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SOLVENT, TEMPERATURE, AND PRESSURE EFFECTS ON THE REACTION BETWEEN TETRACYANOETHYLENE AND STYRENE

Masaru NAKAHARA, Yasutaro TSUDA, Muneo SASAKI, and Jiro OSUGI
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

A new absorption band discovered in the region 300-350 nm by varying solvents, temperature, and pressure was assigned to the zwitterionic intermediate postulated so far in the thermal (2+2) cycloaddition. The PMR spectrum was taken at low temperature. The rate of the intermediate formation depended strongly on solvent polarity.

It is well known that tetracyanoethylene(TCNE) cycloadds thermally to such electron-rich olefins as enol ethers and *p*-methoxystyrene but not to electron-deficient olefins like styrene.1) The idea that the thermal (2+2) cycloaddition proceed *via* 1,4-dipolar intermediates has been developed by Williams *et al.*,2) Gompper and collaborators,3) Huisgen *et al.*,4) and Kelm and coworkers.5) In order to investigate the intermediate and mechanism of the thermal (2+2) cycloaddition, the system of TCNE and styrene is studied here by altering pressure, temperature, and solvent polarity.

When the dichloromethane solution of TCNE is mixed with that of styrene, the charge-transfer(CT) color(red to orange) appears instantaneously and the CT band with its absorption maxima at 395 and 480 nm decreases with time, generating a new absorption band as shown in Fig. 1. Similar spectral change with time can be observed in CCl_4 as seen in Fig. 2, but the rate is about 60 times as slow as that in CH_2Cl_2 and the equilibrium concentration of the new species produced besides π complex is considerably less than that in CH_2Cl_2 if the molar absorption coefficients in both solvents are approximately equal. Since the dielectric constant of CH_2Cl_2 is twice as large as that of CCl_4 (*ca.* 2.2) at room temperature, it can be concluded that the formation rate and the thermodynamic stability of the new species found in the region of 300 to 350 nm increase with increasing solvent polarity. As mentioned above, *p*-methoxystyrene(PMS) cycloadds thermally to TCNE rapidly in a polar solvent like CH_2Cl_2 and very very slowly in a non-polar solvent like CCl_4.2) In the chilled solution of PMS and TCNE in CCl_4, the new species formation is too fast to be followed from the beginning by the usual technique, but if the spectra are measured within a minute of mixing a slight increase of absorption in the corresponding region is really observable with an isosbestic point near 365 nm as shown in Fig. 3. The ultraviolet band discovered can be assigned neither to the cyclobutane derivative2) nor to the anion radical of TCNE.6) According to the foregoing and following experimental results, it would be most probable that the new species found spectroscopically is the zwitterionic intermediate through which some kinds of the two-step cycloadditions have been assumed to be completed.

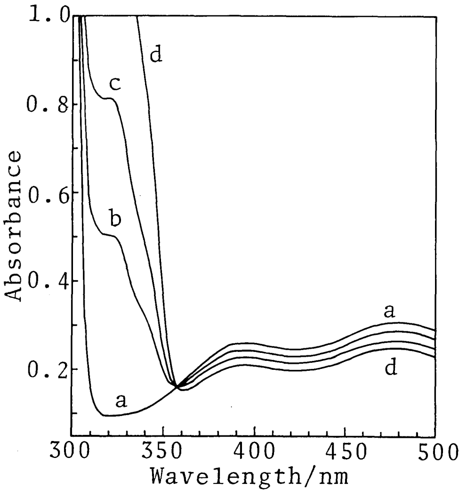


Fig. 1. Time dependence of the electronic spectrum of TCNE and styrene in CH_2Cl_2 at 23°C and 1 atm.
Concentration: TCNE, 1.5×10^{-3} M; styrene, 0.5 M.
a, 30 sec after mixing; b, 18.5 min; c, 47.5 min; d, 14 hr.

