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The Arbuzov Reaction of Alkyl Diphenylphosphinites with 10-Methylacridinium Ion. Kinetic Study on the Formation and the Decomposition of Phosphonium Intermediates

Shinro YASUI,* Kosei SHIOJI,† Masakuni YOSHIHARA,† Toshihisa MAESHIMA,† and Atsuyoshi OHNO††
Tezukayama College, Gakuen-Minami, Nara 631
†Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higashi-Osaka 577
††Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

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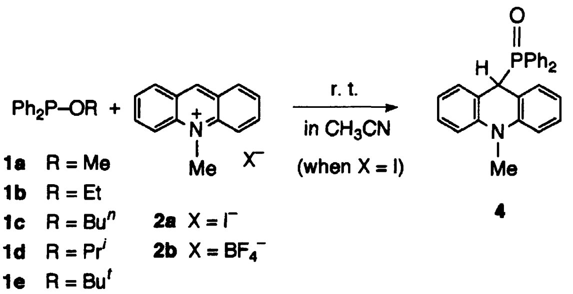
Alkyl diphenylphosphinites (**1**) react rapidly with 10-methylacridinium iodide (**2a**) to afford the corresponding phosphonium ions (**3**), which gradually decompose to phosphine oxide, the expected Arbuzov product. Large difference in the rate of the first (phosphonium-forming) and the second (phosphonium-decomposing) steps enables us independent kinetic investigation for both steps, with which it has been found that the first step obeys second-order kinetics with first-order with respect to **1** and **2a**, respectively. The second step proceeds according to either the S_N2 mechanism when alkyl substituent in **1** is primary or secondary, in which iodide ion acts as a nucleophile, or the S_N1 mechanism when the substituent is tertiary. Closer examination on the first step with activation parameters reveals that the transition state of this step becomes more reactant-like as the substituent in **1** becomes bulkier. For the second step, survey of the activation parameters shows that the breaking of the carbon–oxygen bond in **3** predominates over the formation of the oxygen–phosphorus double bond.

Conversion of trivalent phosphorus compounds to the corresponding pentavalent ones is energetically downhill, and many organic synthetic methods coupled to this exothermic process have been developed so far.[1—6] One of distinct features of these reactions is that the process involves a phosphonium or a phosphorane intermediate. There are therefore two key steps in the reaction, i.e., formation and decomposition of the intermediate, and the mechanisms in both steps have to be well-elucidated in order to obtain desired products in high yields.

The Arbuzov reaction, which proceeds via a phosphonium (or sometimes a phosphorane) intermediate,[7] is a prototype of the mechanistic study on the reactions. There have been, however, very few kinetic studies on the both steps along a certain Arbuzov-type reaction,[8—10] and especially the kinetic investigation on the decomposition of a phosphonium intermediate has scarcely been presented. This is mainly because the intermediate of the Arbuzov reaction is usually transient and its decomposition is too fast to be measured.[11]

We found that the Arbuzov-type reaction takes place between alkyl diphenylphophinites (**1**) and 10-methylacridinium iodide (**2a**) in the dark at room temperature.[12] It was then revealed that the process is composed of rapid formation of a stable phosphonium intermediate and its slow decomposition to the final product, a phosphine oxide **4** (Scheme 1). This reaction system obviously has two advantages for the study upon the mechanisms of the formation and the decomposition of phosphonium ions; the large difference in the rate of phosphonium-forming and -decomposing steps allows us to postulate that both steps are kinetically independent of each other, and the high stability of the phosphonium ion in this system enables full spectroscopic analyses of its structure.



Scheme 1.

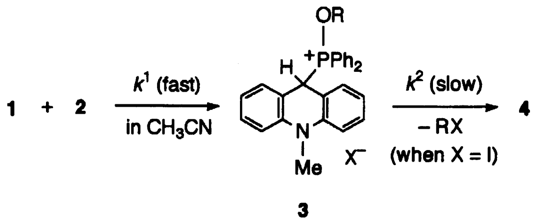
We here discuss the detailed mechanism of this reaction based on the rate constants and the activation parameters for both the formation and the decomposition of the phosphonium intermediate. The study not only portrays a whole story about the single Arbuzov reaction, but also provides a useful information on a favorable structure of trivalent phosphorus compounds to obtain the products in high yields in organic syntheses mediated by a trivalent phosphorus compound.

