Effect of Pressure on Charge-transfer Spectra and Equilibria in Solutions of Tetracyanoethylene and Styrene Derivatives

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Charge-transfer spectra of *trans*-stilbene–, *cis*-stilbene–, 1,1-diphenylethylene–, and α-methylstyrene–TCNE mixtures in chloroform and in 1,2-dichloroethane have been measured at high pressures at 25 °C. The spectra shifted to a lower energy (red shift) with increasing pressure, the two bands in each complex shifting almost in parallel to each other. The shifts are qualitatively interpreted by McRae's theory. The spectral changes in intensity with pressure was analyzed taking account of reversible formation of the EDA complex and 1,4-cycloadduct; only the complex was formed in the stilbene systems. Volume changes for the complex formation are in the range of -4 to -7 cm^3 mol^{-1} and those for the cycloaddtion are in the range of -23 to -30 cm^3 mol^{-1}. The latter slightly increase in magnitude when solvent is changed from chloroform to a more polar solvent, 1,2-dichloroethane.

Disappearance of red color in dichloromethane solution of styrene and tetracyanoethylene (TCNE) was discovered at a high pressure of about 8 kbar (1 bar=0.1 MPa) half a decade ago.[1] The observation has led to finding a new 1,4-cycloaddition between styrene and TCNE with the aid of the quenching method; the electron-donor-acceptor (EDA) complex is transformed to the cycloadduct by the application of pressure.[2,3] Effects of substituents in styrene, solvent polarity, and temperature on the found 1,4-cycloaddition have been investigated to elucidate the reaction mechanism from a kinetic point of view in a series of papers.[4–6] A short paper has been published where effect of pressure on the 1,4-cycloaddition between α-methylstyrene and TCNE in 1,2-dichloroethane is studied.[7] In the present paper, charge-transfer (CT) spectra of *trans*-stilbene–, *cis*-stilbene–, 1,1-diphenylethylene–, and α-methylstyrene–TCNE mixtures in chloroform and in 1,2-dichloroethane have been taken at high pressures and spectral changes in intensity are analyzed by taking account of chemical equilibria involved in each system. The pressure effect allows us to know the volume change accompanying the reversible 1,4-cycloaddition without measuring the partial molal volumes of the reactants and product; in this case, direct density measurements can not be carried out on the product because it is not isolated. The large effect of pressure on the 1,4-cycloaddition is well established here; a decrease of 10—12% in volume accompanies the cycloaddition where two bonds are formed between the component molecules.

Experimental

TCNE, α-methylstyrene, 1,1-diphenylethylene, and *trans*- and *cis*-stilbenes were purified by the method described elsewhere.[3] Solvents were purified by the standard method.

Electronic absorption spectra were recorded on a Shimadzu UV-200S spectrophotometer at 1 bar and on a Union Giken RA-405 spectrophotometer at high pressure. All the other apparatuses and procedures for spectroscopic measurements at high pressure were the same as those in the previous work.[3]

The formation constants for the EDA complex and 1,4-cycloadduct were determined from absorbance of the EDA complex at the first charge-transfer band at each pressure at 25°C. The temperature was regulated to ±0.1 °C and the pressure was measured within ±1%. The concentration of the donor was always much larger than that of TCNE. The concentrations of the donor and the acceptor at high pressure were corrected for compression by using the Tait equation for the solvents.[8]

The partial molal volumes of α-methylstyrene in several solvents were determined by the method described in the previous work.[6]

Results and Discussion

Charge-transfer Spectra. Some typical electronic absorption spectra of the complexes studied here in the visible region are shown in Figs. 1—4 as a function of pressure. Two kinds of intermolecular charge-transfer transitions occur in each complex, while in Figs. 2 and 3, the second transition band lying at a higher energy is markedly obscured by the absorption due to the donor. The band multiplicity can arise from electron donation from the two highest occupied levels in the donor or from electron acceptance at the two lowest unoccupied levels in the acceptor.[9] The latter is not the case in the complexes of TCNE with these styrenes, because the difference in energy between the maxima ($\tilde{\nu}_{\max,1}$ and $\tilde{\nu}_{\max,2}$) of the first and second bands is dependent on the

