Formation Reactions of Phosphorus Ylide–Tetracyanoquinodimethane Complexes

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The complexation reactions of tetracyanoquinodimethane (TCNQ) with phosphorus ylides have been studied. The binding energy is related to the electron density on the ylide atom as controlled by substituents. The degree of charge-transfer in the complex is also controlled by the substituents. The rate of formation of ylide–TCNQ complexes is slow enough to be measured, and a correlation between the reaction rate and the basicity of the ylide atoms was also established.

Molecular complexes formed by charge-transfer interactions exhibit interesting electrical, optical, and magnetic properties. For example, though the electrical conductivity of a pure organic compound may be extremely low, a charge-transfer complex containing it often has high conductivity. Thus, many organic charge-transfer complexes have been synthesized, and recently it was reported that some show the property of superconductivity at low temperatures.[1] Recent studies on new charge-transfer complexes show that the design of the donor is more important than that of the acceptor.

Many kinds of ylides have been synthesized and their properties determined by a variety of physical methods.[2,3] In particular, the ylide bond has unusual valence states in that two kinds of bond character such as the double bond and the dipolar bond exist.[2,4] This suggests that ylides may have interesting properties as donors, because their available electrons are intermediate between typical donors such as the lone-pair electrons of tetramethylenephenylenediamine and the donation of electrons of the double bond of tetrathiafulvalene.[5,6] Thus, we have already reported the syntheses and properties of new charge-transfer complexes containing the ylide as the donor.[5] However, the details of the complexation reactions of the ylide with tetracyanoquinodimethane (TCNQ) were not clarified. Thus, in this paper, we report the kinetics of formation of phosphorus ylide–TCNQ complexes. As the basicity on the ylide carbon (anionic carbon) of phosphorus ylide is controlled by the substituents on the ylide carbon, it is easy to examine the correlation between the basicity of the phosphorus ylide as the donor and the formation of the phosphorus ylide–TCNQ complex.

Of particular interest is our finding that the rate of complex formation is slow enough to be measured by spectroscopic methods and that there is a correlation between the basicity of ylide carbon and the thermodynamic parameters.

Results and Discussion

The phosphorus ylides employed in this study were synthesized by published methods[6] and purified by recrystallization. Structurally related ylides with a variety of substituents were prepared and their basicities range from 4.2 to 6.7.[7]

The reactions of ylides with TCNQ were performed in dry acetonitrile under dry nitrogen. Each acetonitrile solution containing the ylide and TCNQ was stirred under dry nitrogen and the yellowish solution changed to green with time. The visible spectrum of the green solution has three peaks at 680, 743, and 842 nm, showing typical TCNQ radicals.

The charge-transfer complexes were recrystallized by the evaporation of the solvent. The molar ratio of phosphorus ylide to TCNQ was determined by elementary analyses as 1:1. The solid-state i.r. spectra of complexes are not superposable on the spectra of the constituent neutral molecules. That is, all the bands are broad compared with those of the constituent molecules and their frequencies and intensities change. The CN stretching bands appear at 2 180—2 185 cm^{-1}. These values are in the region where the CN stretching modes of the TCNQ anion radical typically appear. The ν(C=O) stretching bands of complexes show a shift (30—60 cm^{-1}) to higher frequencies, indicating an interaction between TCNQ and the ylide carbon ($C^{-}H$).† E.s.r. measurements of ylide–TCNQ complexes were performed to confirm the presence of TCNQ radicals. A strong e.s.r. signal was observed and this observed paramagnetism is explained in terms of an ionic ground state. Each ion has an unpaired electron. They should have independent spin, unless they interact strongly in complexes, and the e.s.r. spectra of such complexes should have two resolved lines or hyperfine structure. In fact, the e.s.r. spectra of sulphilimine–TCNQ complexes showed unsymmetrical structures.[5,8] However, the spectra observed in the present study show only a single line (*g* 2.0025—2.0035), both in tetrahydrofuran and in the solid state, and presumably indicate strong interaction.