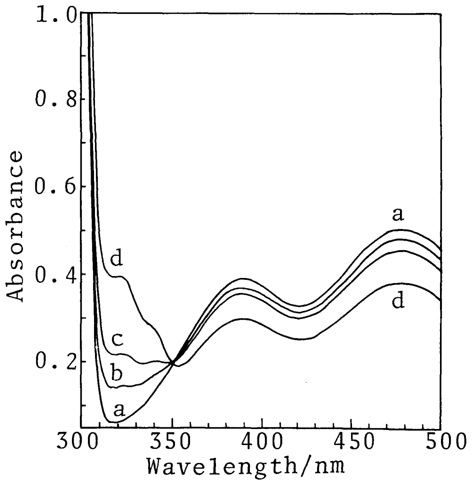


Fig. 2. Time dependence of the electronic spectrum of TCNE and styrene in CCl_4 at 23°C and 1 atm.
Concentration: TCNE, 1.5×10^{-3} M; styrene, 0.5 M.
a, 30 sec after mixing; b, 70.5 min; c, 150.5 min; d, 55 hr.

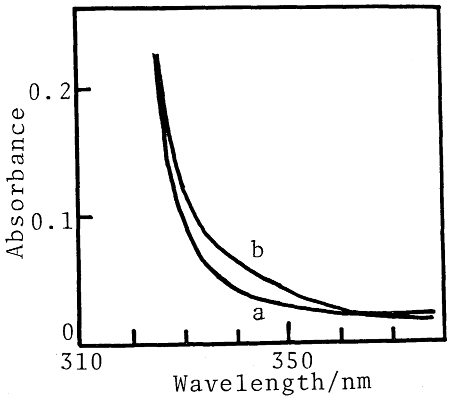


Fig. 3. Time dependence of the electronic spectrum of TCNE and PMS in CCl_4.
Concentration: TCNE, 1.58×10^{-4} M; PMS, 0.184 M.
a, just after mixing; b, ~30 sec.

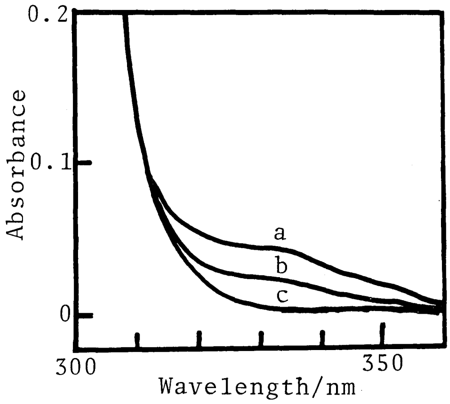


Fig. 4. Temperature effect on the new species formation in CH_2Cl_2.
Concentration: TCNE, ~10^{-4} M; styrene, ~10^{-4} M.
a, just after the chilled solution was diluted; b, 30 min; c, 10 hr.

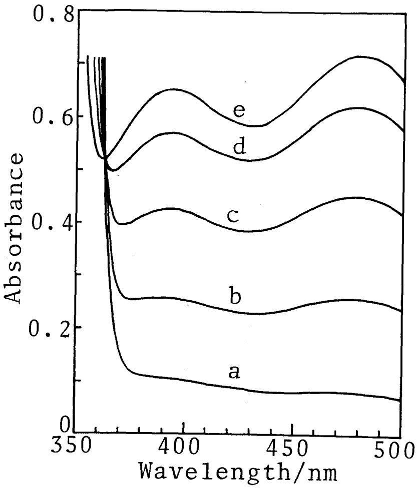


Fig. 5. Recovery of the CT band of TCNE and styrene in CH_2Cl_2 pressurized up to 8 kbar.
Concentration: TCNE, 3×10^{-2} M; styrene, 0.1 M.
Room temperature, 23°C.
a, 9 min after pressure was released; b, 20 min; c, 50 min; d, 100 min; e, 24 hr.