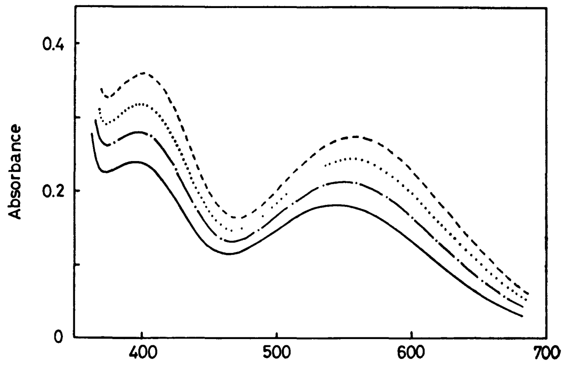

Fig. 1. Absorption spectra of TCNE complex with *cis*-stilbene in chloroform at 25°C at various pressures. $[D]_0=0.1160$ mol dm^{-3}; $[A]_0=5.184\times10^{-3}$ mol dm^{-3} at 1 bar; $l=0.506$ cm.
——, 1 bar; —·—, 500 bar; ····, 1000 bar; -----, 1500 bar.

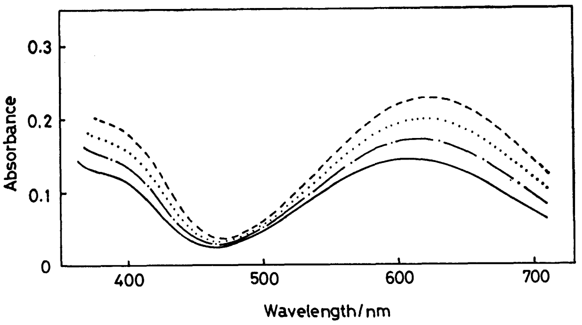

Fig. 2. Absorption spectra of TCNE complex with *trans*-stilbene in chloroform at 25°C at various pressures. $[D]_0=0.1034$ mol dm^{-3}; $[A]_0=2.436\times10^{-3}$ mol dm^{-3} at 1 bar; $l=0.587$ cm.
——, 1 bar; —•—, 500 bar; ••••, 1000 bar; -----, 1500 bar.

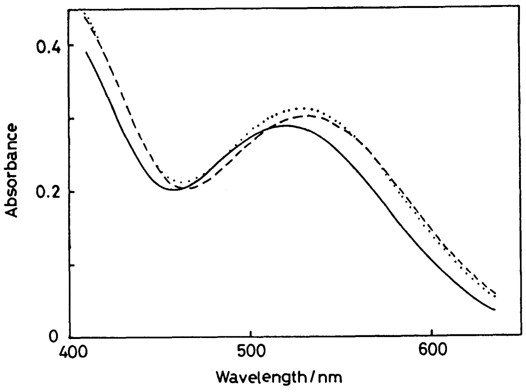

Fig. 3. Absorption spectra of TCNE complex with 1,1-diphenylethylene in chloroform at 25°C at various pressures.
$[D]_0=0.2409$ mol dm^{-3}; $[A]_0=5.184\times10^{-3}$ mol dm^{-3} at 1 bar; $l=0.551$ cm.
——, 1 bar; ••••, 1000 bar; ------, 1500 bar.

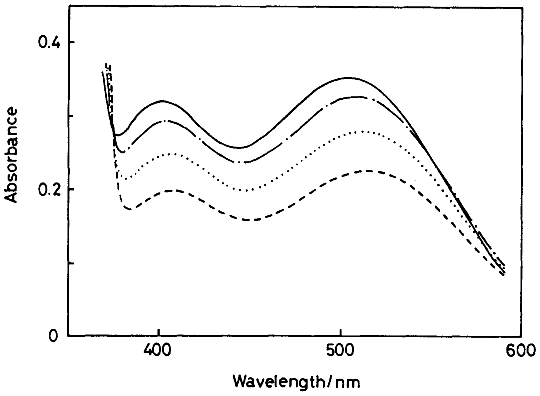

Fig. 4. Absorption spectra of TCNE complex with α-methylstyrene in chloroform at 25°C at various pressures.
$[D]_0=0.3283$ mol dm^{-3}; $[A]_0=4.809\times10^{-3}$ mol dm^{-3} at 1 bar; $l=0.525$ cm.
——, 1 bar; —•—, 500 bar; ••••, 1000 bar; -----, 2500 bar.

