Reactivity and Reaction Mechanism for Reactions of 1,1'-(Azodicarbonyl) dipiperidine with Triphenylphosphines

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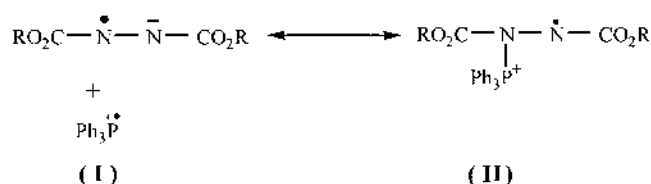
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Reactivity and reaction mechanism for the reactions of 1,1'-(azodicarbonyl) dipiperidine with triphenylphosphines are investigated using kinetic method. The cation radical, $Ph_3\overline{P}$ and the anion radical, -Ṅ-N̄- are produced during the course of the reaction. The cation radical is formed by the transfer of an electron from phosphorus to the nitrogen atom. The anion radical is formed by the addition of the one electron to the azo radical. The rate constants are decreased by electron withdrawing groups while they are increased by electron donating groups present in triphenylphosphine. The electron density increases on nitrogen, while positive charge is developed on phosphorus in the transition state.

Introduction

Phosphazines are usually produced from the reaction of azo compounds with triphenylphosphines.[1-3] The reaction of azodicarboxylate with triphenylphosphine has been suggested to proceed through the formation of triphenylphosphonium cation radical and diazo anion radical[4-6] (I). However a different reaction mechanism is suggested that the reaction occurs through the formation of forming diazo radical (II) rather than diazo anion radical.[7]

$$RO_2C - \overset{\bullet}{N} - \overline{N} - CO_2R \longleftrightarrow RO_2C - \underset{Ph_3\overset{+}{P}}{\overset{|}{N}} - \overset{\bullet}{N} - CO_2R$$

$$+ $$
$$Ph_3\overset{\bullet\bullet}{P}$$

$$(\ I\ ) \qquad\qquad (\ II\ )$$

The hyperfine coupling is affected by the two carboxylate functions on the azodicarboxylate molecule. A different compound, 1,1'-(azodicarbonyl) dipiperidine would be expected to stabilize the diazonium intermediate and also to control the phosphazine product-contributing step. In view of the increased importance of this kind of reactions a new attempt is made to explain in detail the reaction mechanism based on kinetic results. So far the detailed reaction mechanism for this kind of reactions is scarce.

(X = *p*-OCH₃, *p*-CH₃, H, *p*-Cl,*m*-NO₂)
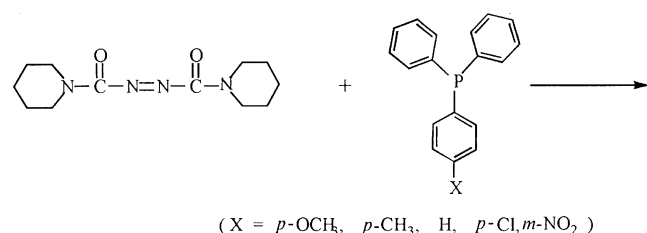
We report here the detailed reaction mechanism and reactivity for the reactions of 1,1'-(azodicarbonyl)dipiperidine with *p*-substituted triphenylphosphine.

Experimental Section

Materials. 1,1'-(Azodicarbonyl)dipiperidine (ADP) and triphenylphosphine (*p*-H) were obtained commercially from Tokyo Kasei Co. (TCI) and recrystallized from acetonitrile. Toluene was purified by distillation based on Timmermans' method.[8]

p-Chlorophenyldiphenylphosphine (*p*-Cl), *p*-methoxyphenyldiphenylphosphine (*p*-OCH₃), *p*-methylphenyldiphenylphosphine (*p*-CH₃), and *m*-trifluoromethylphenyldiphenylphosphine (*m*-CF₃) were synthesized according to literature procedure.[9]

p-Cl; mp 41-43 °C; IR (KBr): 3073 (CH, Ar, s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ7.69 (10H, m, ArH), δ7.42 (2H, m, ArH), δ7.09 (2H, m, ArH) ppm. MS (m/z): 296 (M⁺). *p*-OCH₃; mp 76-78 °C; IR (KBr): 3065 (CH, Ar, s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ7.34 (10H, m, ArH), δ7.28 (2H, m, ArH), δ 6.88 (2H, m, ArH), δ 3.82 (3H, s, OCH₃) ppm. MS (m/z): 292 (M⁺), 183. *p*-CH₃; mp 58-62 °C (from methanol). microanalysis: C₁₉H₁₇P calcd: C, 82.59; H, 6.20%, found: C, 82.62; H, 6.20%. IR (KBr): 3058 (CH, Ar, s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 7.40 (10H, s, ArH), δ 7.00 (4H, s, ArH), δ 2.34 (3H, m, CH₃) ppm. MS (m/z): 276 (M⁺). *m*-CF₃; mp 46-47 °C (from ethanol). microanalysis: C₁₉H₁₄PF₃ calcd: C, 69.09; H, 4.27%, found: C, 68.60; H, 4.24%. IR (KBr): 3060 (CH, Ar, s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ7.61 (10H, m, ArH), δ7.41 (2H, m, ArH), δ 7.38 (2H, m, ArH), ppm. MS (m/z): 330 (M⁺).