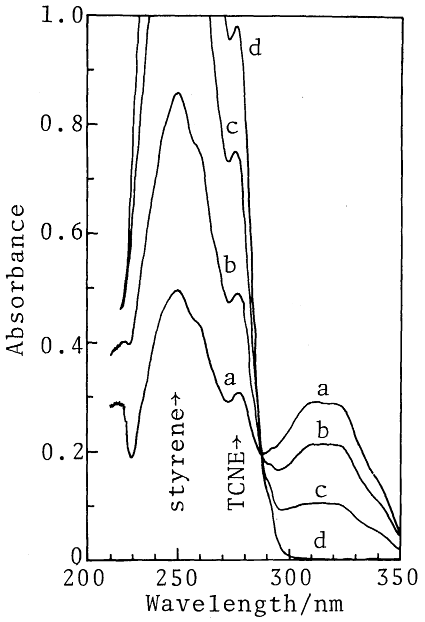


Fig. 6. Decay of the new species accumulated by the pressure of 8 kbar.
Concentration: TCNE, ~10^{-4} M; styrene, ~10^{-4} M.
Room temperature, 23°C.
a, 10 sec after the quenched solution was diluted; b, 10 min; c, 30 min; d, 16 hr.

By letting down temperature, solvent polarity can be increased without changing solvent species. When 4×10^{-2} M equimolar solution of TCNE and styrene in CH_2Cl_2 allowed to stand for a long time after mixing is cooled down to -78°C and quickly diluted to *ca.* 10^{-4} M at room temperature, a very small absorption corresponding to the new species is also detected in this concentration range where π-complex formation is negligible. The new species increased by lowering temperature decays slowly at room temperature, as can be seen in Fig. 4. Whether the new species may be formed *via* the π complex or directly from the donor and acceptor molecules, the formation of the new species from TCNE and styrene is exothermic. Therefore, the new species must have much larger solvation energy than the parent molecules have as a whole, overcoming any energy increase resulting from some breaking and making of chemical bonds. This temperature effect on the absorption spectrum also supports the present assumption that the new species may be identified with the zwitterionic intermediate.

Pressure can also make solvent polarity greater with a solvent species fixed. As can be seen from the electronic spectra of the solution quenched after being pressurized in Figs. 5 and 6, the influence of pressure on the new species formation is most drastic. Especially in Fig. 6, the well resolved spectrum of the new species is revealed; it has two absorption peaks of similar intensity in the range of 310 to 325 nm. Since it is confirmed$^{7)}$ that the volume changes for the formation of most π complexes

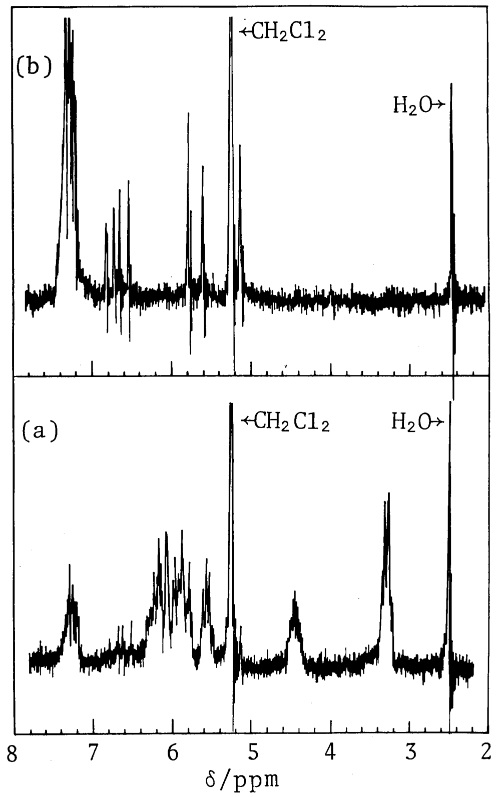


Fig. 7. PMR spectra of TCNE and styrene solution in CD_2Cl_2 pressurized up to 8 kbar for 1.5 hr.
Internal reference, TMS.
Measured at 100 MHz, 0°C, and 1 atm.
Concentration: TCNE, ~0.5 M; styrene, ~0.15 M.
(a), 30 min after the pressure of 8 kbar was released and quickly quenched to -78 °C; (b), after the solution was left to stand for 6 hr at 25°C so that it might recover the initial equilibrium state.

are usually negative, the pressure-induced disappearance of the present π complex must be considered to be caused directly by its conversion into the new species or indirectly by the consumption of the starting reactants. Thus we would have either of the following reaction schemes,

$$D + A \overset{K_1}{\rightleftarrows} \pi \underset{TS_1}{\overset{K_2}{\rightleftarrows}} I \underset{TS_2}{\xrightarrow{\times}} \text{Cycloadduct}, \qquad (1)$$

and

$$\pi \overset{K_1^{-1}}{\rightleftarrows} D + A \underset{TS_1'}{\overset{K_2'}{\rightleftarrows}} I \underset{TS_2}{\xrightarrow{\times}} \text{Cycloadduct}, \qquad (2)$$