(i) *Equilibrium Constants of Formation of Complexes.*—To clarify the type of reaction involved in charge-transfer complex formation, the ratio of molar concentration of the ylide and TCNQ was changed and the intensity of absorption of TCNQ radicals at 842 nm was measured. The total molar concentration of ylide and TCNQ was 3.674×10^{-3}M through these experiments. The Figure shows that the maximum of absorbance is observed when the ratio of molar concentration of ylide to TCNQ is 1. Hence, the 1:1 complex of ylide and TCNQ is formed in this solution and we conclude that equilibrium (1) exists. The

$$\text{Ylide} + \text{TCNQ} \overset{K}{\rightleftharpoons} [\text{Ylide}]^{+\cdot}[\text{TCNQ}]^{-\cdot} \qquad (1)$$

equilibrium constant for this reaction is expressed by equation (2) where C = concentration of charge-transfer complex at

$$K = [\mathrm{C}]/([\mathrm{C_y} - \mathrm{C}][\mathrm{C_t} - \mathrm{C}]) \qquad (2)$$

equilibrium, C_y = initial concentration of ylide, and C_t = initial concentration of TCNQ. Analysis of the equilibrium constant (K) by Benesi and Hildebrand results in equation (3),[9] where b = breadth of cell, $A = \log(I_0/I)$, and ε_0 = true molar extinction coefficient. In this experiment, the molar concentration of TCNQ in acetonitrile was 100 times higher than that of ylide. We can then replace $[C_t - C]$ with $[C_t]$ in equation (2)

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† The ν(C=O) stretching bands of the salts, the phosphorus ylide–TCNQ complexes, and the phosphorus ylides for ylide (**2**) are 1 662, 1 560, and 1 527 cm^{-1} and for ylide (**3**) are 1 689, 1 600, and 1 540 cm^{-1}.

Table 1. The equilibrium constant (*K*) and thermodynamic quantities of ylide–TCNQ charge-transfer complexes and the related data[e]

	K						
	30 °C	40 °C	50 °C	$-\Delta H^a$	$-\Delta S^b$	$pK_a{}^c$	$\nu_{max.}{}^d$
(1) $Ph_3P{=}CHCOC_6H_4OMe$ (*p*)	835 (±5)					6.7	1 503
(2) $Ph_3P{=}CHCOC_6H_5$	438 (±5)	358 (±5)	300 (±5)	11.1 (±0.1)	23.0 (±0.1)	6.0	1 527
(3) $Ph_3P{=}CHCOC_6H_4NO_2$ (*p*)	38.2 (±0.5)	32.5 (±0.5)	28.8 (±0.5)	2.9 (±0.1)	2.4 (±0.1)	4.2	1 540—1 500

[a] Binding energy (kcal mol^{-1}). [b] Binding entropy (cal K^{-1} mol^{-1}). [c] Basicity.[7] [d] ν(C=O) stretching band (cm^{-1}).[10] [e] The figures in parentheses are errors.

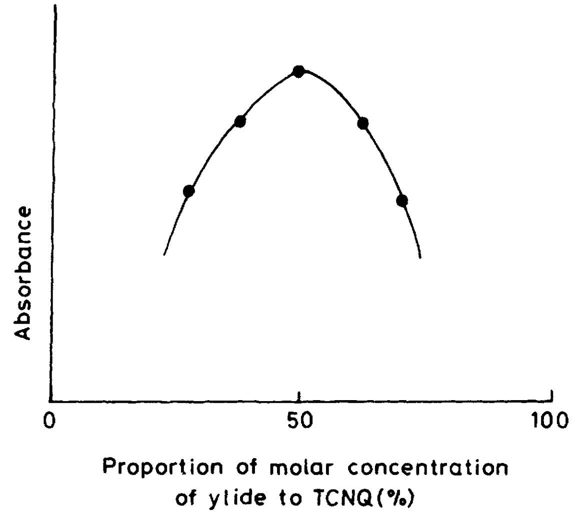
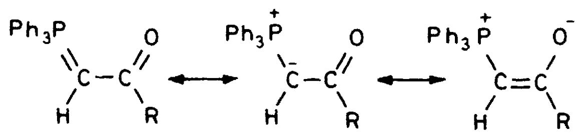