donors.[10,11] Each band maximum shifts toward a lower energy (red shift) with increasing pressure, as found in other EDA complexes.[12] The frequency shifts between 1 and 1500 bar are in the range of −200 to −400 cm^{-1} kbar^{-1}. Causes for the red shift are pressure-induced increases in the refractive index and dielectric constant of the solvent according to McRae's theory.[13] The excited state much polar than the ground state is stabilized more at higher pressures, and as a result, the energy gap between the ground and excited states is reduced to some extent by pressure. The difference between $\tilde{\nu}_{\mathrm{max},1}$ and $\tilde{\nu}_{\mathrm{max},2}$ is independent of pressure within an experimental uncertainty of 10^2 cm^{-1} as follows; $(\tilde{\nu}_{\mathrm{max},2}-\tilde{\nu}_{\mathrm{max},1})/10^2$ cm^{-1} in chloroform at 1, 500, 1000, and 1500 bar are 68.3, 68.4, 69.4, and 69.8 for the *cis*-stilbene complex and 50.3, 49.7, 50.6, and 50.5 for α-methylstyrene complex, respectively. A similar behavior is found for the biphenyl–TCNE complex, while the two bands of the naphthalene–TCNE complex are reported to behave differently from each other.[14] In that case, existence of isomeric forms of the complex is proposed on the basis of the nonparallel shifts, but the present result of the parallel shifts of the two bands suggest some similarity in polarity between the excited states of the first and second bands.[15]

Spectral Intensities and Chemical Equilibria. An increase, a decrease, and a complicated variation in absorbance with increasing pressure are observed in the solutions of stilbenes (Figs. 1 and 2), α-methylstyrene (Fig. 4), and 1,1-diphenylethylene (Fig. 3), respectively. The increase is due to the formation of the EDA complex promoted by pressure and the decrease is caused by the transformation of the complex to the 1,4-cycloadduct which is promoted by pressure more than the complex formation. Thus, the following reversible reactions,

$$\mathrm{D}+\mathrm{A} \overset{K_c}{\rightleftharpoons} \text{EDA Complex} \tag{1}$$

and

$$\mathrm{D}+\mathrm{A} \overset{K_c}{\rightleftharpoons} \text{EDA Complex} \overset{K_1}{\rightleftharpoons} \mathrm{P} \tag{2}$$

occur in solutions of TCNE with stilbenes and in those with α-methylstyrene and 1,1-diphenylethylene, respectively.[4] Here, D, A, and P denote the donor, the acceptor, and the 1,4-cycloadduct, respectively, and K_c and K_1 are, respectively, expressed by

$$K_c=\frac{[\mathrm{EDA}]}{[\mathrm{D}][\mathrm{A}]} \tag{3}$$

and

$$K_1=\frac{[\mathrm{P}]}{[\mathrm{EDA}]}, \tag{4}$$

where the square brackets indicate the concentration of each species. The equilibrium constants in Eqs. 3 and 4 can be determined, respectively, by the Scott equations

$$\frac{[\mathrm{D}]_0[\mathrm{A}]_0 l}{A_e}=\frac{1}{K_c\varepsilon_{\max}}+\frac{1}{\varepsilon_{\max}}[\mathrm{D}]_0 \tag{5}$$

and

$$\frac{[\mathrm{D}]_0[\mathrm{A}]_0 l}{A_e}=\frac{1}{K_c\varepsilon_{\max}}+\frac{1+K_1}{\varepsilon_{\max}}[\mathrm{D}]_0, \tag{6}$$

where $[\mathrm{D}]_0$ and $[\mathrm{A}]_0$ are the initial concentration of the

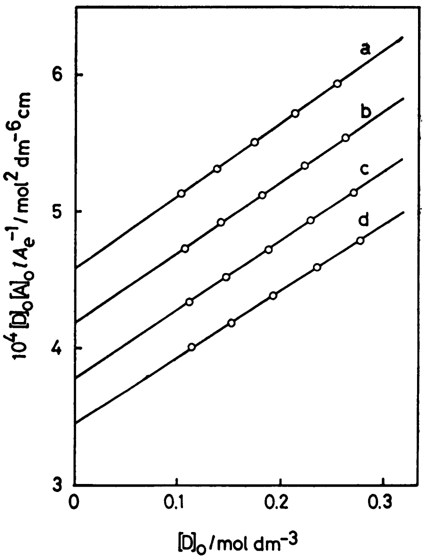

Fig. 5. Scott plots for *trans*-stilbene–TCNE system in chloroform at 25°C at various pressures.
(a), 1 bar; (b), 500 bar; (c), 1000 bar; (d), 1500 bar.

