The nature of reaction 4 is not presently known. Decomposition of $RhH(P(i\text{-}Pr)_3)_2$ may be indicative of the formation of as-yet-uncharacterized clusters. The orange, plate-like crystals which also grew in the reaction solution (see Experimental Section) may contain the elusive complex $[RhH(P(i\text{-}Pr)_3)_2]_2$[5] but none of these crystals diffracts X-rays, and the true nature of the remaining compound(s) is presently unknown.

Acknowledgment. We are indebted to Johnson Matthey, Inc., Malvern, Pa., for the loan of Rh metal used in this work. This work was kindly supported by the National Science Foundation (CHE76-10335) and the Japanese Society for the Promotion of Science. Support is also acknowledged from the Japan-U.S. Cooperative Science Program (GR021/INT 77-07152). We also wish to thank Dr. P. J. Domaille of E. I. du Pont de Nemours and Co. for valuable assistance with the line shape analysis calculations.

Supplementary Material Available: A listing of observed and calculated structure amplitudes and a table of alkyl hydrogen atom positions (29 pages). Ordering information is given on any current masthead page.

Mechanism of Thermal Decomposition of *trans*-Diethylbis(tertiary phosphine)palladium(II). Steric Effects of Tertiary Phosphine Ligands on the Stability of Diethylpalladium Complexes

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Abstract: *trans*-$[PdR'_2(PR_3)_2]$ with a series of alkyl groups and tertiary phosphine ligands of various steric bulkiness (R' = Et, PR_3 = PMe_2Ph (**1**), PEt_3 (**2**), PEt_2Ph (**3**), $PMePh_2$ (**4**), $PEtPh_2$ (**5**); R' = Pr (**6**), Bu (**7**), PR_3 = PMe_2Ph) are thermolyzed in solution by β-elimination processes liberating alkane and alkene in a 1:1 ratio. Kinetic studies on thermolysis of *trans*-$[PdEt_2(PR_3)_2]$ revealed that they decompose obeying the first-order rate law with respect to the concentration of the palladium complexes. Thermolysis predominantly proceeds from the four-coordinated complex without dissociation of the tertiary phosphine ligand. The minor parallel thermolysis pathway involving the dissociation of the phosphine is completely blocked by addition of the phosphine. Activation enthalpies for thermolysis of the ethylpalladium complexes having various steric bulkiness were virtually constant in the range of 26.0 ± 1.0 kcal/mol whereas activation entropies showed considerable variation with increasing bulkiness of the phosphine. Thermolysis of *trans*-$[Pd(CH_2CD_3)_2(PMePh_2)_2]$ (**8**) cleanly liberated $CH_2{=}CD_2$ and CH_2DCD_3 with a small isotope effect ($k_H/k_D = 1.4 \pm 0.1$). The kinetic results together with examination of the molecular model suggest that the interaction between the bulky phosphine ligands and the ethyl groups causes the destabilization of the Pd–Et bonds. A thermolysis mechanism consistent with the kinetic results assuming an activation state distorted from the square-planar ground state is proposed.

Introduction

Tertiary phosphines are employed in a variety of transition-metal-promoted reactions to control the reaction courses.[2] Understanding of their influence on the stability and reactivity of organometallic species involved in these reactions is expected to provide essential information in clarifying the reaction mechanisms and further designing suitable catalytic reactions promoted by transition-metal catalysts. Effectiveness of tertiary phosphines as auxiliary stabilizing ligands of transition-metal alkyls is well-known as exemplified by an increasing number of successful isolations of transition-metal alkyls having tertiary phosphine ligands.[2e] Although some proposals have been made for accounting for the stability of transition-metal alkyls,[3] the exact reason for the stabilization effect of the tertiary phosphine ligands is still far from clear. The role of tertiary phosphine ligands in stabilizing transition-metal alkyls may be accounted for in terms of electronic and steric factors. An attempt to interpret the stabilization effect of tertiary phosphines and related ligands in terms of the electronic effect as the increase in the ligand field energy to cause the electronic excitation of transition-metal alkyls has been made by Chatt and Shaw,[4] whereas Wilkinson pointed out the importance of the role of auxiliary ligands as a blocking agent to hinder the occurrence of β elimination as the most frequently observed decomposition pathway.[5] There are some examples that show the dissociation of tertiary phosphines is quite important in initiating the thermolysis of transition-metal alkyls,[6] but other examples indicate that explanation of the role of the auxiliary ligands in transition-metal alkyls merely as the blocking agent for the β-elimination process is insufficient.[7] For getting more information concerning the role of the stabilizing ligands on transition-metal alkyls, we have undertaken the kinetic study of thermolysis of

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Table I. IR[a] and ^{1}H NMR[b] Data of *trans*-[$PdEt_2(PR_3)_2$]

	IR data			^{1}H NMR data[c]			
	Pd–Et group			Pd–Et		P–R	
PR_3	ν(C–H)	δ(C–H)	ν(Pd–C)	$-CH_3$	$-CH_2-$	$-CH_3$	$-CH_2-$
PMe_2Ph, **1**	2880 s 2820 s	1135 s 1350 m	452 s	0.92 t[d]	0.36 q[d]	1.68 t[e]	
PEt_3, **2**	2875 s 2825 s	1145 s 1360 m	455 s	*g*	0.33 q[d]	1.12 qui[d]	1.82 m
PEt_2Ph, **3**	2875 s 2800 s	1135 s 1350 m	440 s	1.31 t[d]	0.71 q[d]	0.92 qui[d]	1.92 m
$PMePh_2$, **4**	2890 s 2830 s	1140 m 1355 m	455 s	0.41 t[f]	0.05 q[f]	1.99 t[f]	
$PEtPh_2$, **5**	2900 s 2840 s	1140 s 1355 m	455 m	0.55 t[f]	0.17 q[f]	1.23 qui[f]	2.41 m

[a] KBr disk, in cm^{-1}. [b] 100 MHz, chemical shifts are in δ values with respect to tetramethylsilane as an external or internal standard (downfield positive). Solvent: acetone-d_6 (**1**, **2**); toluene-d_8 (**3**); CD_2Cl_2 (**4**, **5**). Temperature (°C): 25 (**2**); −20 (**1**, **3**); −40 (**4**, **5**). [c] Multiplicity abbreviations are as follows: t, triplet; q, quartet; qui, quintet; m, multiplet. [d] Coupling constants, in Hz, 8. [e] Coupling constants in Hz, 2. [f] Coupling constants are obscured due to broadening. [g] Chemical shift is obscured due to the signals of P–C–CH_3 protons.

