ether and a contribution from a change in solvation. The latter is negligibly small for a weak complex.[9,16] Thus, it may be suggested that the e.d.a. complex with a donor of lower ionization potential may be stabilized even for a longer separation between the donor and the acceptor. The result that $-\Delta V_1$ of (3) is smaller than those of (1) and (2) is explained by this concept.

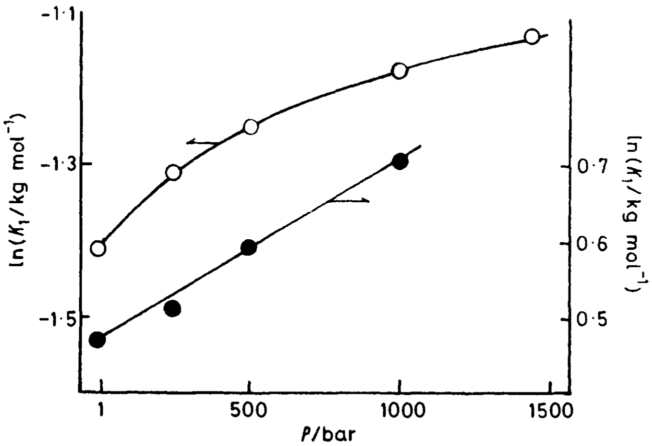
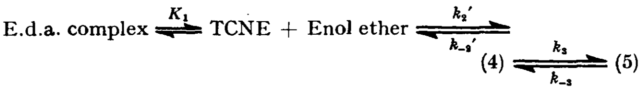


FIGURE 2 Dependence of equilibrium constant K_1 on pressure for TCNE + (2) and TCNE + (3) in chloroform at 25 °C: ○, TCNE + (2); ●, TCNE + (3)

Kinetics of Cycloaddition Reaction.—The cycloaddition reaction between TCNE and an enol ether has been presumed to proceed through a zwitterionic transition state or intermediate.[7,10] Jouanne *et al.* have pointed out that the e.d.a. complex should exist not as an intermediate but as a dead-end product (Scheme 2).[10] They emphasized that equivalence should be achieved between the second-order rate constants, k_{TCNE} and $k_{\mathrm{e.d.a.}}$, which were determined from equations (4a and b), respectively.



SCHEME 2

$$-\mathrm{d[TCNE]}/\mathrm{d}t = k_{\mathrm{TCNE}}\mathrm{[TCNE][ether]} \qquad (4a)$$

$$-\mathrm{d[e.d.a.]}/\mathrm{d}t = k_{\mathrm{e.d.a.}}\mathrm{[TCNE][ether]} \qquad (4b)$$

They ruled out Scheme 1 for the reason that the expressions for k_{TCNE} and $k_{\mathrm{e.d.a.}}$ differed from each other. That view, however, seems doubtful for the following reasons. First, the rate expression (4b) is a little curious with reference to the practical analysis required to determine $k_{\mathrm{e.d.a.}}$. The rate representing the change of the e.d.a. complex apparently obeys equation (1b) under pseudo-first order conditions. Thus, the definition of $k_{\mathrm{e.d.a.}}$ in equation (4b) does not seem to correspond to the phenomenological analysis. A second question occurs in the assumptions made in developing the rate equation. When they derived the expression for k_{TCNE}, a steady state was approximated for the e.d.a. complex concentration; on the other hand, the equilibrium between the reactants and the e.d.a. complex was assumed when $k_{\mathrm{e.d.a.}}$ was determined. We imagine that they justified these different assumptions because the quantity of the e.d.a. complex is in practice much smaller when k_{TCNE} is determined. It is understood, however, that different assumptions whether steady state or equilibrium, usually gives different expressions, and so k_{TCNE} and $k_{\mathrm{e.d.a.}}$ must be compared using the same assumptions.