Figure. Absorbance *versus* the proportion of molar concentration of ylide to TCNQ. Total concentration of ylide and TCNQ in all solutions is 3.674×10^{-3}M

and use the Benesi–Hildebrand equation as shown in equation (3). A value of *K* is calculated for each set of experimental

$$\frac{C_y b}{A} = \frac{1}{K\varepsilon_0}\frac{1}{C_t} + \frac{1}{\varepsilon_0} \qquad (3)$$

measurements; that is, $C_y b/A$ values are plotted as a function of $1/C_t$, and the equilibrium constant (*K*) is calculated from the slope of these plots for each ylide. The reactions of complexation of ylide and TCNQ in acetonitrile reach equilibrium after 20—30 h. The equilibrium constants of the various ylides are summarized in Table 1, which also contains the binding energies ($-\Delta H$) and the binding entropies ($-\Delta S$) calculated from the Van't Hoff equation. When the reaction of ylide (**1**) with TCNQ proceeded above 40 °C, the colour of the solution changed from green to blue and a new peak appeared at 630 nm in the visible spectrum. Probably, this peak is not due to the charge-transfer complex, but results from the reaction products of a subsequent reaction *via* the ylide–TCNQ charge-transfer complex. Thus, the binding energy and the binding entropy of ylide (**1**)–TCNQ complex were not measured. The equilibrium constant of the ylide (**1**)–TCNQ complex at 30 °C is contained in Table 1.



(I) (II) (III)

The phosphorus ylides employed in this study have the three-component resonance (**I**)—(**III**). Resonance structure (**II**) is a characteristic electronic structure for an ylide in which the ylide carbon has very strong basicity. Resonance structure (**III**) tends to make the oxygen atom more basic than the case without resonance. There are three possible locations that might be considered as the donor site in these ylides, the lone pairs of the ylide carbon, the lone pairs of the oxygen atom, and the π electrons of the double bond. Table 1 contains the ylide carbon basicity and the i.r. values of ν(C=O) reported previously.[7,10] The order of basicity of the ylide carbon is the same as that of the equilibrium constant as shown in Table 1. This suggests a stronger interaction between the TCNQ molecule and the ylidic carbon (C^-H) of the phosphorus ylide. In fact, the ν(C=O) stretching bands of the ylide–TCNQ complex are higher than those of the ylide. The type of orbital would also affect the ability of the donor. However, according to the values of the ^{13}C–^{31}P coupling constant reported previously,[10] the hybridization of the ylide carbon of ylides (**1**)—(**3**) is similar to sp^2.

The binding energy ($-\Delta H$) in these complexes is proportional to the equilibrium constant (*K*), probably due to the similarity in structure of the complexes. Generally, when the binding energy ($-\Delta H$) increases, the freedom of both components of a charge-transfer complex decreases, and consequently the binding entropy ($-\Delta S$) increases. The experimental results for these complexes are consistent with the above conclusion. It should be noticed that the binding energy of the ylide (**2**)–TCNQ complex is much larger than that of the ylide (**3**)–TCNQ complex, though the structures of the ylides are very similar. The value for the ylide (**2**)–TCNQ complex is comparable with that of trimethylamine–I_2 complex, which is representative of the strong charge-transfer complexes of I_2 in various aromatic solvents.[11] This large difference between two complexes would come only from differences in the donor character of the ylide carbon. This fact indicates that the binding energy of the new complex is controlled by the substituents of the ylides as expected. This is also a characteristic feature of ylide–TCNQ complexes, namely, the degree of charge-transfer in the complex is controlled by the substituent on the ylide.

(ii) *Reaction Rate of Formation of Charge-transfer Complex*.—The formation reactions of ylide–TCNQ complexes reach equilibrium after 20—30 h as described above. However, the initial reaction rates depend on the kinds of phosphorus ylides. The kinetic data for the initial rates are summarized in Table 2. The initial reactions of ylide with TCNQ approximately obey the second-order rate equation, *i.e.*, the plots of $\log[(b - x)/(a - x)]$ *versus* *t* fall on a straight line, where *x* represents the decrease in concentration of a reactant in a given time, and *a* and *b* are the initial concentrations.

Table 2. Rate constants (k) and activation parameters of formation of ylide–TCNQ charge-transfer complexes[d]

	k[a]				
	30 °C	40 °C	50 °C	$\Delta H^{\ddagger b}$	$-\Delta S^{\ddagger c}$
Ylide (**1**)	8.66 (±0.05)	10.72 (±0.05)	13.00 (±0.05)	3.46 (±0.05)	42.9 (±0.5)
Ylide (**2**)	3.20 (±0.05)	4.23 (±0.05)	5.30 (±0.05)	4.30 (±0.05)	42.1 (±0.5)
Ylide (**3**)	0.53 (±0.01)	0.70 (±0.01)	0.97 (±0.01)	5.37 (±0.05)	42.2 (±0.5)

[a] Rate constant (l mol^{-1} min^{-1}). [b] Enthalpy of activation (kcal mol^{-1}). [c] Entropy of activation (cal K^{-1} mol^{-1}). [d] The figures in parentheses are errors.