diethylpalladium complexes having various tertiary phosphines as continuation of our effort to clarify the thermolysis mechanisms of various transition-metal alkyls.[8]

In view of the utility of palladium-promoted reactions conducted in the presence of tertiary phosphine ligands,[2,9] examination of behavior of palladium alkyls having tertiary phosphine ligands and clarification of the influence of the phosphine ligands on the palladium-promoted reactions are quite desirable. However, studies on the behavior of well-characterized simple palladium alkyls having tertiary phosphines have been quite limited.[10] The recently isolated dialkylbis(tertiary phosphine)palladium(II) complexes have been found to provide convenient materials for the kinetic study on thermolysis mechanism of palladium alkyls. A series of *trans*-[PdR_2L_2] type complexes where R = Et, Pr, and Bu with various tertiary phosphines decompose via β-elimination pathways liberating alkanes and alkenes in a 1:1 ratio. The kinetic study on thermolysis of *trans*-[$PdEt_2(PR_3)_2$] revealed that the β elimination is not blocked by the presence of tertiary phosphines but rather *accelerated* by bulky tertiary phosphines. The strong steric effect of tertiary phosphines to destabilize the palladium ethyls observed here, for the first time to our knowledge, is in contrast with the electronic effect of tertiary phosphines on stability of copper alkyls.[8d] Kinetic studies on thermolysis of *trans*- and *cis*-dimethylpalladium complexes and *cis*-diethylpalladium complexes which decompose through reductive elimination pathways will be reported separately.[12]

Results

Preparation and Characterization of *trans*-[$PdR'_2(PR_3)_2$]. The *trans*-diethylpalladium complexes having a range of tertiary phosphine (PR_3) ligands of various basicities and steric bulkiness have been prepared by the reactions of [$Pd(acac)_2$] (acac = pentane-2,4-dionato ligand) with $AlEt_2(OEt)$,[11] or more preferably with $Al_2Et_3(OEt)_3$, in the presence of PR_3 ligands (PR_3 = PMe_2Ph (**1**), PEt_3 (**2**), PEt_2Ph (**3**), $PMePh_2$ (**4**), $PEtPh_2$ (**5**)). The employment of the ethylaluminum compounds is suitable for obtaining the trans isomers whereas ethyllithium gives cis isomers.[12] The trans isomers are sometimes contaminated with the cis isomers, but the latter can be removed by recrystallization. Since most complexes are thermally unstable and not amenable to microanalysis, they were characterized by macroscopic palladium analysis and acidolysis with concentrated H_2SO_4 and by means of IR and ^{1}H NMR spectroscopy. The IR and ^{1}H NMR data are listed in Table I. The ^{1}H NMR spectra of *trans*-[$PdEt_2(PR_3)_2$] having the methyl-substituted phosphines (**1** and **4**) showed the characteristic triplets, whereas those having the ethyl-substituted phosphine (**2**, **3**, and **5**) showed the apparent quintets supporting the trans configuration.

Table II. Gases Evolved on Thermolysis of *trans*-[$PdEt_2(PR_3)_2$][a]

run	PR_3	additive[b] (mol/L)	evolved gas ratio C_2H_4	C_2H_6	C_4H_{10}	$^1/_2\Sigma$-Et/Pd[c]
1	PMe_2Ph, **1**	st (0.22)	0.49	0.51	0.00	0.95
2	PEt_3, **2**	st (0.22)	0.49	0.51	0.00	1.03
3	PEt_2Ph, 3	st (0.22)	0.49	0.49	0.02	1.03
4	$PMePh_2$, 4	st (0.22)	0.48	0.49	0.03	0.98
5	$PMePh_2$, 4	py (0.31) st (0.13)	0.46	0.54	0.00	0.93
6	$PMePh_2$, 4	py (0.62) st (0.09)	0.48	0.52	0.00	1.00
7	$PMePh_2$, 4	$AsPh_3$ (0.18)	0.49	0.51	0.00	0.97
8	$PMePh_2$, 4	PPh_3 (0.21)	0.49	0.51	0.00	0.97
9	$PMePh_2$, 4	$PMePh_2$ (0.13)	0.49	0.51	0.00	0.93
10	$PMePh_2$, 4	$PMePh_2$ (0.75)	0.44	0.56	0.00	1.02
11	$PEtPh_2$, 5	st (0.22)	0.49	0.49	0.01	1.02

[a] Conditions: [complex] ≈ 0.05 mol/L, at room temperature, in toluene. [b] Key: st, styrene; py, pyridine. [c] $^1/_2\Sigma Et/Pd = \{^1/_2(C_2H_4 + C_2H_6) + C_4H_{10}\}/(complex)$.

Dipropyl and dibutyl analogues having dimethylphenylphosphine ligands have been prepared analogously, but attempts to prepare isopropyl and *tert*-butyl analogues resulted in failure with decomposition of complexes. Thermolysis studies discussed below have been carried out mainly with the diethylpalladium complexes.

Thermolysis Products of *trans*-[$PdEt_2(PR_3)_2$]. Thermolysis of *trans*-[$PdEt_2(PR_3)_2$] in toluene as well as in the solid state[11] liberates ethane and ethylene together with a negligible amount of butane. Thermolysis of *trans*-[$PdPr_2(PMe_2Ph)_2$] and *trans*-[$PdBu_2(PMe_2Ph)_2$] gives likewise propane and propylene and butane and butene-1, respectively. Addition of olefins or tertiary phosphines to the toluene solution containing *trans*-[$PdEt_2(PR_3)_2$] caused the liberation of quantitative amounts of ethane and ethylene as represented by eq 1 and summarized in Table II. In thermolysis in the absence of these additives the liberation of

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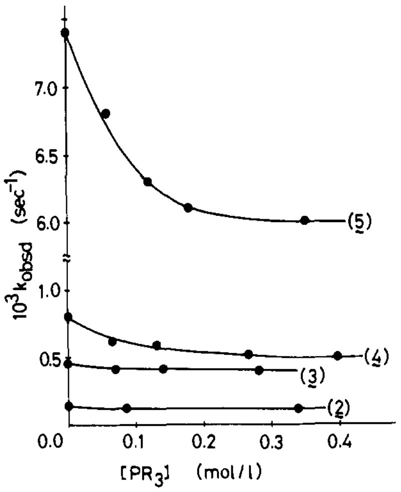
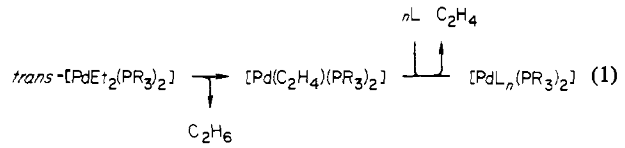