Table 1. Formation constants (K_c/mol^{-1} dm^3) of EDA complexes in chloroform at 25 °C at various pressures

Donor	P/bar			
	1	500	1000	1500
trans-Stilbene[a)]	1.16	1.23	1.34	1.42
cis-Stilbene[b)]	0.415	0.424	0.467	0.493
α-Methylstyrene[c)]	0.422	0.443	0.452	0.466
1,1-Diphenylethylene[d)]	0.312	0.329	0.353	0.369

a) $\varepsilon_{\max}$ is 1880, 1940, 1960, and 2040 mol^{-1} dm^3 cm^{-1} at 1, 500, 1000, and 1500 bar, respectively. b) $\varepsilon_{\max}$ is 1950, 2090,2050, and 2100 mol^{-1} dm^3 cm^{-1} at 1, 500, 1000, and 1500 bar, respectively. c) $\varepsilon_{\max}$ is taken to be 1760 mol^{-1} dm^3 cm^{-1} from Ref. 4. d) $\varepsilon_{\max}$ is taken to be 1660 mol^{-1} dm^3 cm^{-1} from Ref. 4.

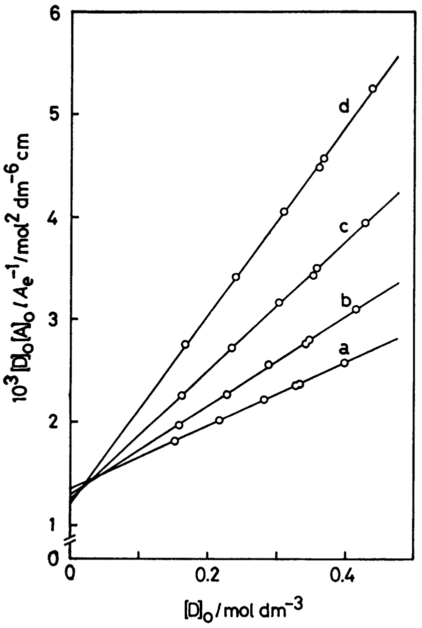

Fig. 6. Scott plots for α-methylstyrene–TCNE system in chloroform at 25°C at various pressures.
(a), 1 bar; (b), 500 bar; (c), 1000 bar; (d), 1500 bar.

donor and acceptor, respectively, l is the path length (0.5—0.6 cm), A_e is the equilibrium absorbance at $\tilde{\nu}_{\max,1}$, and $\varepsilon_{\max}$ is the molar absorption coefficient.

When spectra in the *trans*-stilbene–TCNE system like those in Fig. 2 are measured at high pressures over a wide range of $[\mathrm{D}]_0$, the left-hand side of Eq. 5 can be plotted against $[\mathrm{D}]_0$ as shown in Fig. 5. The plots are linear at each pressure and provide K_c and $\varepsilon_{\max}$ from their slopes and intercepts (see Eq. 5). Similar plots are obtained in the *cis*-stilbene–TCNE system. The results are summarized in Table 1 as a function of pressure; actually, the formation constants increase with increasing pressure.

Figure 6 illustrates plots of the left-hand side of Eq. 6 against $[\mathrm{D}]_0$ for the α-methylstyrene–TCNE system in chloroform; the intercept, $1/(K_c\varepsilon_{\max})$ becomes smaller and the slope, $(1+K_1)/\varepsilon_{\max}$ becomes larger as pressure increases, both K_c and K_1 increasing with pressure. Similar plots are obtained for the α-methylstyrene–TCNE system in 1,2-dichloroethane and for the 1,1-diphenylethylene–TCNE system in chloroform and in 1,2-dichloroethane. We can not determine the pressure dependence of $\varepsilon_{\max}$ in the present case where the two kinds of equilibria are involved. Hence, we use the values of $\varepsilon_{\max}$ at 1 bar[4,6] to determine the values of K_c and K_1 at high pressures. The determined values of K_c and K_1 are listed in Tables 1 and 2 and 3 and 4, respectively. The values of K_c/mol^{-1} dm^3 and K_1 at 1 bar for the α-methylstyrene–TCNE system in chloroform are comparable with those obtained by a kinetic method,[4] 0.436 and 4.12, respectively, and the values in 1,2-dichloroethane with 0.084 and 11.6,[6] respectively. The values of K_c/mol^{-1} dm^3 at 1 bar for the 1,1-diphenylethylene–TCNE system in chloroform is in reasonable agreement with the kinetically determined one, 0.306, whereas the K_1 value is smaller than that determined kinetically, 3.51 for some unknown reason.[4]