The rate constants are summarized in Table 2 which also contains the thermodynamic parameters of activation. The rate constants increase with increasing temperature and are affected by the substituents. The increase with temperature is caused by the increase of the rate of diffusion and the number of collisions. The substituent effect is very important in order to clarify the factors by which the reaction rate is affected. The calculated entropies of activation are independent of the kinds of substituents, but the enthalpies of activation are dependent on the substituents. Each reaction proceeds *via* an activated complex composed of each ylide and TCNQ, and the structure of the activated complexes must be similar, because the entropies of these complexes are almost constant as shown in Table 2. This similarity is reasonable because ylides (**1**)—(**3**) have similar structures and the only point of difference is the substituent attached to the aromatic ring. Thus, the difference in the reaction rates caused by the substituents comes from the enthalpies of activation. The differences in the enthalpies are caused by the basicity of the ylide carbon, because a linear relationship between the basicity and the reaction rate is observed. When this linear relationship is represented by the form $\log k = m(\mathrm{p}K_a) + c$, the values of m and c are 0.43 and −1.77 at 50 °C, 0.43 and −1.87 at 40 °C, and 0.43 and −1.99 at 30 °C, respectively. This result indicates that the electron density on the reaction site of the donor molecule is an important factor in the formation of a charge-transfer complex. This conclusion was supported by other results in which sulphilimines were used as donor.[8]

Generally, the rate of formation of a charge-transfer complex is very high. In the case of the reaction of $\mathrm{Ph_3P{=}CHCOOMe}$ with TCNQ, the rate is *ca.* 10^4 l mol^{-1} min^{-1}.* However, the rate of reaction of phosphorus ylides with an aryl group with TCNQ is slow enough to be measured. Thus, the mechanism and main factors of formation of charge-transfer complexes can be determined.

The substituent effect was also examined by the Hammett method. In this case, the reaction constants (ρ) are −1.06 to −1.17. That the value of reaction constant (ρ) is negative indicates that the rate constant increases with increasing electron density at the reaction site. As the values of the reaction constant are not large, the substituent effect for this reaction is not strong compared with other reactions. This result is reasonable because there is a considerable distance between the main reaction site (ylide carbon) and the substituents.

Experimental

The ylides employed in this study were prepared by published methods.[6] Ylides with the appropriate basicity were selected from a series of phosphorus ylides reported already,[7] and were purified by recrystallization. TCNQ (tetracyanoquinodimethane) was purified by recrystallization and sublimation.

A Hitachi 340 spectrometer was employed for measurements of electronic spectra. The spectrometer was equipped with a HAAKE G temperature regulated cell holder, and a constant temperature was maintained by circulating water through the cell holder. I.r. spectra were determined using a Hitachi 260-10 spectrometer. E.s.r. spectra were recorded using a JEOL JES-FE3X instrument. N.m.r. spectra were determined using a JEOL GX 270 (270 MHz) spectrometer.

In order to measure the equilibrium constants of ylide–TCNQ complexes by the Benesi–Hildebrand method, a *ca.* 100-fold concentration of TCNQ over that of ylide was used, *i.e.*, the concentrations of ylides and TCNQ are 1×10^{-5} and 1×10^{-3}—3×10^{-3}M, respectively.

The rate constants for formation of complexes were measured by spectroscopic methods, and the concentrations of ylide (**1**)—(**3**) used in this experiment were 2.44×10^{-3}, 1.81×10^{-3}, and 2.35×10^{-2}M, respectively. The TCNQ and ylide solutions, which were equimolar and which were separately prepared, were mixed under nitrogen just before measurement. After mixing, aliquot portions of solution were periodically withdrawn, and the absorption was measured. As the reaction of $\mathrm{Ph_3P{=}CHCOOMe}$ with TCNQ proceeded rapidly, the concentration of $\mathrm{Ph_3P{=}CHCOOMe}$ employed in this experiment was 5×10^{-5}M and the reaction was carried out in the cell. In these complexation reactions, the biggest peak, at 842 nm, of TCNQ radicals was used to determine the equilibrium constants and rate constants.

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* This value was measured by the method for phosphorus ylides having aryl groups.

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