Figure 1. The effect of addition of the same tertiary phosphine as that originally coordinated to the complex on the thermolysis of *trans*-[PdEt$_2$(PR$_3$)$_2$]. Conditions: [complex] ≈ 0.025 mol/L, at 25.5 °C, in toluene.

ethylene was hindered by formation of ethylene-coordinated complexes.



$$trans\text{-}[PdEt_2(PR_3)_2] \xrightarrow[C_2H_6]{} [Pd(C_2H_4)(PR_3)_2] \underset{}{\overset{nL\ \ C_2H_4}{\rightleftarrows}} [PdL_n(PR_3)_2] \quad (1)$$

L = olefin; n = 1 or 2

The study of the olefin-coordinated complexes has been reported separately.[13] The results shown in Table II clearly indicate that the thermolysis proceeds through a β-elimination pathway. Thermolysis of *trans*-[Pd(CH$_2$CD$_3$)$_2$(PMePh$_2$)$_2$] (**8**) liberated cleanly CH$_2$=CD$_2$ and CH$_2$DCD$_3$ without formation of any H/D scrambled products.

$$trans\text{-}[Pd(CH_2CD_3)_2(PMePh_2)_2] \xrightarrow{L} [Pd(L)(PMePh_2)_2] + CH_2{=}CD_2 + CH_2DCD_3$$

The clean formation of CH$_2$=CD$_2$ and CH$_2$DCD$_3$ was confirmed on the basis of IR and mass spectral results (see Experimental Section).

Kinetic Studies. The rate of evolution of ethane and ethylene was followed by measuring the amount of the gases evolved on thermolysis of the palladium diethyls in toluene containing such additives as styrene or tertiary phosphine. While addition of the additives is required to liberate ethylene quantitatively, variation of the styrene concentration did not affect the thermolysis rate.[14] Invariance of the composition of the gases evolved during the thermolysis carried out in the presence of the olefin was also confirmed. The thermolysis proceeded for any tertiary phosphine-coordinated complexes obeying a first-order rate law in the palladium ethyl concentration up to 80–90% decomposition.

The Effects of Addition of Tertiary Phosphines and Other Ligands on the Thermolysis Rates. In contrast to the complete inhibition of thermolysis of *cis*-[PtBu$_2$(PPh$_3$)$_2$][6a] and to considerable retardation of thermolysis of [CoEt$_2$(acac)(PR$_3$)$_2$][8e] by addition of the tertiary phosphine ligands, thermolysis of the toluene solutions of *trans*-[PdEt$_2$(PR$_3$)$_2$] (**2**–**5**) was only slightly retarded by tertiary phosphine as shown in Figure 1. The rate of thermolysis of **1** having the least bulky phosphine at 25.5 °C was too small to observe the effect of addition of PMe$_2$Ph. The investigation at the higher temperature, 32.0 °C, only revealed the presence of a minor retardation effect of the phosphine, the observed first-order rate constant, k_{obsd}, being diminished to 0.21 × 10^{-3} s^{-1} in the presence of 0.43 mol/L of PMe$_2$Ph from the value of 0.23 × 10^{-3} s^{-1} in the absence of the phosphine. The plots of k_{obsd} against the reciprocal of the added PR$_3$ concentration gave straight lines for complexes **2**–**5** as shown in Figure 2.

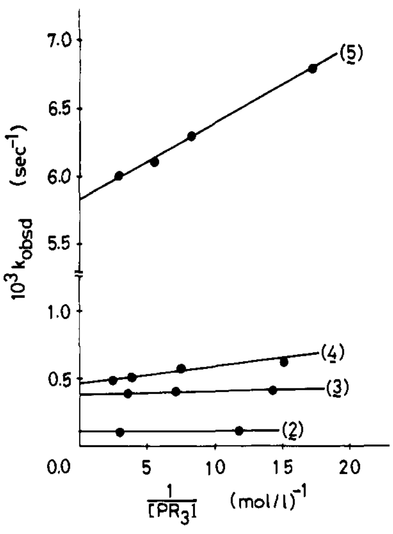
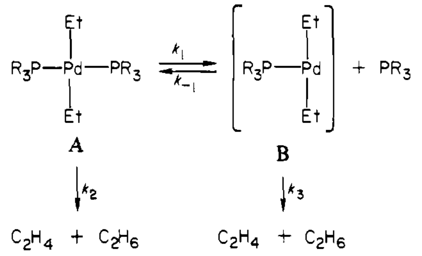


Figure 2. Plots of k_{obsd} vs. 1/[PR$_3$], at 25.5 °C.

Scheme I. Thermolysis Pathways of *trans*-[PdEt$_2$(PR$_3$)$_2$]



The results indicate that the thermolysis proceeds through two parallel pathways as represented in Scheme I, one through the undissociated species *trans*-[PdEt$_2$(PR$_3$)$_2$] and the other through a partially dissociated species [PdEt$_2$(PR$_3$)], the former pathway constituting the predominant route.

Assumption of Scheme I as the thermolysis mechanism with small rate constants k_2 and k_3 compared with k_1 and k_{-1} leads to the kinetic expression

$$\begin{aligned} -\frac{d}{dt}[PdEt_2]_{total} &= k_2[A] + k_3[B] \\ &= \frac{k_2[PR_3] + k_3K}{K + [PR_3]}[PdEt_2]_{total} \\ &= k_2 + \frac{K(k_3 - k_2)}{K + [PR_3]}[PdEt_2]_{total} \qquad (2) \end{aligned}$$

where $K = k_1/k_{-1}$ and $[PdEt_2]_{total} = [A] + [B]$. Hence

$$k_{obsd} = k_2 + K(k_3 - k_2)/(K + [PR_3]) \qquad (3)$$

$$k_{obsd} = k_2 + K(k_3 - k_2)/[PR_3] \qquad (4)$$

if $K \ll [PR_3]$. The assumption that the equilibrium constant K is much smaller than the concentration of the added PR$_3$ is reasonable since the ^{1}H NMR spectra of *trans*-[PdEt$_2$(PR$_3$)$_2$] show no sign of the presence of free PR$_3$ in the examined concentration range. Equation 4 is consistent with the experimental results as demonstrated by Figure 2.