Results and Discussion

Reaction of 1 with 2. When solutions of **1** and **2a** in equimolar amounts in acetonitrile were mixed in the dark at room temperature, reddish-brown color from **2a** disappeared immediately, and the prolonged reaction finally gave a white precipitate. These observations indicate that the reaction takes place through rapid formation of an intermediate followed by its slow decomposition to the final product. The chemical shift in ^{31}P NMR (δ=27 from H_3PO_4 in $CDCl_3$) as well as the spectral data from ^{1}H and ^{13}C NMR (listed in Experimental Section) of the precipitate shows that the precipitate is (9,10-dihydro-10-methyl-9-acridinyl)diphenylphosphine oxide (**4**), the expected Arbuzov product from **1** and **2a**. The structure was also confirmed by elemental analysis as well as mass spectroscopy. The yield was nearly quantitative.

When 10-methylacridinium tetrafluoroborate (**2b**) was used in place of the iodide salt **2a**, immediate disappearance of the reddish-brown color from **2b** was observed upon mixing the two components. No precipitate appeared when **1a**—**d** reacted with **2b**, whereas the reaction of **1e** (R=Bu^t) with **2b** finally gave **4** in a nearly quantitative yield as was observed in the reactions with **2a**. These observations imply that iodide ion participates in the decomposition of the intermediate except for the reaction of **1e** (vide infra).

Structure of the Intermediate. In order to determine the structure of the intermediate, the reactions of **1a**—**e** with **2a** in CD_3CN were analyzed by NMR spectroscopy. The intermediates were stable enough at room temperature to perform full spectroscopic analyses on either proton-decoupled ^{31}P or ^1H NMR except for the reaction of **1a** (R=Me).[13] The values of the chemical shifts obtained on ^{31}P and ^1H NMR spectra are listed in Tables 1 and 2, respectively, along with those for the starting materials **1a**—**e**. The ^{31}P NMR chemical shift observed in the reaction of **1b** with **2b** corroborates that **1** reacts with acridinium cation to form the same kind of intermediate irrespective of its counter anion. The phosphorus signals from the intermediates exhibit upfield shift when compared with those from the starting materials **1a**—**e**. The chemical shifts in this region can be assigned to phosphonium salts **3a**—**e**[14—16] but not to pentavalent phosphoranes.[14,17] It is thus concluded that the reaction of **1** with **2a** proceeds via the phosphonium ion **3** as the intermediate as depicted in Scheme 2.



Scheme 2.

The values of the chemical shifts of protons in the substituent R in **3a**—**e** are not largely different from the corresponding ones in **1a**—**e**, respectively, which suggests that the R group in **3** does not release electrons to the phosphonium center. In fact, the Hammett plots of ^{31}P NMR chemical shifts from **1a**—**e** and **3a**—**e** against the Taft σ^*-values for the R group in the form of RCH_2[18,19] give linear lines, respectively, providing a slightly larger value of the slope (ρ^*-value) for **1** than for **3** (Fig. 1). In other words, the extent of electron demand to the R group is smaller in the phosphonium center of **3** than in the neutral phosphorus atom of **1** indicating that this cationic center of **3** is stabilized by other factor(s) than the electron-donating participation by the OR group.

A phosphonium ion with a bulky substituent such as neopentyl group on the oxygen of the P–O bond is stable due to a crowded structure of the substituent which prevents a nucleophile from approaching the reaction center (α-carbon in the substituent).[8,20] Such a steric factor, however, seems unimportant here, because even the ethyl derivative (**1b**) forms a relatively stable phosphonium ion. Examination with CPK molecular models indicates that aromatic substituents on the phosphorus atom in **3** provide no steric hindrance against the attack of a nucleophile. Mesomeric contribution from the adjacent phenyl groups, therefore, is responsible for the stabilization of **3**.[21] The dihydroacridinyl group, to which the positive charge cannot be transferred from the phosphorus via π-system, would have little effect for the stabilization of **3**, if any. Indeed, trialkyl phosphites, which has no phenyl group, react very rapidly with **2** to afford the corresponding phosphates.[22] The reactions of the phosphites proceed probably through a similar but

Table 1. ^{31}P NMR Chemical Shifts of **1** and **3** in CD_3CN

	δ/ppm$^{a)}$		
Compound	**1**	**3**$^{b)}$	
a (R=Me)	116.5	—$^{c)}$	(60.0)$^{d)}$
b (R=Et)	110.6	57.1	(57.1)$^{d)}$
c (R=Bu^n)	111.3	57.1	
d (R=Pr^i)	105.0	54.3	
e (R=Bu^t)	85.6	38.5	

a) From 85% H_3PO_4. b) Obtained in the reaction of **1** with **2a** unless otherwise noted. c) The intermediate formed from the reaction of **1a** with **2a** (X=I) decomposed too rapidly to perform NMR analyses. d) The values in parentheses denote the chemical shift obtained in the reaction of **1** with **2b** ($X=BF_4$).

