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THE CHARGE-TRANSFER INTERACTION AND SUCCESSIVE THERMAL (2+2)CYCLO-ADDITION OF α,β-UNSATURATED ETHERS WITH TETRACYANOETHYLENE

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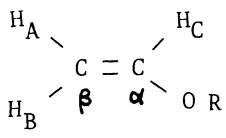
An equilibrium study on the formation of 1:1 α,β-unsaturated ether-tetracyanoethylene complexes, and a kinetic study on the successive (2+2)cycloaddition reaction were made in $CHCl_3$ and CCl_4 in the temperature range 10-40°C by the spectrophotometric method. The behavior of the charge-transfer complexes in the initial process of this reaction was considered.

Recently Williams, Wiley, and McKusick[1] found that tetracyanoethylene(TCNE) cycloadds thermally to electron-rich olefins under very mild conditions. In this reaction a characteristic color appears immediately after mixing, and then gradually diminishes. The complete disappearance of the color possibly corresponds to the end-point of the reaction. However, the mechanism of this reaction has not been investigated in detail. In the present report, it is found that α- and β-

Table 1. The CT spectra with TCNE and H_C chemical shifts of the donors.

	Donor	λ_{CT}	H_C τ value in CCl_4
REACTIVE[a]	vinyl 2-chloroethyl ether(V2-ClEE)	403 nm	3.64 ppm
	vinyl methyl ether(VME)	410	3.60
	vinyl ethyl ether(VEE)	428	3.70
	vinyl n-butyl ether(Vn-BE)	432	3.72
	vinyl isobutyl ether(Vi-BE)	436	3.74
	cis-propenyl ethyl ether(cis-PEE)	480	4.20
	trans-propenyl ethyl ether(trans-PEE)	480	3.90
	isobutenyl ethyl ether(IBEE)	518	4.42
	2,3-dihydro pyran	471	
	1,2-diethoxy ethylene	582	
	p-methoxystyrene	586	
NONREACTIVE[b]	pentene-1	340	4.3
	pentene-2	404	4.7
	2-methyl-2-butene	467	4.9
	tetramethylethylene	562	
	cyclohexene	420	
	styrene	475	

a) "REACTIVE" indicates that the cycloadducts could be identified by the product analyses(IR, UV, NMR and elemental analysis). b) "NONREACTIVE" indicates that the cycloadducts could not be identified.

substituents in the unsaturated ethers have considerably large effects on the NMR spectra, on the charge-transfer(CT) bands, and on the relative reactivities both in the complex formation and in the (2+2)cycloaddition reaction.

The donors used in this study, their corresponding CT bands with TCNE and ^{1}H-NMR chemical shifts of H_C of the donors are shown in Table 1. It is found that the effects of β-substituents are much larger than those of alkoxy groups on CT bands and τ values of H_C. All the chemicals were purified by the usual ways and the reacting solutions were prepared immediately before the use. Thermostated water was circulated around the quarz observation-cell compartment (optical path length is 10 mm), and the donor and acceptor solution reservoirs. Donor and acceptor solutions were mixed directly in the observation cell. Initial absorption measurements could be made within 6 sec. The kinetic and equilibrium experiments were carried out with the donors in large excess over the acceptor ((D)=0.2-1.2M and (A)=ca.10^{-3} M). The cycloaddition reaction was followed by observing the CT maximum band; during the reaction, in the NMR spectra only the reactant ether and the cycloadduct were observed and nothing else could be found. The pseudo-first order rate constant was obtained by Guggenheim's plot. The initial association constant was obtained by Benesi-Hildebrand(B-H) plot. In the case of reacting systems, we made use of the absorbance value obtained from the extrapolation of Guggenheim's plot to zero time to take the B-H plot. The value of ε did not have so much variation among the donors used; 2000±50 in $CHCl_3$ and 1400±100 in CCl_4.