An alternative mechanism involving the five-coordinated species [PdEt$_2$(PR$_3$)$_3$] in the thermolysis of *trans*-[PdEt$_2$(PR$_3$)$_2$] in the presence of the added phosphine may be excluded on the basis of failure to observe such species at high concentrations of the added PR$_3$ by NMR spectroscopy and also from the minimal

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[14] The decomposition rate constants (10$^3 k_{obsd}$, s^{-1}) of **1**–**5** in the presence of styrene are as follows (concentration of styrene is in parentheses, mol/L): **1** (at 32 °C), 0.23 (0.11), 0.22 (0.44); **2** (at 25.5 °C), 0.14 (0.11), 0.14 (0.44); **3** (at 25.5 °C), 0.45 (0.11), 0.45 (0.44); **4** (at 25.5 °C), 0.80 (0.11), 0.81 (0.35); **5** (at 25.5 °C), 4.0 (0.11), 3.9 (0.44).

Table III. k_2 Values for the Thermolysis of *trans*-[$PdEt_2(PR_3)_2$][a]

	PMe_2Ph (1)	PEt_3 (2)	PEt_2Ph (3)	$PMePh_2$ (4)	$PEtPh_2$ (5)
cone angle (θ), deg	122	132	136	136	140
pK_a	6.25	8.65	6.78	4.65	4.91
10^3k_2, s^{-1}	0.085[b]	0.11	0.38	0.46	5.82
ln k_2	−9.37	−9.12	−7.88	−7.68	−5.15

[a] The values obtained from Figure 2. See text. [b] The values obtained by extrapolation of values at higher temperatures to the value at 25.5 °C.

Table IV. The Effects of Addition of Various Tertiary Phosphines on the Thermolysis Rate Constants of *trans*-[$PdEt_2(PEt_2Ph)_2$] (3)[a]

	additive				
	PMe_2Ph	PEt_2Ph	$PEtPh_2$	PPh_3	P(*c*-Hex)$_3$
cone angle (θ), deg	122	136	140	145	170
concn of additive, mol/L	0.12	0.14	0.12	0.13	0.13
10^3k_{obsd}, s^{-1}	0.12	0.41	1.03	1.38	2.83

[a] [3] ≈ 0.025 mol/L, at 25.5 °C, in toluene.

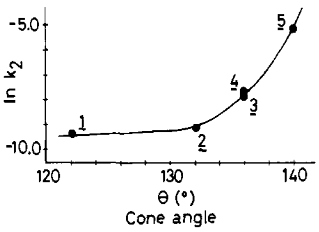

Figure 3. Plot of ln k_2 vs. θ, at 25.5 °C.

Table V. The Effects of Addition of Various Ligands on the Decomposition Rates of *trans*-[$PdEt_2(PMe_2Ph)_2$] (1)[a]

run	additive (mol/L)[b]	10^3k_{obsd}, s^{-1}
1		0.10
2	py (0.031)	5.3
3	py (0.077)	10.8
4	py (0.093)	12.5
5	py (0.124)	18.1
6	py (0.093) PMe_2Ph (0.038)	0.14
7	$AsPh_3$ (0.032)	7.9
8	NPh_3 (0.029)	0.15

[a] [1] ≈ 0.025 mol/L, at 27.0 °C, in toluene containing 0.11 mol/L of styrene. [b] py, pyridine.

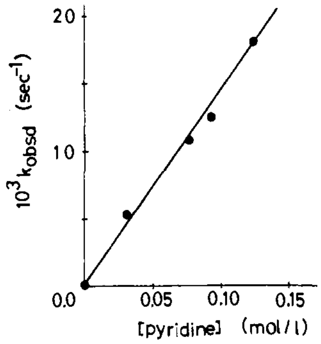

Figure 4. The effect of addition of pyridine on the decomposition rates of *trans*-[$PdEt_2(PMe_2Ph)_2$] (1) at 27.0 °C in the presence of styrene. [complex] ≈ 0.025 mol/L.

influence of the added PR_3 of the high coordinating abilities such as PMe_2Ph, PEt_3, and PEt_2Ph. The intercepts of k_{obsd} values at $1/[PR_3] = 0$ correspond to k_2 values in Scheme I and eq 4, representing the thermolysis rate constants of the undissociated four-coordinate species. The k_2 values for thermolysis of complexes **1**–**5** at 25.5 °C are summarized in Table III together with Tolman's cone angles θ[15] representing the steric bulkiness of the phosphine ligands and the pK_a values of the conjugate acid of the tertiary phosphines to stand for the basicities of the tertiary phosphines.[16] Table III reveals the correlation of the thermolysis rate of *trans*-[$PdEt_2(PR_3)_2$] with the cone angles but not with the basicities of PR_3. Figure 3 demonstrates the pronounced increase in the thermolysis rate of *trans*-[$PdEt_2(PR_3)_2$] with increase in the cone angle of the coordination tertiary phosphine over the θ value of ~132°.

Since the range of the steric bulkiness of the phosphines coordinated in the isolated palladium ethyls **1**–**5** covers rather limited cone angles (θ = 122–140°), the effect of addition of tertiary phosphines of wider range of steric bulkiness to the solution containing **3** was examined. The results shown in Table IV indicate that the addition of phosphines of greater cone angles than that of PEt_2Ph accelerates the thermolysis rate of **3** originally coordinated with PEt_2Ph in the order of $PEtPh_2$ < PPh_3 < P(*c*-Hex)$_3$ whereas addition of the less bulky phosphine PMe_2Ph caused the decrease in the thermolysis rate. Since the ligand exchange of the square-planar phosphine-coordinated complexes is known to proceed with retention of the configuration[17] and in fact the replacement of the coordinated phosphine ligands in **3** with an excess of PMe_2Ph gave *trans*-[$PdEt_2(PMe_2Ph)_2$)] (**1**) (see Experimental Section), addition of PR_3 ligands other than PEt_2Ph presumably gives the partly or totally exchanged $PdEt_2$ complex retaining the trans configuration. The results in Table IV suggest that the thermolysis of such exchanged species is accelerated with replacement by the bulkier phosphines.