The e.d.a. complex is believed to exist in equilibrium either on the pathway to the cycloaddition step or in a dead-end. It is known that the cycloreversion does occur but it is slow enough [9,11] not to be observed in the course of the disappearance of the e.d.a. complex. The zwitterionic intermediate (4) has not been identified but is believed to exist in a steady state. Thus, k_{-3}/k_3 and/or k_{-2} (or k_{-2}') in either Scheme 1 or 2 are considered to be very small, and k_2 (or k_2') is held to be the rate-determining step. According to Scheme 1, the pseudo-first-order rate constant k_{obs} is represented by equation (5) which refers to the decrease of either TCNE or e.d.a. complex. If the reaction proceeds by Scheme 2, k_{obs} is represented by equation (6). These reaction schemes are

$$k_{\mathrm{obs}} = k_2K_1d/(1 + K_1d) \qquad (5)$$

$$k_{\mathrm{obs}} = k_2'd/(1 + K_1d) \qquad (6)$$

kinetically indistinguishable. For the time being, Scheme 1 is taken into account as similar to the [2π + 4π] cycloaddition between TCNE and 9,10-dimethylanthracene.[17] A plot of k_{obs} *versus* $K_1d/(1 + K_1d)$ for TCNE + (2) system is shown in Figure 3. A similar plot is also obtained from the TCNE + (3) system. In both cases the experimental points lie on a good straight line passing the origin at each pressure. Thus the slope corresponds to k_2, and cycloreversion is regarded as almost negligible.

The volume of activation $\Delta V_2^‡$ for the step from the e.d.a. complex to the cycloadduct was calculated by relationship (7) (see Figure 4). The values of k_2 and

$$-RT(-\ln k_2/\partial p)_T = \Delta V_2^‡ \qquad (7)$$

$\Delta V_2^‡$ thus calculated are given in Table 3. The present values of k_2 at 1 bar are a little smaller than those determined previously,[13] but the sequence (3) < (1) < (2) is conserved. In the cycloaddition step, there is a trend that the decreasing electron density at the β-carbon of an enol ether brings about a larger value of $-\Delta V_2^\ddagger$. Table 4 gives ^{13}C n.m.r. chemical shifts of enol ethers cited from the literature.[18-20] An upfield shift means an increase in electron density. If the transition state has partial bonding between the β-carbon of an enol ether and the olefinic carbon of TCNE, which is very similar to (4), the enol ether with a more electron deficient β-carbon will require a larger degree of structural contraction. This tendency was recognized in comparison with the stepwise [2π + 4π] cycloaddition between TCNE and styrene derivatives.[21] α-Methylstyrene, the β-carbon chemical shift of which is δ 81.3 p.p.m.,[20] gave $\Delta V_2^\ddagger < -40$ cm^3 mol^{-1} for the reaction step from the e.d.a. complex to the 1,4-adduct.[21b] The large negative value of $\Delta V_2^\ddagger$ shows that cycloaddition takes place through a highly polar transition state. As many workers have pointed out,[5,9,10,22] the dipole moment of the transition state is estimated as *ca.* 15—19 D. Variation of the enol ether will not much affect the contribution from the solvation term, since the charge separation in the transition states will not be much changed.[22] The present results also suggest that the transition state is a zwitterion similar to (4).

TABLE 3

Rate constants k_2 and volumes of activation $\Delta V_2^\ddagger$ for cycloaddition reaction from e.d.a. complex at 25 °C

		p/bar				
	Ether	1	250	500	1 000	1 500
$10^2 k_2$/s^{-1}	(1) [a]	5.3 ± 0.2	6.9 ± 0.2	9.3 ± 0.3	16.1 ± 0.4	27.1 ± 0.5
	(2)	10.5 ± 0.5	14.4 ± 0.6	18.8 ± 0.7	37.8 ± 1.5	63.5 ± 2.5
	(3)	2.8 ± 0.1	4.6 ± 0.2	6.7 ± 0.3	14.7 ± 0.6	
$\Delta V_2^\ddagger$/cm^3 mol^{-1}	(1) [a]	−28.0 ± 2.0				
	(2)	−30.8 ± 1.5				
	(3)	−41.8 ± 1.5				

[a] Ref. 9.