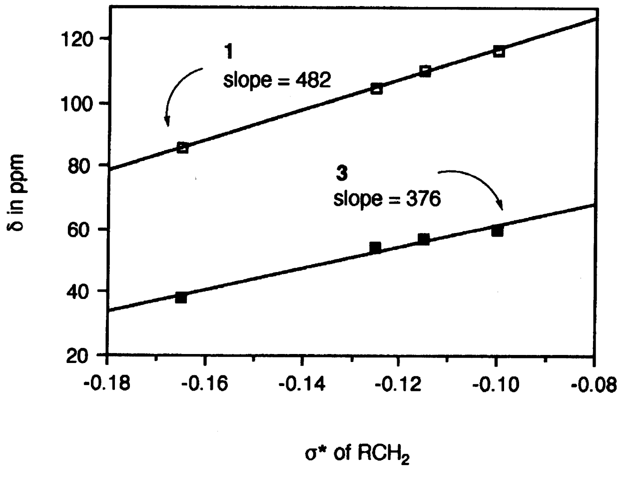


Fig. 1. The Hammett plots of ^{31}P NMR chemical shifts of **1** and **3** vs. Taft σ^*.

Table 2. ^{1}H NMR Spectral Data of **1** and **3** in CD_3CN[a)]

Compnd.	X	9-H[b,c)]	10-Me[d)]	Aromatic[e)]	Alkane protons in R
1a	—	—	—	7.35—7.54	3.64 (3H,d;$^3J_{PH}$=13.80 Hz)
1b	—	—	—	7.30—7.54	1.29 (3H,t), 3.93 (2H,dq;$^3J_{PH}$=9.89 Hz)
1c	—	—	—	7.30—7.54	0.90 (3H,t), 1.39 (2H,tq), 1.65 (2H,tt), 3.85 (2H,dt;$^3J_{PH}$=9.19 Hz)
1d	—	—	—	7.30—7.54	1.28 (6H,d), 4.17 (^{1}H,dsep;$^3J_{PH}$=8.66 Hz)
1e	—	—	—	7.30—7.55	1.39 (9H,s)
3a	BF_4	6.15 (16.0)	2.71	6.75—8.59	3.65 (3H,d;$^3J_{PH}$=12.2 Hz)
3b	I	6.28 (18.9)	2.54	6.74—8.57	1.21 (3H,dt;$^4J_{PH}$=1.31 Hz), 3.92 (2H, dq;$^3J_{PH}$=6.85 Hz)
	BF_4	6.15 (18.9)	2.53	6.74—8.57	1.21 (3H,dt;$^4J_{PH}$=1.10 Hz), 3.92 (2H,dq;$^3J_{PH}$=6.40 Hz)
3c	I	6.31 (18.9)	2.54	6.88—7.92	0.84 (3H,t) 1.40 (2H,tq) 1.54 (2H,dtt;$^4J_{PH}$=1.00 Hz) 3.86 (2H, dt;$^3J_{PH}$=6.1 Hz)
	BF_4	6.17 (18.9)	2.52	6.93—7.93	0.83 (3H,t), 1.30 (2H,tq), 1.54 (2H,dtt;$^4J_{PH}$=1.00 Hz) 3.84 (2H,dt;$^3J_{PH}$=6.27 Hz)
3d	I	6.32 (19.0)	2.49	6.71—7.93	1.13 (6H,dd;$^4J_{PH}$=0.80 Hz), 4.39 (1H, desp;$^3J_{PH}$=6.20 Hz)
	BF_4	6.16 (18.9)	2.49	6.72—7.93	1.14 (6H,dd;$^4J_{PH}$=0.90 Hz), 4.37 (1H,desp;$^3J_{PH}$=7.96 Hz)
3e	I	5.45 (21.6)	2.74	6.75—7.76	1.72 (9H,d;$^4J_{PH}$=1.00 Hz)

a) δ (ppm) from TMS. Spectra were obtained on a 200 MHz apparatus. b) 1H, d. c) The values in parentheses denote coupling constants $^2J_{P-9-H}$ in Hz. d) 3H, s. e) 18H, m.

much less stable phosphonium intermediate.