Table V shows the effect of addition of ligands other than tertiary phosphines on the thermolysis rate of **1**. The thermolysis rate of **1** is markedly accelerated by addition of pyridine (runs 1–5) and triphenylarsine (run 7) whereas only a minor acceleration effect was observed on addition of triphenylamine (run 8). Figure 4 shows the linear increase in the k_{obsd} value at 25.5 °C with increase in the concentration of pyridine added to the toluene solution containing **1**. These effects may be accounted for by assuming the exchange reaction with replacement of the originally coordinated ligands PMe_2Ph by pyridine or $AsPh_3$. The marked acceleration effect by addition of pyridine which is less bulky than the tertiary phosphines may be an indication of the contribution of electronic factors. Addition of an excess of PMe_2Ph to the pyridine-containing system effectively suppressed the acceleration effect of pyridine (run 6).

Although addition of styrene does not accelerate the thermolysis of the *trans*-[$PdEt_2(PR_3)_2$] complexes, addition of more electronegative olefins such as dimethyl maleate and methyl acrylate slightly increased the thermolysis rate, the k_{obsd} values of 0.80×10^{-3} s^{-1} at 25.5 °C observed in the presence of styrene being raised to 1.0 and 0.90×10^{-3} s^{-1} when 0.35 mol/L each of dimethyl maleate and methyl acrylate was added to the solution containing **4**. The acceleration effect was totally hampered by addition of $PMePh_2$. The results are in sharp contrast with the behavior of diethyl(bipyridine)nickel(II) whose thermolysis is markedly accelerated by addition of electronegative olefins.[8b]

Estimation of Kinetic Parameters and Isotope Effect. Activation parameters for thermolysis of **1**–**5** were derived from Arrhenius plots of the thermolysis rates of undissociated four-coordiante species. For complexes **3**–**5** the thermolysis rates were measured in the presence of added phosphine in the concentration of 0.4 mol/L, whereas for complexes **1** and **2** whose thermolyses are not affected by addition of the same phosphine as coordinated in the complexes the thermolysis rates were measured in the presence

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(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(16) pK_a values of tertiary phosphines were calculated by the equation of $pK_a = 7.85 - 2.67\Sigma\sigma^*$: Kosolapoff, G. M.; Maier, L. "Organic Phosphorus Compounds"; Wiley-Interscience: New York, 1972; Vol. 1.

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Table VI. Activation Parameters for the Thermolysis of *trans*-$[PdEt_2(PR_3)_2]$ at 300 K[a]

	PMe_2Ph (1)	PEt_3 (2)	PEt_2Ph (3)	$PMePh_2$ (4)	$PEtPh_2$ (5)
E_a,[b] kcal/mol	26.4	26.5	26.9	27.0	26.3
$\Delta H^{\ddagger}$,[b] kcal/mol	25.8	25.9	26.3	26.4	25.7
$\Delta S^{\ddagger}$,[c] eu	9.3	10.6	14.0	14.7	17.5
$\Delta G^{\ddagger}$,[b] kcal/mol	23.0	22.7	22.1	22.0	20.5

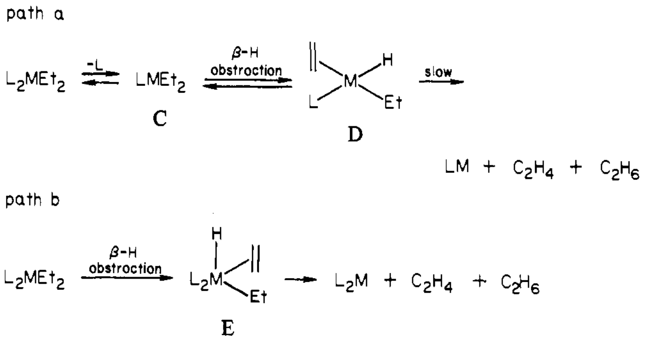
[a] Conditions: **1**, **2**, styrene (0.11 mol/L) was added; **3**, PEt_2Ph (0.40 mol/L) was added; **4**, $PMePh_2$ (0.41 mol/L) was added; **5**, $PEtPh_2$ (0.41 mol/L) was added; [complex] ≈ 0.025 mol/L, in toluene. [b] Experimental error ±1.0 kcal/mol. [c] Experimental error ±1.0 eu. 1 cal = 4.18 J.

of styrene. The results summarized in Table VI show little variance of $\Delta H^{\ddagger}$ values on variation of the coordinated tertiary phosphine ligands whereas the $\Delta S^{\ddagger}$ values are all positive and increase with the increase in steric bulkiness of the coordinated phosphines.

The isotope effect (k_H/k_D) derived from thermolysis of *trans*-$[Pd(CH_2CD_3)_2(PMePh_2)_2]$ (**8**) as compared with the thermolysis rate of undeuterated complex **4** in the presence of $PMePh_2$ (0.27 mol/L) or styrene (0.11 mol/L) was found to be 1.4 ± 0.1. The isotope effect observed here is smaller than the reported isotope effects of 2.29 ± 0.20 in the thermolysis of $[C_6H_{13}CD_2CH_2Ir(CO)(PPh_3)_2]$[18] and of 2.30 ± 0.05 in that of $[Co(CH_2CD_3)_2(acac)(PMe_2Ph)_2]$[8c] but significantly greater than the value expected for the secondary isotope effect.[19] The absence of H/D scrambling in the remaining ethyl groups of **8** and in the evolved gases suggests that β elimination is an irreversible process in contrast to the thermolysis behavior of the platinum analogues.[6a,8h]

Discussion

The kinetic study described here revealed several important features of the thermolysis behavior of the *trans*-$[PdEt_2(PR_3)_2]$ type complexes: (i) The thermolysis proceeds by a clean β-hydrogen elimination mechanism without involving the hydrogen scrambling and with a small isotope effect of $k_H/k_D = 1.4 \pm 0.1$. (ii) Thermolysis takes place predominantly from the undissociated four-coordinate species. (iii) The coordination of sterically demanding phosphine destabilizes the palladium ethyl rather than stabilizing the complex by blocking the site for β elimination. Most of these observations are unprecedented and merit the discussion in comparison with the reported results on thermolysis of transition-metal alkyls.