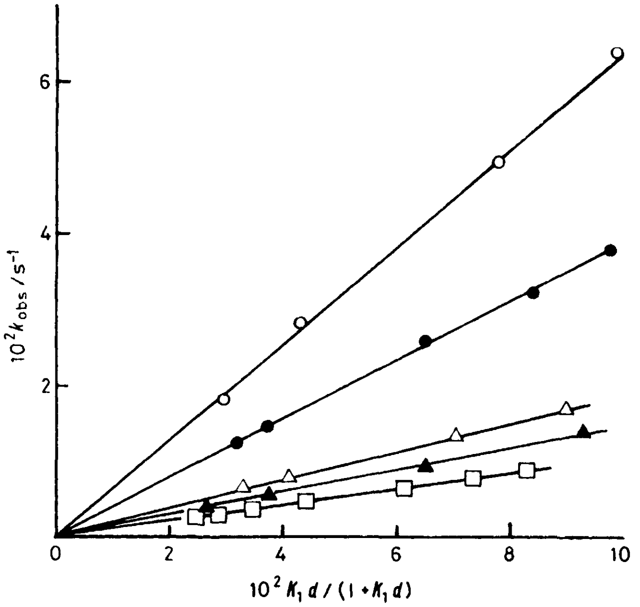


FIGURE 3 Dependence of pseudo-first-order rate constant k_{obs} on enol ether concentration for TCNE + (2) at 25 °C: □, 1 bar; ▲, 250 bar; △, 500 bar; ●, 1 000 bar; ○, 1 500 bar

There is a remarkable difference due to β-methyl substitution on both ΔV_1 and $\Delta V_2^\ddagger$. However, in the sum of ΔV_1 and $\Delta V_2^\ddagger$, the effect is less remarkable since an enol ether of smaller ΔV_1 gives a larger $\Delta V_2^\ddagger$. The sum $\Delta V_1 + \Delta V_2^\ddagger$ should approximately correspond to the overall volume of activation $\Delta V_{exp}^\ddagger$ at 1 bar, an expression employed by Jouanne *et al.*[10] or Isaacs *et al.*,[7] who determined it from the disappearance of TCNE. Our values of this sum are close to those of Isaacs *et al.* in CH_2Cl_2 and CCl_4 but less negative than those of Jouanne *et al.*, though the reason is not clear at present.

TABLE 4

^{13}C N.m.r. chemical shifts of olefinic carbons of enol ethers [a]

Ether	α-Carbon	β-Carbon
(1)	41.6 [b]	107.6 [b]
	39.7 [c]	108.5 [c]
(2)	40.6 [c]	107.8 [b]
		108.1 [c]
(3)	>47.7 [d]	92.5 [d]

[a] Chemical shift in p.p.m. from CS_2. [b] Ref. 18. [c] Ref. 19. [d] The value given here is for ethyl *cis*-propenyl ether.[18] The additional β-methyl substituent brings about a shift of the α-carbon to higher magnetic field and of the β-carbon to lower field.[18,20]

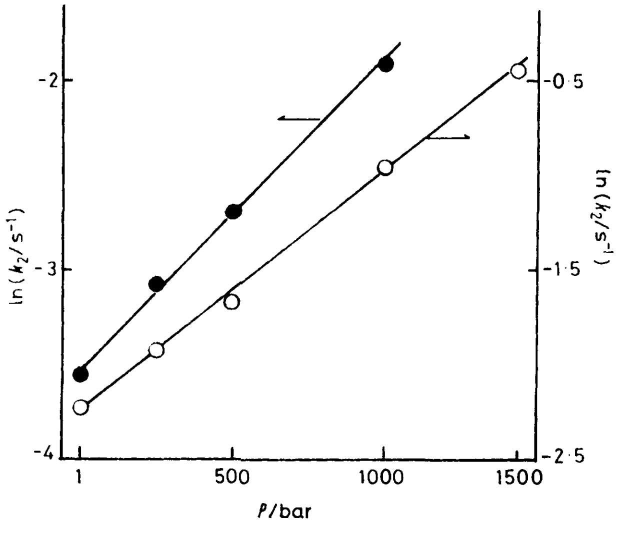


FIGURE 4 Dependence of rate constant k_2 on pressure for ○, TCNE + (2) and ●, TCNE + (3) in chloroform at 25 °C

We have hitherto considered the volumetric data according to Scheme 1. On the other hand, if the reaction proceeds by Scheme 2, the sum of $\Delta V_1 + \Delta V_2^{\ddagger}$ corresponds to $\Delta V_2'^{\ddagger}$, as required by equation (6). As Isaacs *et al.* have pointed out, the highly negative value of the volume of activation is due to the polar character of the transition state, but it seems unlikely that such a large negative volume of activation is brought about by a single reaction step even if the transition state is of high polarity. Moreover, the value of -55 cm^3 mol^{-1} by Jouanne *et al.*[10] seems difficult to rationalize. In conclusion, on the basis of volumetric considerations, it is likely that the cycloaddition takes place according to Scheme 1.

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