Volume Changes for Reactions. Volume change

Table 2. Formation constants (K_c/mol^{-1} dm^3) of EDA complexes in 1, 2-dichloroethane at 25 °C at various pressures

Donor	P/bar					
	1	300	600	900	1200	1500
α-Methylstyrene[a)]	0.094	0.097	0.101	0.104	0.117	0.126
1,1-Diphenylethylene[b)]	0.072	0.075	0.078	0.081	0.084	0.087

a) $\varepsilon_{\max}$ is taken to be 3330 mol^{-1} dm^3 cm^{-1} from Ref. 6. b) $\varepsilon_{\max}$ is taken to be 3000 mol^{-1} dm^3 cm^{-1}.

TABLE 3. FORMATION CONSTANTS (K_1) OF 1,4-CYCLOADDUCTS IN CHLOROFORM AT 25 °C AT VARIOUS PRESSURES

Donor	P/bar			
	1	500	1000	1500
α-Methylstyrene	4.44	6.67	10.0	15.1
1,1-Diphenylethylene	2.15	2.90	4.35	6.11

TABLE 4. FORMATION CONSTANTS (K_1) OF 1,4-CYCLOADDUCTS IN 1,2-DICHLOROETHANE AT 25 °C AT VARIOUS PRESSURES

Donor	P/bar					
	1	300	600	900	1200	1500
α-Methylstyrene	10.8	14.1	18.3	23.2	30.1	39.5
1,1-Diphenylethylene	2.91	4.26	6.08	7.90	10.3	13.1

(ΔV_c) accompanying the EDA-complex formation and that (ΔV_1) for the 1,4-cycloaddition are determined from the thermodynamic relation,

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} + \Delta m\cdot\kappa, \tag{7}$$

where R, K, P, T, ΔV, Δm, and κ are the gas constant, the equilibrium constant (K_c or K_1), the pressure, the temperature, the volume change (ΔV_c or ΔV_1), the change in the molecular number for the reaction ($\Delta m = -1$ for K_c and 0 for K_1), and the isothermal compressibility of the solvent, respectively. Plots of ln K *vs.* P are linear within the experimental error in every case. Typical plots for α-methylstyrene–TCNE system in chloroform are shown in Fig. 7. The values of ΔV_c and ΔV_1 obtained thus are given in Table 5, where the volume changes, $\Delta V_R = \Delta V_c + \Delta V_1$, for the overall reactions from the donor and the acceptor in the two solvents are included.

The volume changes accompanying the complex formation are in the range of −4 to −7 cm^3 mol^{-1}. The relatively small negative values are found also for other TCNE complexes.[12,16] There is no general correlation between ΔV_c and $-RT \ln K_c$ in the series of donors studied here.

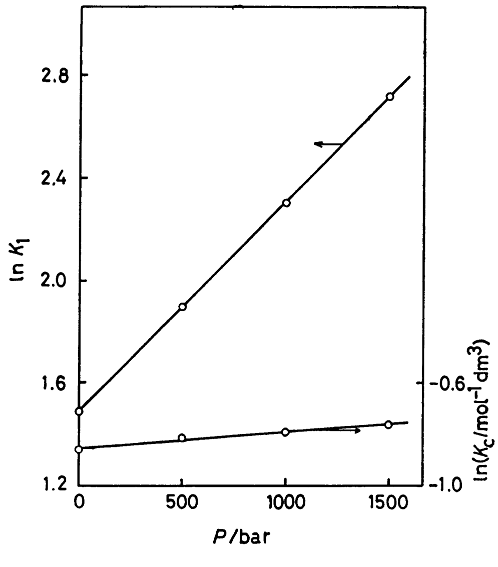

Fig. 7. Plots of ln K *vs.* P for α-methylstyrene–TCNE system in chloroform at 25°C.

TABLE 5. VOLUME CHANGES (ΔV_c, ΔV_1, AND ΔV_R/cm^3 mol^{-1}) IN CHLOROFORM AT 25 °C

Donor	ΔV_c	ΔV_1	ΔV_R
trans-Stilbene	−5.8±1.9	—	—
cis-Stilbene	−5.4±0.5	—	—
α-Methylstyrene	−4.0±0.2 (−6.9±0.6)[a]	−20±1 (−21±1)[a]	−24±1 (−28±1)[a]
1,1-Diphenylethylene	−5.2±0.2 (−5.1±0.0)[a]	−18±1 (−25±1)[a]	−23±1 (−30±1)[a]

a) In 1,2-dichloroethane.