Kinetics for the Formation of 3. The reaction of **1** with **2** to form **3** obeyed second-order kinetics with first-order with respect to **1** and **2**, respectively (see Experimental Section). The second-order rate constants k^1 obtained at a variety of temperatures for each substrate are reported in Table 3 together with the activation parameters calculated from k^1's. The reactions of **1b** and **1c** with **2b** afforded the identical values in the rate constant to those for the reactions with **2a**, respectively, within experimental error revealing that a counter anion exerts no influence on the reaction rate in this step. There is a rough tendency that the reaction rate increases in the order of the substituent R in **1**=primery<secondary<tertiary, which seems to indicate that a steric factor controls the rate in this step only to a small extent. However, more detailed discussion should be given based on the activation parameters.

The plot of the entropies vs. the enthalpies of activation for the reactions of **1a**—**e** ($\Delta S^{\ddagger}_{1}$ and $\Delta H^{\ddagger}_{1}$, respectively) shows an isokinetic relationship with the isokinetic temperature β=390 K (Fig. 2), which means that the free energy of activation $\Delta G^{\ddagger}_{1}$ around 390 K must be almost constant irrespective of R. Figure 3 clearly demonstrates that negligible change in $\Delta G^{\ddagger}_{1}$ with different R's results from compensation of large changes in $\Delta H^{\ddagger}_{1}$ and $\Delta S^{\ddagger}_{1}$.[23)] Since both the reactant and the product in this step have a positive charge, both the reactant-like and the product-like transition states would be solvated to a similar extent. Therefore, the contributions to the activation parameters from solvation for these two extremes would be similar. On the other hand, a tighter association between the reagents in the transition state results in a less favorable $\Delta S^{\ddagger}_{1}$, and it would likely accompany a stronger interaction between the reagents, lowering $\Delta H^{\ddagger}_{1}$.[24)] In other words, as the transition state becomes more product-like, $\Delta H^{\ddagger}_{1}$ becomes smaller and $\Delta S^{\ddagger}_{1}$ becomes smaller (more negative) due to the association of the reagents. Thus, the smallest value of $\Delta H^{\ddagger}_{1}$ and the most negative value of $\Delta S^{\ddagger}_{1}$ observed in the reaction of **1a** (R=Me) indicate that the transition state is product-like in this case (Structure I in Scheme 3). On the contrary, the largest value of $\Delta H^{\ddagger}_{1}$ and the least negative value of $\Delta S^{\ddagger}_{1}$ observed in the reaction of **1e** (R=Bu^t) manifest the reactant-like transition state (Structure III in Scheme 3). Clearly, the bulkiness of the substituent R plays a crucial role to determine the structure of the transition state. The origin of the irregular change in $\Delta H^{\ddagger}_{1}$ and $\Delta S^{\ddagger}_{1}$ observed for **1b** (R=Et) is not clear, but may be explainable in the term of the less solvated structure of the transition state; a "medium-sized" substituent such as ethyl group provides an opportunity that the posi-

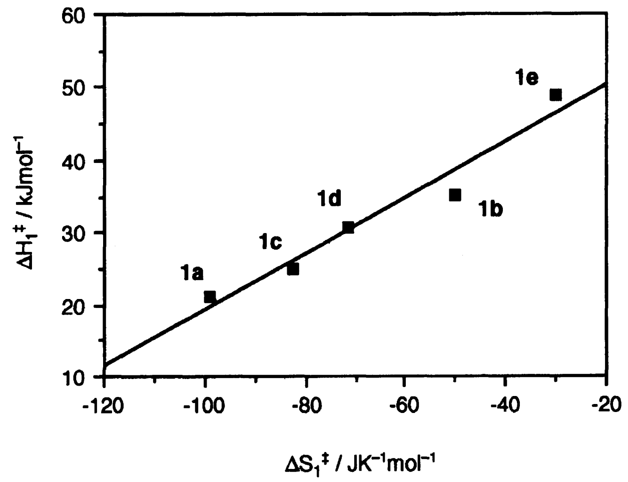


Fig. 2. $\Delta H^{\ddagger}_{1}$-$\Delta S^{\ddagger}_{1}$ relationship in the reaction of **1** with **2a** to form **3**.