Apparatus and Characterization. The synthesized samples were characterized before using. Melting points were measured on a Büchi 510 melting point apparatus. IR spectra were recorded on a Bruker IFS 55 spectrophotometer. ¹H NMR spectra were measured on a Bruker AC-200 (FT, 200 MHz) spectrometer and are reported in parts per million downfield from tetramethylsilane. Mass spectra (MS) were obtained on a Hewlett-Packard 5890- AX505WA [column: HP ultra 2 (SE-54, 5% phenylmethylsilicon, 50m × 0.2 mm × 0.3 μm), 70eV, EI].

EPR spectra were obtained on a Bruker ESP 300E X-band

spectrometer, and the g values were calibrated with 2,2-diphenyl-1-picrylhydrazyl using Bruker ER035M NMR gaussmeter. All samples were 0.30 mL and were contained in 3-mm cylindrical quartz EPR tubes. All spectra were obtained at 0.2-G modulation amplitude, a modulation frequncy of 100 kHz, and an incident microwave power of 8 mW. The field-frequency lock accessory was operated automatically programmed with automatic frequency control modulation amplitude correction over the attenuation range. Spin concentration measurements were carried out on a dual TE_{104} rectangular cavity. UV-vis spectra for kinetics were recorded on a Shimadzu UV-240 spectrophotometer, and the cell temperature was calibrated by using a Cu/constant thermocouple.

Kinetic Run. The reaction rates were followed by photochemical method on a UV-vis spectrophotometer and the k_{obs} values were obtained by the Guggenheim method.[10] Kinetic determinations were done by following the decreasing amount of reactant *vs.* time, by using UV/vis spectrophotometer. The kinetic runs were carried out at 438 nm for maximum wavelength of *m*-CF$_3$, 442 nm for *p*-Cl, 437 nm for *p*-H, 442 nm for *p*-CH$_3$ and 442 nm for *p*-OCH$_3$ respectively. Figure 1 shows a typical spectrophotometric kinetic measurement.

Results and Discussion

The pseudo-first order rate constants, k_{obs} are linearly correlated with the concentration of *p*-substituted phenyldiphenylphosphine. The second order rate constants, k_2 have been determined from the following equation (1),

$$k_{obs} = k_2 [p\text{-X}] \tag{1}$$

where [*p*-X] represents the concentration of *p*-substituted phenyldiphenylphosphine.
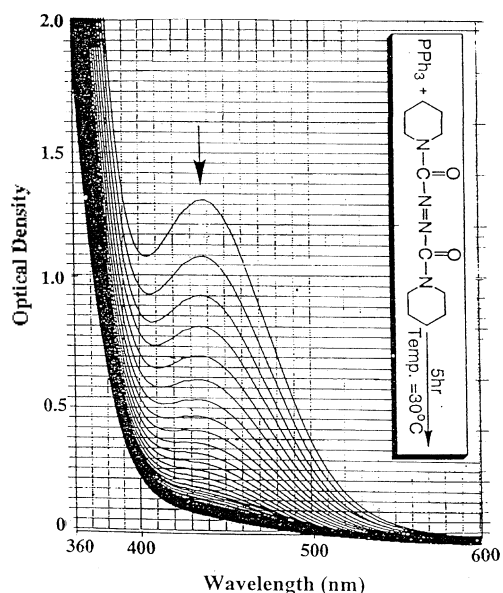

Figure 1. The spectra of the reaction 1,1'-(azodicarbonyl) dipiperidine with triphenylphosphine as a function of reaction time in toluene solution at 30 °C ($\lambda_{max} = 437$ nm).