The reaction volumes(ΔV_R) for the 1,4-cycloadditions studied in the present work are comparable with those reported so far for many other 1,4-cycloadditions (−30 to −40 cm^3 mol^{-1}).[17] The difference (4—7 cm^3 mol^{-1}) in ΔV_R between chloroform and 1,2-dichloroethane is probably due to the polarity of the adduct for the following reason. The partial molal volume of α-methylstyrene varies little in the solvent used here; its value at 25 °C is 132.5±0.3, 132.3±0.3, 131.3±0.3, and 130.8±0.1 cm^3 mol^{-1} in 1,2-dichloroethane, dichloromethane, chloroform, and carbon tetrachloride, respectively. The partial molal volume of TCNE sparlingly soluble in these solvents are 107, 107, and 106 cm^3 mol^{-1} in 1,2-dichloroethane, dichloromethane, and carbon tetrachloride, respectively.[6,18] Thus, the partial molal volumes of the donor and the acceptor depend little on solvent polarity in these solvents. It is clarified in the previous paper[6] that the cycloadduct has a relatively large dipole moment as a result of the symmetry breakdown in the TCNE moiety. In consequence, the partial molal volume of the polar adduct is expected to be smaller in 1,2-dichloroethane than in chloroform. If this is the case, the reaction volume becomes larger in magnitude in 1,2-dichloroethane than in chloroform as observed.

References

1) M. Nakahara, Y. Tsuda, M. Sasaki, and J. Osugi, *Chem. Lett.*, **1976**, 731.

2) M. Nakahara, Y. Uosaki, M. Sasaki, and J. Osugi, *Rev. Phys. Chem. Jpn.*, **47**, 119 (1977).

3) M. Nakahara, Y. Uosaki, M. Sasaki, and J. Osugi, *Bull. Chem. Soc. Jpn.*, **53**, 3395 (1980).

4) Y. Uosaki, M. Nakahara, and J. Osugi, *Bull. Chem. Soc. Jpn.*, **54**, 2569(1981).

5) Y. Uosaki, M. Nakahara, and J. Osugi, *Bull. Chem. Soc. Jpn.*, submitted.

6) Y. Uosaki, M. Nakahara, and J. Osugi, *Bull. Chem. Soc. Jpn.*, in press.

7) Y. Uosaki, M. Nakahara, M. Sasaki, and J. Osugi, *Chem. Lett.*, **1979**, 727.

8) D. M. Newitt and K. E. Weale, *J. Chem. Soc.*, **1951**, 3092.

9) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London (1969).

10) T. Matsuo and H. Aiga, *Bull. Chem. Soc. Jpn.*, **41**, 271 (1968).

11) J. Bendig, B. Dobslaw, D. Kreysig, and J. Sauer, *J. Prakt. Chem.*, **318**, 618 (1976).

12) A. H. Ewald, *Trans. Faraday Soc.*, **64**, 733 (1968).

13) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

14) J. R. Gott and A. I. Maisch, *J. Chem. Phys.*, **39**, 2229 (1963).

15) When we apply McRae's theory[13] to the two bands under the same conditions, we can expect cancellation of the dispersion term *etc.* and also neglect of the dipole moment of the ground state much smaller than the dipole moment (μ_E) of the excited state. In the present case, therefore, McRae's formula is simplified as

$$\{\tilde{\nu}_{\max,2}(P)-\tilde{\nu}_{\max,1}(P)\} - \{\tilde{\nu}_{\max,2}(1)-\tilde{\nu}_{\max,1}(1)\} = -\frac{\mu_{E,2}{}^2-\mu_{E,1}{}^2}{hca^3}\cdot\frac{n(P)^2-n(1)^2}{\{2n(P)^2+1\}\{2n(1)^2+1\}},$$

where $n(P)$ is the refractive index of the solvent at pressure P, h is Planck's constant, c is the velocity of light, and a is the effective radius of the complex. The above equation shows that if the left-hand side is zero, $\mu_{E,2}$ is equal to $\mu_{E,1}$.

16) T. Nakayama, *Rev. Phys. Chem. Jpn.*, **49**, 25, (1979).

17) T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978).

18) F. K. Fleischmann and H. Kelm, *Tetrahedron Lett.*, **1973**, 3733.