In thermolysis of a square-planar transition-metal diethyl of the type $[MEt_2L_2]$ via β-elimination pathways, paths a and b are conceivable. Path a involves the preliminary ligand dissociation to provide a coordinatively unsaturated species (C) which undergoes the β-hydrogen elimination to give a square-planar hydridoethyl complex coordinated with ethylene and further reductive elimination of the hydridoethyl complex gives the thermolysis products. When the hydrogen abstraction process, C → D, and its reverse process are rapid and reversible compared with the ensuing slow steps, hydrogen scrambling[6,8e,18,20] and sometimes the isomerization of the branched to linear alkyls are observed for the alkyls higher than ethyl.[8h,21] Path b proceeds without ligand dissociation and consequently the five-coordinate intermediate E is to be considered, if the formation of the hydrido–ethyl–ethylene intermediate of a meaningful lifetime should be involved. The behavior of *trans*-$[PdEt_2(PR_3)_2]$ distinctly differs from that of *cis*-$[PtR_2(PR_3)_2]$ studied in detail.[6a,8h] The kinetic study supporting the occurrence of thermolysis mainly from the undissociated four-coordinate complex suggests that the β elimination takes place in a sterically congested state. Examination of the molecular structure of *trans*-$[PdEt_2(PR_3)_2]$ using a CPK model reveals the considerable steric repulsion between the ethyl groups and the phosphine ligands. Figure 5 depicts the interaction between the ethyl groups and the phosphine ligands with covalent bond radii proposed by Pauling[22] and cone angles of phosphines by Tolman.[15] It is clearly seen that the free rotation of the ethyl groups around the Pd–C bonds is severely restricted and even in the most favorable situation, where the methyl groups are directed perpendicularly to the molecular plane, considerable steric repulsion is expected between the ethyl groups and the bulky phosphine ligands. It is natural to assume that the sterically more demanding phosphines would destabilize the palladium ethyls since the lengthening of Pd–C bonds would release the steric interaction.

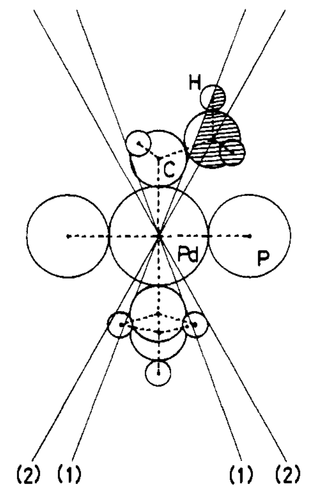


Figure 5. A possible structure of *trans*-$[PdEt_2PR_3)_2]$: (1) PR_3 = $PEtPh_2$ (θ = 140°), (2) PR_3 = PMe_2Ph (θ = 122°); atomic radius (Å), Pd = 1.31, P = 1.10, C = 0.77, H = 0.32; bond angle, Pd–C–C = C–C–H = 109.28°.

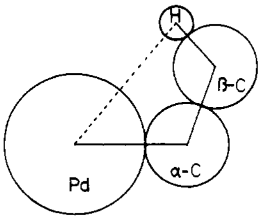


Figure 6. A geometry of a Pd–Et group: atomic radius (Å), Pd = 1.31, P = 1.10, C = 0.77, H = 0.32; bond angle, Pd–C–C = C–C–H = 109.28°.

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(19) The secondary isotope effect of 1.07 in thermolysis of *fac*-$[PtX(Me)_3(PR_3)_2]$ has been reported: Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.

(20) Chatt, J.; Coffey, R. S.; Gough, A.; Thompson, D. J. *J. Chem. Soc. A* **1968**, 190.

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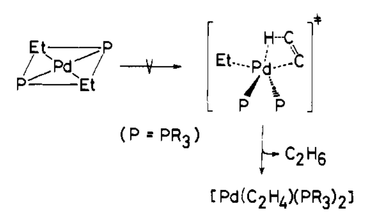
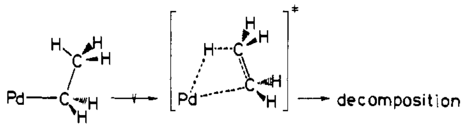
(22) Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960. Covalent bond radius (Å): Pd, 1.31 (dsp^3); P, 1.10 (sp^3); C, 0.77 (sp^3); H, 0.32 (s).

Scheme II



Failures to prepare isopropyl- and isobutylpalladium complexes and successful preparation of propyl and butyl analogues are in line with the assumption of the steric repulsion between the alkyl groups and the phosphine ligands.

As previously pointed out[8d] the distance between the central atom and the β hydrogen of the ethyl group is considerably large to have any significant interaction between the palladium and the β hydrogen in the ground state (Figure 6). We suspect that for the palladium and a β hydrogen to interact causing the hydrogen abstraction by palladium, the lengthening of the Pd–C bond accompanied by bending of the Pd–C_α–C_β angle is required at the activated state as shown in eq 5. If lengthening of the Pd–C bonds, distortion of the square-planar trans configuration, and other processes are involved to achieve the transition state for causing the β elimination, the hydrogen abstraction would constitute part of the whole rearrangement process and the reason for the small isotope effect may be understood. It is tempting to speculate further on the possible configuration of the activation complex. Bending away of the two phosphine ligands from the square molecular plane and approach of a β hydrogen at one of the ethyl groups toward palladium through the space above the molecular plane would bring the complex to a configuration close to the trigonal-bipyramid structure as shown in Scheme II. The relief of the strain existing on the ground state by acquiring the transition state coupled with release of the solvent interacted with the planar ground-state complex may be responsible for the positive values of activation entropies which were observed to increase with increase of the steric bulkiness. It is noted that a theoretical prediction for the transition state in β elimination of square-planar transition-metal alkyls is in agreement with the proposed structure for the transition state.[23]



(5)

Examination of the molecular model also suggests that the approach of an olefin toward palladium above the molecular plane would be difficult. The indication of only minor activation effects by addition of very electronegative olefins is in line with the observation using the model. The result is in contrast with the strong activation effect of electronegative olefins on [NiEt$_2$(bpy)].[8b] Although the strong interaction of the olefins with the nickel complex may be partly due to the higher electron density on the nickel complex which would give more electrons by back-donation to the olefins, the main factor for the stronger interaction with the nickel complex is ascribed to the less steric interaction between the olefin and the flat bipyridine complex as can be clearly seen on its molecular model.

Thermolysis of *cis*-[PdMe$_2$(PR$_3$)$_2$] and *cis*-[PdEt$_2$(PR$_3$)$_2$], on the other hand, proceeds by reductive elimination pathways evolving predominantly ethane and butane, respectively, and the reductive elimination is severely hindered by addition of tertiary phosphines, as will be reported separately.[12] It has been further established that there exist some energy barriers between the partly dissociated T-shaped *trans*-[PdR$_2$L] and *cis*-[PdR$_2$L] species.[12] The contrast between their thermolysis behavior with that of the present trans complex is striking. It is interesting to note that the *reductive elimination* of the *cis*-dialkylpalladium requires the predissociation of the phosphine ligand whereas the dissociation is not a prerequisite to cause *the β elimination* against the generally held view that the tertiary phosphine ligand serves to block a site for β elimination.[5]

Experimental Section

All manipulations were carried out under an atmosphere of nitrogen or argon or in vacuo. Solvents, pyridine, and olefins were dried in the usual manner, distilled, and stored under a nitrogen atmosphere.