Table 1. The Second Order Rate Constants ($k_2 \times 10^3$ M^{-1}sec^{-1}) and Thermodynamic Parameters for the Reactions of 1,1'-(Azodicarbonyl)dipiperidine with *p*-Substituted Phenyldiphenylphosphine in Toluene at 303, 308 and 313K

Temp (K)	*m*-CF$_3$ (438 nm)	*p*-Cl (442 nm)	*p*-H (437 nm)	*p*-CH$_3$ (442 nm)	*p*-OCH$_3$ (442 nm)
303	1.95	2.78	4.42	8.02	11.4
308	2.79	3.97	6.63	11.3	17.1
313	3.62	5.16	8.84	14.5	22.7
Ea (Kcal · mol^{-1})	11.7	11.7	13.0	11.2	12.9
$\Delta H^\neq$ (Kcal · mol^{-1})	11.1	11.1	12.4	10.6	12.3
$-\Delta S^\neq$ (Kcal · mol^{-1})	34.2	33.5	28.3	33.1	26.7
$-\Delta G^\neq$ (Kcal · mol^{-1})	21.6	21.4	21.1	20.8	20.5

Good second order kinetics are observed ($r \geq 0.9982$) in all cases. Table 1 summarizes the second order rate constants, k_2 for the reactions of ADP with *p*-X.

The second order rate constants are increased by electron donating groups and decreased by electron withdrawing groups.

The effect of substituents on the rate constants given in Table 1 is examined with help of Hammett equation.[11]

$$\log(k/k_0) = \rho\sigma_x \tag{2}$$

where *k* and k_0 are the rate constants for the reactions of ADP with *p*-X and those for of the reaction of ADP with unsubstituted triphenylphosphine (*p*-H) respectively. σ_x is the substituent parameter.

The reaction parameters, ρ-values, are in the range $-1.02 \sim -1.06$. These values indicate that the phosphorus atom becomes more positive in the transition state relative to the ground state and bond formation is more advanced.
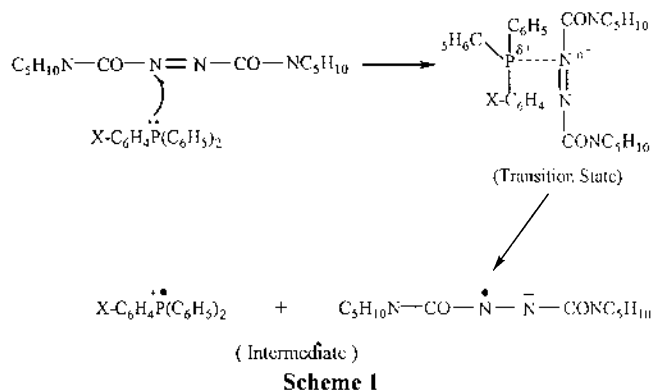
Our kinetic results show that a rigid transition state exists before forming triphenylphosphonium radical cation or diazo radical anion.

Previously Jenkins[3] reported that the triphenylphosphonium radical cation and the diazo radical anion were formed as a result of direct attack of triphenylphosphine on diethylcarboxylate in the reaction of azodicarboxylate with triphenylphosphine as shown in equation (3)

$$RO_2C-N\overset{\frown}{=}N-CO_2R \longrightarrow Ph_3\overset{+}{P} + RO_2C-\overset{\cdot}{N}-\overline{N}-CO_2R$$

$$Ph_3P: \tag{3}$$
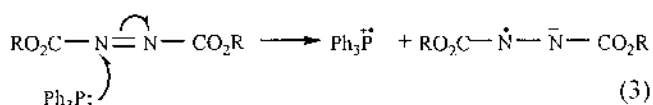
Our kinetic results show that in the reactions of ADP with *p*-X the transition state lies within the range of reactants and the intermediates as shown in Scheme 1 which is somewhat different from Jenkins' result.

The activation parameters are shown in Table 1. Generally the Hammett equation is expressed in the form of standard molar free energy[12] as shown in equation (4).

$$C_5H_{10}N—CO—N=N—CO—NC_5H_{10} \longrightarrow$$

X-C$_6$H$_4$P(C$_6$H$_5$)$_2$

(Transition State)

X-C$_6$H$_4$P(C$_6$H$_5$)$_2$ +   C$_5$H$_{10}$N—CO—N— N—CONC$_5$H$_{10}$

(Intermediate)

Scheme 1

$$\delta\Delta G^{\pm} - \rho_{AR} \, \delta\Delta G \, ^{\phi}{}_{AR} \qquad (4)$$

where ΔG is the free energy of activation for the substituted aromatic compound, p-X and $\Delta G^{\phi}{}_{AR}$ is the corresponding value for the unsubstituted triphenylphosphine (p-H).

The correlation parameter, ρ_{AR} is almost constant as 0.972-1.023 ≃ 1.00. This means that the reactions of ADP with p-X are unaffected by the variation in ΔG for the reaction involving the substituent X in p-X. This shows that the activation enthalpy compensates the activation entropy in this reaction series.