The plot of the experimental ionization potentials of the donors[2] against ν_{CT} is linear as seen in Fig.1. It is found that the complex stoichiometry is 1:1 from the continuous variation plot. The ^{1}H-NMR chemical shifts of H_C and -OCH_2- in the complexed isobutenyl ethyl ether(IBEE) are about 0.1 ppm to the lower field in comparison with the isolated IBEE in CCl_4, and the other protons do not show any shift. According to these facts, it could be concluded that a characteristic color in the system is due to the formation of the CT complex. The thermodynamic parameters for the complex formation are listed in Table 2. The heat and entropy of formation(ΔH° and ΔS°) are determined from the temperature dependence of Kε value assuming ε to have no temperature dependence and using the equation $R\ln K\varepsilon = -\Delta H^\circ(1/T) + \Delta S^\circ + R\ln\varepsilon$. A good linear relation is obtained for the plot of $R\ln K\varepsilon$ vs. 1/T. The obtained values of ΔH° and ΔS° are negative and have similar magnitudes to those of the common π-π complexes.

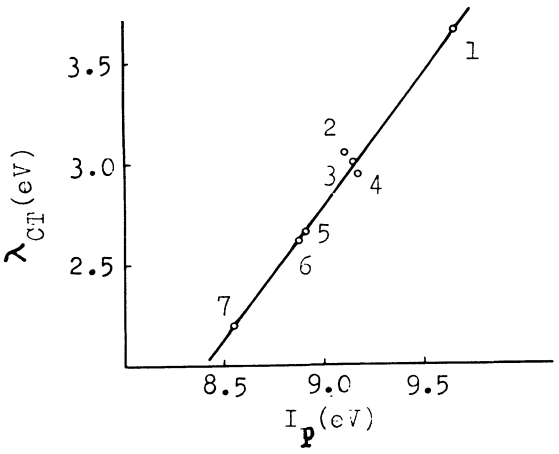


Fig. 1. Frequencies of the CT bands for some TCNE complexes plotted against the ionization potentials of the donors.
1:pentene-1 2:pentene-2 3:VME
4:cyclohexene 5:2-methyl-2-butene
6:styrene 7:tetramethylethylene

Table 2. The thermodynamic parameters for the TCNE complex formation equilibria.

Donor	K (1 mol^{-1}) 10°C	20°C	30°C	40°C	ΔH° (kcal mol^{-1})	ΔS° (e.u.)	Solvent
IBEE	2.16	1.91	1.34		-3.9	-12.2	CCl_4 [a]
	0.74	0.65	0.52		-3.0	-9.0	$CHCl_3$
cis-PEE	-	0.91	-	0.67	-2.9	-10.0	CCl_4
	0.24	0.21	0.18	-	-2.3	-10.0	$CHCl_3$
trans-60-PEE[b]	-	0.18	-	-			$CHCl_3$
VEE	-	0.33	-	0.27	-1.7	-8.0	CCl_4
	0.10	0.094	0.088	-	-1.0	-5.5	$CHCl_3$
Vi-BE	0.084	0.078	0.072	-			$CHCl_3$
VME	-	0.073	0.071	-			$CHCl_3$
V2-ClEE	-	-	0.05	-			$CHCl_3$
styrene	-	0.93	-				CCl_4
p-methoxystyrene	-	4.5	-				CCl_4

a) 95 vol.% CCl_4-5 vol.% CH_2Cl_2. b) The trans isomer of PEE could not be completely separated from the cis isomer, and trans-60-PEE indicates the PEE containing 60% trans isomer.

The obtained values of log K are plotted against $\tilde{\nu}_{CT}$ in Fig.2. The linearity of the lines A and B in Fig.2 suggest rather strongly that the electronic effect dominantly controls the relative stability in TCNE-unsaturated ether complex formation.[3] By the gradient of these plots the value of b^2 in Mulliken's simple resonance theory[4] can be obtained; it is about $0.04a^2$, which is in reasonable agreement with the value determined for some other π-π complexes by IR or dipole moment measurement.[5] The line C shows a similar relationship in molecular iodine(I_2)-nonsubstituted unsaturated ether(alkyl vinyl ether) complexes.[6] In this case the difference in the mesomeric effect of various alkoxy groups seems to be clearer.