Infrared spectra were recorded on a Hitachi 295 spectrometer using KBr pellets. NMR spectra were measured on a JEOL PS-100 spectrometer. ^{1}H NMR signals are referred to tetramethylsilane as internal or external standard. Analysis of the gases evolved by the reactions was carried out by gas chromatography (Shimadzu GC-3BF) after collecting gases using a Toepler pump, by which the volumes of gases were also measured. Analysis of the gases dissolved in solution was also carried out by gas chromatography (Shimadzu GC-6A). Analysis of palladium content was performed by the colorimetric method using 1-nitroso-2-naphthol as a color-producing reagent.[24] The complete ionization of the palladium metal in the complex was achieved by treating the sample with a hot aqua regia.

Triethylphosphine (Strem) was used as purchased. Dimethylphenylphosphine, diethylphenylphosphine, diphenylmethylphosphine, and diphenylethylphosphine were prepared by the reactions of PPhCl$_2$ and PPh$_2$Cl, respectively, with RMgX (R = Me, X = I; R = Et, X = Br). *trans*-[PdEt$_2$(PEt$_3$)$_2$] (**2**) and *trans*-[PdEt$_2$(PMePh$_2$)$_2$] (**4**) were prepared by the reactions of [Pd(acac)$_2$], Al$_2$Et$_3$(OEt)$_3$,[25] and tertiary phosphines according to the method described previously.[11] Characterization of **2** and **4** was carried out on the basis of their IR and NMR spectra and elemental analysis.

Preparation of *trans*-[PdR′$_2$(PR$_3$)$_2$] (PR$_3$ = PMe$_2$Ph, R′ = Et (1), Pr (6), Bu (7); PR$_3$ = PEt$_2$Ph, R′ = Et (3); PR$_3$ = PEtPh$_2$, R′ = Et (5)). To the heterogeneous red mixture of [Pd(acac)$_2$] (1.5 g, 5 mmol), PMe$_2$Ph (1.5 mL, 11 mmol), and diethyl ether (30 cm^3) cooled at −70 °C, Al$_2$Et$_3$(OEt)$_3$ (6.0 mL, 20 mmol) was added dropwise. On raising the temperature of the mixture gradually, it became homogeneous at −30 °C. The solution was stirred for several hours at 0 °C. After concentration of the solution to ca. 10 mL, cooling at −70 °C overnight yielded a white precipitate, which was filtered, washed with a small amount of Et$_2$O at the same temperature, and dried in vacuo. The product was recrystallized from cold Et$_2$O to yield white crystals of *trans*-[PdEt$_2$(PMe$_2$Ph)$_2$] (**1**) (0.54 g, 25%).

Similarly obtained were *trans*-[PdPr$_2$(PMe$_2$Ph)$_2$] (**6**) and *trans*-[PdBu$_2$(PMe$_2$Ph)$_2$] (**7**) by the use of respectively AlPr$_2$(OEt) and AlBu$_2$(OEt) in place of Al$_2$Et$_3$(OEt)$_3$. *trans*-[PdEt$_2$(PEt$_2$Ph)$_2$] (**3**) and *trans*-[PdEt$_2$(PEtPh$_2$)$_2$] (**5**) were also prepared analogously by using PEt$_2$Ph and PEtPh$_2$, respectively, in place of PMe$_2$Ph. Complex **5** could not be purified by recrystallization due to its poor solubility.

Since these complexes are too unstable for microanalysis, their characterization was carried out by means of IR and ^{1}H NMR spectroscopy, macroscopic analysis of Pd, and determination of the amount of alkane evolved on acidolysis with concentrated H$_2$SO$_4$. IR: **6**, δ_{C-H} = 1345 and 1115 cm^{-1}, ν_{Pd-C} = 550 cm^{-1}; **7**, δ_{C-H} = 1360 and 1115 cm^{-1}, ν_{Pd-C} = 550 cm^{-1}. ^{1}H NMR (δ at −40 °C): **6** (in CD$_3$COCD$_3$), 0.36 (quintet, Pd–CH$_2$–, 4 H), 0.92 (multiplet, Pd–C–CH$_2$–, 4 H), 0.69 (triplet, Pd–C–C–CH$_3$, 6 H), 1.71 (triplet, P–CH$_3$ 12 H), 7.56 and 7.91 (multiplet, P–Ph, 10 H); **7** (in CD$_2$Cl$_2$), 0.16 (broad, Pd–CH$_2$–, 4 H), 0.92 (broad, Pd–C–CH$_2$–CH$_2$–, 8 H), 0.60 (broad, Pd–C–C–C–CH$_3$, 6 H), 1.60 (triplet, P–CH$_3$, 12 H), 7.36 and 7.58 (multiplet, P–Ph, 10 H). Anal. Calcd for 1 (C$_{20}$H$_{32}$P$_2$Pd): Pd, 24.1. Found: Pd, 24.4. Calcd for **6** (C$_{22}$H$_{36}$P$_2$Pd): Pd, 22.7. Found: Pd, 22.7. Calcd for **7** (C$_{24}$H$_{40}$P$_2$Pd): Pd, 21.4. Found: Pd, 21.3. Calcd for **3** (C$_{24}$H$_{40}$P$_2$Pd): Pd, 21.4. Found: Pd, 21.8. Calcd for **5** (C$_{32}$H$_{40}$P$_2$Pd): Pd, 17.9. Found: Pd, 18.0. The amounts of corresponding alkanes evolved by acidolysis with concentrated H$_2$SO$_4$ (mol/mol of complex): **1** (C$_2$H$_6$), 1.8; **6** (C$_3$H$_8$), 1.4; **7** (C$_4$H$_{10}$), 1.4; **3** (C$_2$H$_6$), 1.8; **5** (C$_2$H$_6$), 1.9.

Kinetic Studies. A 20-mL Schlenk tube containing a toluene solution (4 mL) of the complex (about 0.05 g) and the additive (styrene or tertiary phosphine) was connected to a vacuum line equipped with a mercury manometer, and the system was evacuated. The Schlenk tube was placed in a thermostated bath (HAAKE Type FK-2) controlled to ±0.5 °C. The rate constants for thermolysis of the complex were obtained by measuring the volume of the gas evolved with time. It was confirmed

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[24] Cheng, K. L. *Anal. Chem.* **1954**, *26*, 1894.