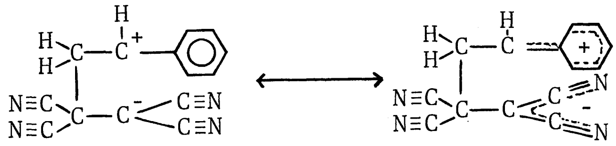
where D, A, π, I, K's, and TS's denote, respectively, styrene, TCNE, the π complex, the intermediate, formation constants, and transition states. The equilibrium (K_2) between the π complex and the new species and that ($K_2'=K_1K_2$ from thermodynamic indistinguishability between the two schemes) between the component molecules and the new species are shifted toward the new species to a great extent by the application of 8 kbar. The pressure dependences of K_2 and K_2', estimated respectively from the initial and final absorbances in Figs. 5 and 6, give immensely large negative volume changes, the absolute values of which exceed those of the activation volumes (-50 to -40 cm^3/mol) reported$^{5)}$ for the cycloaddition reactions of TCNE to enol ethers in CH_2Cl_2. This is what would be expected from the identification of the new species with the

Table 1. Assignment of the PMR spectra

in styrene			
7.5~7.2 ppm	6.8, 6.7, 6.65, and 6.5 ppm	5.8 and 5.6,	and 5.25 and 5.1 ppm
		cis H	*trans* H
$-C_6H_5$	$=CH-$	$CH_2=$	
in the new species			
6.4~5.5 ppm	4.6~4.3 ppm	3.4~3.2 ppm	
$-C_6H_5 \leftrightarrow =C_6H_5^+$	$-\overset{+}{C}H- \leftrightarrow -CH=$	$-CH_2-$	

zwitterion, because this zwitterion can be an intramolecular contact ion pair and have higher polarity and smaller intrinsic volume than the transition states before and after the intermediate on the reaction pathway. Moreover, in the case of TCNE and styrene the transition state TS_2 seems to be much higher in free energy than TS_1 or TS_1' in any solvent at any pressure, while in the case of TCNE and *p*-methoxystyrene TS_2 can be either higher or lower depending on the solvent.

Taking advantage of the striking influence of pressure on the new species formation equilibrium, we can make TCNE dissolve in CH_2Cl_2 much beyond the solubility (< 0.1 M at room temperature) at 1 atm that we may take the PMR spectrum (a) in Fig. 7 mainly of the new species, which differs substantially from that of the cycloadduct of TCNE and *p*-methoxystyrene measured in acetone-d_6. On the basis of the chemical shifts and the corrected (for the contribution of the untransformed styrene to the spectrum (a)) relative areas of the peaks in Figs. 7 (a) and (b), the assignment listed in Table 1 has been attempted. Each hydrogen peak of the new species appears in higher field than the corresponding one of styrene in Fig. 7 (b). The up-field shifts of methylene and methine protons seem to indicate the double bond in styrene gets more saturated. The ring protons of the new species locate in higher field than those of the monoarylcarbonium ions in strong acid solutions.8) This difference may be attributed to the electric field and the anisotropic magnetic field in the zwitterion. When the spin of methine proton is decoupled, the methylene protons do not become a singlet. According to these informations, the molecular structure of the intermediate could be depicted as,



The infrared spectra of the CH_2Cl_2 solutions of TCNE and styrene are taken along the same procedure as in the measurement of the PMR spectra. The stretching band of the double bond (1635 cm^{-1}) and those (4 absorptions from 1400 to 1600 cm^{-1}) between the carbon atoms in the ring of styrene all decrease when the pressure is applied to the solution. The strong absorptions due to the stretching of C≡N in TCNE at 2240 and 2270 cm^{-1} decrease when the pressure of 8 kbar is applied, and recover gradually at atmospheric pressure. These infrared studies seem to indicate that the new species found has the molecular structure pictured above.

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