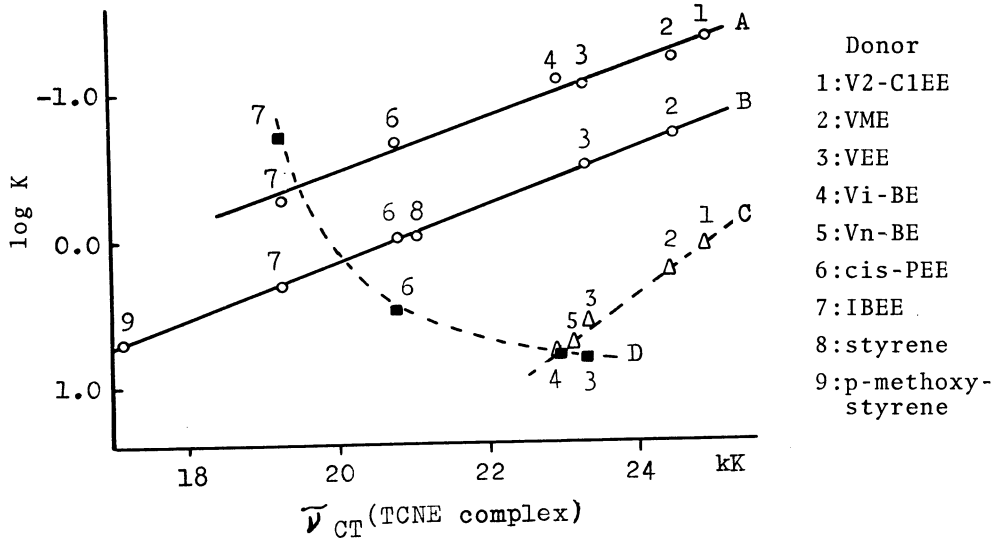


Fig.2. A plot of log K vs. frequencies of the charge-transfer bands for some TCNE complexes.
A: TCNE at 30°C in $CHCl_3$ B: TCNE at 20°C in CCl_4
C: I_2 at 23°C in isooctane
D: Ag^+ at 20°C in ethylene glycol

However, the line D shows a contrary trend in Ag^+-unsaturated ether complexes as reported by Fueno et al.[7] These plots indicate that the effect of β-methyl groups on the stability of Ag^+-ether complexes is negative on the contrary to that of TCNE-ether complexes. This trend of the substituent effect in Ag^+ complexes could be interpreted by considering that the interaction distance between the donor and acceptor is much smaller than the sum of their van der Waals radii so that the steric hindrance of the β-methyl group may become important. As a matter of fact, a similar phenomenon is observed in another case; the TCNE-olefin complexes studied by the present authors exhibit gradual increases in stability with increasing the double-bond substitution, in contrast to Ag^+-olefin and I_2-olefin complexes[8] where the complexes become more unstable with increasing substitution at the double bond.

There are linear relationships between log K and τ value of H_C as seen in Fig.3. The ^{13}C-NMR spectra reported by other authors,[9,10] ^1H-NMR spectra and an extended Hückel molecular orbital calculation by the present authors show that π-electron density on the α-carbon of an olefinic double bond increases and that on the β-carbon decreases as alkoxy groups become bulkier or the number of β-substituents increases. Then it could be supposed that the interaction of π-electron on the α-carbon with TCNE is more important than that of π-electron on the β-carbon with TCNE in the complex formation.