To further explore the intermediates as shown in Scheme 1 we have performed EPR measurements. Figure 2 shows the EPR spectra which are obtained from the reaction of ADP (2 mmol : 1 eqiv.) with p-X (p-H, 0.5M in solution: 1 equiv.).

An ambiguous spectrum was obtained by the Gaussian line firstly scanned on the EPR as shown in (1) in Figure 2. To see a clear spectrum, the base-line cross over method is adopted as a kind of the phase-sensitive technique, then a good spectrum is collected as shown in (4) in Figure 2. The g-value and the hyperfine coupling constant, A are shown as g = 10.131 and A = 16G. The g factor and the A factor are in agreement for the separation into three lines due to hyperfine interaction with the nitrogen nucleus.[13]

The more detailed EPR spectra were collected on the EPR as shown in Figure 3. The mole ratio of ADP: p-X(p-H) is changed as 1 : 1 → 1 : 2 → 1 : 5 while scanning on the EPR.
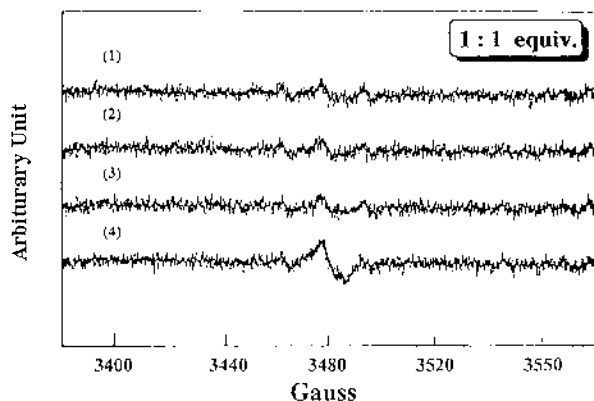
Figure 2. EPR spectra of the radical for the reaction of 1,1'-azodicarbonyldipiperidine (1 equiv.) and triphenylphosphine (1 equiv.) in toluene at room temperature.
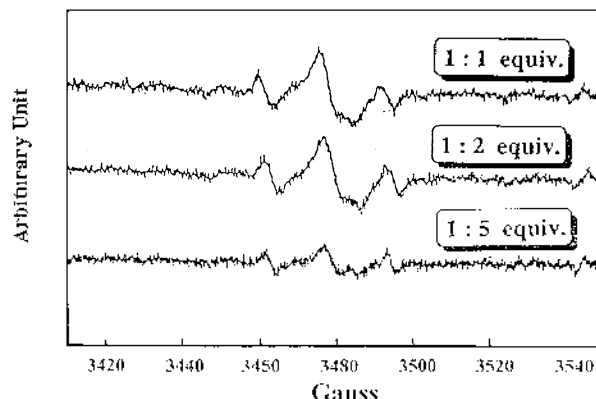
Figure 3. Evolution of EPR spectra for radical containing two nuclei with I = 1/2 when they are equivalent.

The central lines show 3462G, 3478G and 3494G. When the concentration of nucleophile (p-X; p-H) is changed as 1 (equiv.) → 2 (equiv.) → 5 (equiv.), the intensity is decreased. It is caused by the resonances of nitrogen nucleus and methine proton nucleus. This kind of observation has been reported for the reaction of the triphenylphosphinium radical cation with the diazo radical anion.[14] Our results of EPR spectra indicate the formation of arendiazonium salts.[15] It seems that the step in which the diazo radical anion is formed does not depend on whether the two phenyl rings or the two piperidine rings are connected to the diazo function in the reaction series of diazo reaction centers with triphenylphosphines. However, the EPR spectrum shows different intensity when different connection exists between the diazo center and the dicarboxylate. This occurs when the mole ratio as 1 : 1 of azo function and triphenylphosphine[16] is reduced.

It is caused by the amount of triphenylphosphonium cation radical, Ph$_3$P When the concentration of triphenylphosphine is high, the formation of Ph$_3$P is altered and it reduces the amount of -N-N-. When an excess amount of triphenylphosphine attacks the diazo function it produces a stable diazo radical (-N-N-) rather than diazo anion radical (-N-N-).

Therefore the radical anion species are produced by intermolecular electron transfer from the triphenylphosphine to the diazo function below an equivalent concentration of triphenylphosphine.

In conclusion, triphenylphosphine and p-substituted phenyldiphenylphosphines are good nucleophiles to attack the nucleophilic center, diazo function in the reactions of 1,1'-(azodicarbonyl)dipiperidine with p-substituted phenyldiphenylphosphines.

A kind of diazo anion radical is produced with triphenylphosphonium cation radical as transient.

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