[25] In a previous paper[11] we used AlEt$_2$(OEt) as an alkylation reagent. Later, we found that Al$_2$Et$_3$(OEt)$_3$ was more suitable for the preparation of *trans*-[PdEt$_2$(PR$_3$)$_2$] complexes with respect to the yield of the complex. Al$_2$Et$_3$(OEt)$_3$ was prepared by the reaction of AlEt$_3$ and EtOH in a molar ratio of 2/3 under a nitrogen atmosphere at −20 to 0 °C.

by means of GLC that the compositions of the gases evolved by the reactions did not vary through the reaction courses.

Preparation of *trans*-[Pd(CH$_2$CD$_3$)$_2$(PMePh$_2$)$_2$] (8) and Its Thermolysis in Toluene. *trans*-[Pd(CH$_2$CD$_3$)$_2$(PMePh$_2$)$_2$] (**8**) was prepared by the reaction of [Pd(acac)$_2$], PMePh$_2$, and Al(CH$_2$CD$_3$)$_2$(OEt)[8g] in a similar manner to the preparation of **4**. **8** was identified by means of IR spectroscopy: ν_{C-D} (KBr disk, in cm^{-1}) = 2180, 2150, 2100, 2050 cm^{-1}. The isotopic purity of **8** (97%) was determined by analyzing the ^{1}H NMR spectrum of (CD$_3$CH$_2$)$_2$CO derived from **8** by the reaction with CO,[11] since **8** itself was poorly soluble in solvents to allow the accurate determination of the deuterium content in **8**.

Gases evolved on thermolysis of **8** (about 0.025 mol/L) in toluene (4 mL) containing styrene (0.11 mol/L) or PMePh$_2$ (0.27 mol/L) at 25.5 °C were collected and analyzed by IR spectroscopy and mass spectrometry. The IR spectrum revealed that ethylene evolved on thermolysis consisted solely of CH$_2$CD$_2$: ν_{C-D} (cm^{-1}) 946 and 752.[8e] Evolution of C$_2$D$_4$H$_2$ was confirmed by means of mass spectrometry.

Ligand Exchange Reaction of *trans*-[PdEt$_2$(PEt$_2$Ph)$_2$] (3) with PMe$_2$Ph. To a colorless solution (3 mL) of *trans*-[PdEt$_2$(PEt$_2$Ph)$_2$] (0.18 g, 0.36 mmol) in Et$_2$O cooled at −70 °C, PMe$_2$Ph (0.15 mL, 1.1 mmol) was added with a syringe. After stirring of the solution for 2 h, the solution was concentrated to yield a white precipitate. The precipitate was filtered, washed with a small amount of Et$_2$O at −70 °C, and dried in vacuo at −10 °C. The precipitate was identified as *trans*-[PdEt$_2$(PMe$_2$Ph)$_2$] (1) (0.13 g, 84%) on the basis of the IR spectrum.

Acknowledgment. The authors are indebted to Dr. Takakazu Yamamoto and Dr. Sanshiro Komiya for their helpful discussion. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan.

α-Deuterium Isotope Effects in Benzyl Halides. 2. Reaction of Nucleophiles with Substituted Benzyl Bromides. Evidence for a Change in Transition-State Structure with Electron-Donating Substituents

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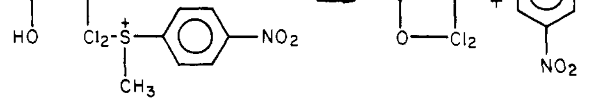
Abstract: Rates and α-D isotope effects have been determined for the following substrates and nucleophiles: *p*-methoxybenzyl bromide (Et$_3$N, SCN$^-$, N$_3^-$, OH$^-$, S$_2$O$_3^{2-}$), benzyl bromide (Et$_3$N, SCN$^-$, N$_3^-$, OH$^-$, S$_2$O$_3^{2-}$), and *p*-nitrobenzyl bromide (Et$_3$N, SCN$^-$, N$_3^-$, S$_2$O$_3^{2-}$). In nearly all cases the second-order rate constant for each nucleophile goes though a minimum for the unsubstituted compound while the α-D isotope increases monotonically in the sequence *p*-NO$_2$ > *p*-H > *p*-OCH$_3$. These results are consistent with an increasing "looseness" of the S$_N$2 transition state as the substituent on the aromatic ring becomes more electron donating.

Introduction

Nearly 30 years ago Kohnstam[1] suggested that as the nucleophile becomes weaker in the S$_N$2 reactions of *p*-methoxybenzyl chloride (I) and *p*-phenoxybenzyl chloride (II), the charge on the benzylic carbon increases. Thus, the sum of the bond orders between the α-carbon–nucleophile bond and the α-carbon–leaving group bond was less for weak nucleophiles than for strong nucleophiles. For example, I solvolyzes (S$_N$1) 135-fold as rapidly as II while in the S$_N$2 reactions of these two substrates the rate of I vs. II is dependent on the strength of the attacking nucleophile. With weak nucleophiles such as NO$_3^-$ a 139-fold rate enhancement was observed whereas for strong nucleophiles such as N$_3^-$ a 4.9-fold rate enhancement was found. Schematically, this may be represented as in Figure 1.

In recent years analysis of the S$_N$2 transition state using the reacting bond rule[2] and O'Ferrall[3]–Jencks[4] diagrams has afforded deeper insight into this reaction.[5-7] Harris[6] has summarized several predictions concerning S$_N$2 reactions of benzyl systems by using these O'Ferrall type reaction coordinate diagrams. For solvolysis of substituted benzyl tosylates and chlorides the experimental changes in m, k_H/k_D, k_{OTS}/k_{Cl}, and $k_{\text{ethanol}}/k_{H_2O}$ are as predicted for a transition state midway between reactants and products for a change to electron-donating substituents.

In a series of significant papers Schowen[8-10] has shown how α-D isotope effects can be used to deduce the "tightness" of the S$_N$2 transition state and how steric compression may lead to enzymatic accelerations in enzyme-mediated methyl transfer. Specifically, Schowen[8] has reported α-D isotope effects for reactions 1 and 2. Once again, the poorer nucleophile furnishes the looser transition state.



$$k_{H_2}/k_{D_2} = 1.17 \pm 0.02$$

Westaway and Ali[11] have studied the reaction of substituted phenyldimethylbenzylammonium ions with thiophenoxides in DMF (Figure 2). Secondary α-D isotope effects, nitrogen-leaving

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