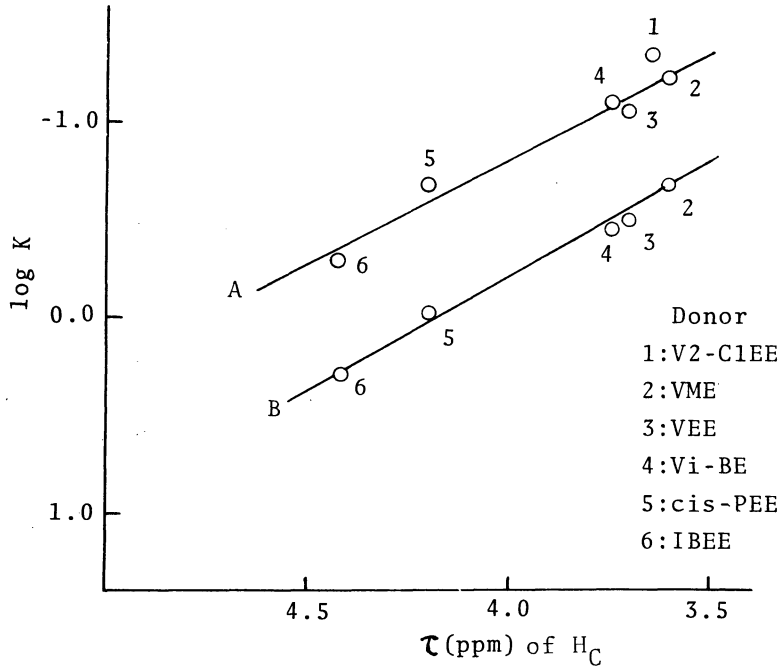


Fig.3. A plot of log K vs. H_C chemical shift. A: at 30°C in $CHCl_3$ B: at 20°C in CCl_4

The second order rate constant k_{II} (pseudo first order rate constant divided by the initial donor concentration(D)) decreases with increasing (D) for cis-propenyl ethyl ether(cis-PEE) and IBEE-TCNE systems, but is independent of (D) within the experimental errors for the vinyl ethyl ether(VEE)-TCNE system etc. Those phenomena could be satisfactorily interpreted by the next reaction scheme(1) or (2), though Rappoport[11] proposed Scheme(3) based on the kinetic study in the electrophilic substitution reaction of TCNE and aromatic amines. Schemes(1) and (2) are in agreement with the decrease of the rate constant k_{II} with the increase in (D) for cis-PEE and IBEE-TCNE systems, although in the case of Scheme(3) increase in (D) must increase the corresponding rate constant k_{II} unless $K(D) \gg 1$. The value of k_{II} is independent of (D) for the VEE-TCNE system etc. because in Eq.(1-2) or (2-2) $K(D) \ll 1$, and then $k_{II}=k_rK$ or k_r' respectively. As discussed extensively by Andrews and Keefer,[12] however, the kinetic method alone does not enable us to dis-

Scheme(1) Scheme(2) Scheme(3)

$$A + D \underset{}{\overset{K}{\rightleftharpoons}} C \xrightarrow{k_r} P \qquad C \underset{}{\overset{K}{\rightleftharpoons}} A + D \xrightarrow{k'_r} P \qquad A + D \underset{}{\overset{K}{\rightleftharpoons}} C \quad C + D \xrightarrow{k''_r} P + D$$

$$\frac{d(C)}{dt} = -\frac{k_r K(D)(C)}{1 + K(D)} \quad (1\text{-}1) \qquad \frac{d(C)}{dt} = -\frac{k'_r (D)(C)}{1 + K(D)} \quad (2\text{-}1) \qquad \frac{d(C)}{dt} = -\frac{k''_r K(D)^2 (C)}{1 + K(D)} \quad (3\text{-}1)$$

$$k_{II} = \frac{k_r K}{1 + K(D)} \quad (1\text{-}2) \qquad k_{II} = \frac{k'_r}{1 + K(D)} \quad (2\text{-}2) \qquad k_{II} = \frac{k''_r K(D)}{1 + K(D)} \quad (3\text{-}2)$$

$$\frac{1}{k_{II}} = \frac{(D)}{k_r} + \frac{1}{k_r K} \quad (1\text{-}3) \qquad \frac{1}{k_{II}} = \frac{1}{k'_r} + \frac{K(D)}{k'_r} \quad (2\text{-}3) \qquad \frac{1}{k_{II}} = \frac{1}{k''_r K(D)} + \frac{1}{k''_r} \quad (3\text{-}3)$$

tinguish between Scheme(1) in which the complex lies on the reaction co-ordinate and Scheme(2) in which the complex formation is a side reaction in a rapid equilibrium with free donor and acceptor. For cis-PEE and IBEE-TCNE systems the plot $1/k_{II}$ against (D) has fairly good linearity as seen in Fig.4, and then the rate constant k_r, k'_r and the initial association constant K are determined by these plots. It is also found that the association constant K obtained from this kinetical plot is in good accordance with that previously determined by the B-H plot. The obtained kinetic parameters are listed in Table 3.

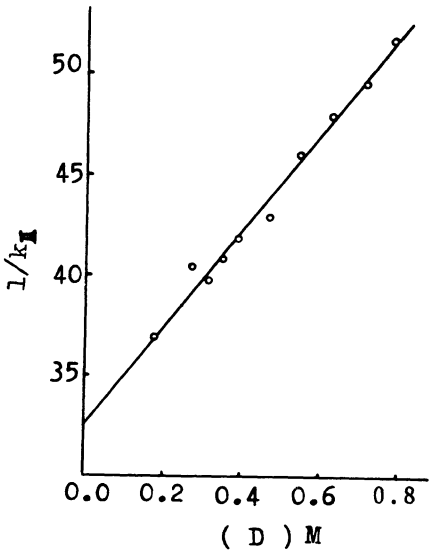


Fig.4. A plot of $1/k_I$ vs. the initial donor concentration (D). Donor:IBEE

Table 3. The kinetic parameters for the cycloaddition reactions in $CHCl_3$.

Donor		10°C	20°C	30°C	E_a c)	$\Delta S^{\neq}$ d)
cis-PEE	k_r a)	1.0×10^{-1}	1.4×10^{-1}	2.3×10^{-1}	6.9	-41
	k'_r b)	2.5×10^{-2}	3.1×10^{-2}	4.1×10^{-2}	4.4	-52
IBEE	k_r	2.8×10^{-2}	4.7×10^{-2}	7.1×10^{-2}	8.2	-39
	k'_r	2.1×10^{-2}	3.1×10^{-2}	3.7×10^{-2}	5.2	-50
VEE	k_r	4.4×10^{-2}	6.8×10^{-2}	1.0×10^{-1}	7.3	-41
	k'_r	4.4×10^{-3}	6.4×10^{-3}	9.1×10^{-3}	6.8	-48
Vi-BE	k_r	-	-	1.5×10^{-1}		
	k'_r	-	-	1.1×10^{-2}		
VME	k_r	-	-	1.0×10^{-2}		
	k'_r	-	-	7.3×10^{-4}		
V2-ClEE	k_r	-	-	2.0×10^{-3}		
	k'_r	-	-	1.0×10^{-4}		

a) sec^{-1}
b) $M^{-1}\ sec^{-1}$
c) kcal mol^{-1}
d) e.u.

As seen in the interesting plots of log k_r and log k_r' against $\tilde{\nu}_{CT}$ in Fig.5, each curve is not linear with a shallow minimum in contrast to that of the complex formation (Fig.2). There is no complete similarity between the substituent dependence of the transition state and that of the CT complex. Thus, the reactivity difference between in the cycloaddition reaction and in the complex formation seems not to be explained concurrently merely in terms of the electronic structure of the ground state of the reactant ethers. In order to explain the negative slope of log k_r or log k_r' against $\tilde{\nu}_{CT}$ for cis-PEE and IBEE in Fig.5, some steric effects are to be taken account of in addition to the electronic effect as in the case of the negative contribution of a β-methyl group to the stability in the complex formation of Ag^+-unsaturated ether complexes. The activation entropy is very large negative ca. -50 e.u. in Scheme(2), while the entropy of the complex formation is ca.-10 e.u. It seems that the transition state of this reaction is much more rigid than the initial stage.

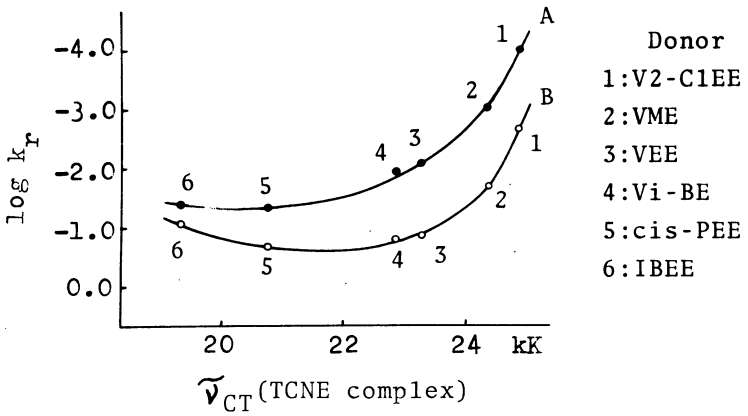


Fig.5. A plot of log k_r vs. frequencies of the charge-transfer bands for some TCNE complexes.
A: log k_r' B: log k_r

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