Table 3. Kinetic Parameters for the Reaction of **1** with **2a** to form **3** in Acetonitrile[a)]

	$k^1\times10^{-3}$/dm^3 mol^{-1} s^{-1}				
Temp/°C	**1a**	**1b**	**1c**	**1d**	**1e**
25	8.46	10.1	11.7	4.38	0.438
41	15.1	23.3 (22.2)[b)]	21.1 (22.2)[b)]	9.88	1.52
50	17.2	32.6	27.9	12.0	2.07
$\Delta H_1{}^{\ddagger}$ (kJ mol^{-1})	21.0±4.1	35.2±1.1	25.1±0.6	30.8±5.7	48.8±8.2
$\Delta S_1{}^{\ddagger}$ (J K^{-1} mol^{-1})	−99.2±13.3	−50.2±3.4	−82.6±2.0	−71.5±18.5	−30.0±26.5
$\Delta G_1{}^{\ddagger}{}_{300}$ (kJ mol^{-1})	50.8±0.2	50.3±0.1	49.9±0	52.3±0.2	57.8±0.3

a) In the dark. b) The values in parentheses denote the rate constants for the reaction of **1** with **2b**.

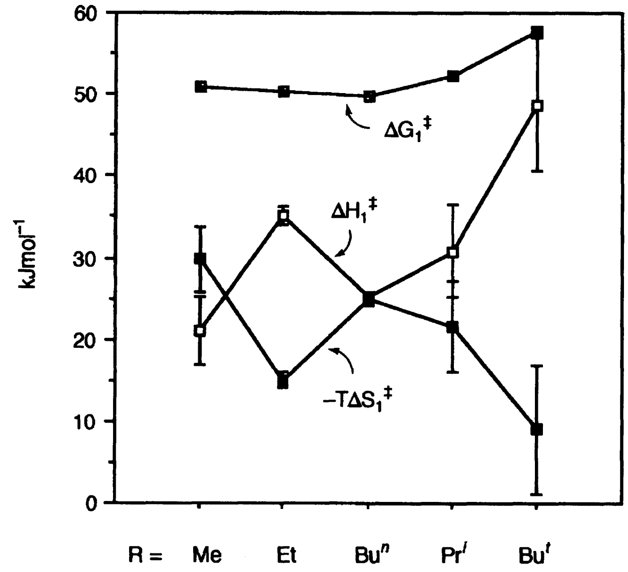
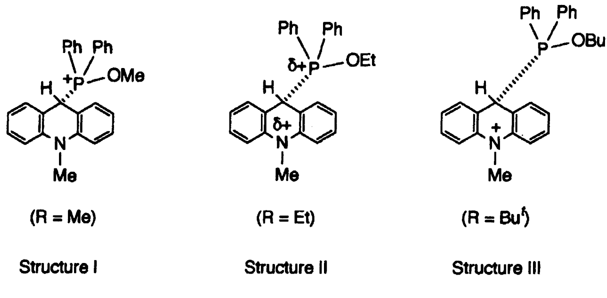


Fig. 3. Dependence of the activation parameters on the bulkiness of the substituent R in the formation of **3**. The substituents are arranged along the abscissa according to increasing order of the bulkiness of R from the left to the right.



Scheme 3.

tive charge delocalizes not only on the phenyl groups but also on the dihydroacridinyl moiety in the transition state (Structure II in Scheme 3), which decreases the degree of the solvation and consequently increases both $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$.

As anticipated by the examination with CPK molecular models, **3e** (R=Bu^t) might have the most strained structure, which means that **3e** is the least stable among the phosphonium ions **3a**—**e**. So, the transition state for the formation of **3e** would be the latest among those for **3a**—**e**, as the Hammond postulate states.[25)] However, the reverse situation was indeed observed, apparently interfering with this postulate. Structural change of the transition state with the change of the substituent R therefore should be large enough so that the change of the mechanism is no longer continuous.

Interestingly, the data from the work on the Menschutkin reaction of *N*,*N*-dialkylanilines with methyl iodide provide an isokinetic trend similar to that observed in the present study, in which $\Delta H^{\ddagger}$ increases with $\Delta S^{\ddagger}$ as the alkyl substituent becomes bulkier.[26)] This may indicate that the larger the alkyl substituent(s), the more reactant-like the transition state.

Kinetics for the Decomposition of 3 to 4. Since the rate for the decomposition of **3** to **4** is much slower than that for the formation of **3**, the rate for the former step can be followed spectrophotometrically without interference from the latter step. The rates were measured under the pseudo-first-order conditions in the presence of a 20—80 times excess amount of tetraethylammonium iodide. It was then confirmed that **3a**—**d** decompose to **4** according to second-order kinetics with first-order with respect to **3** and iodide ion, respectively (see Experimental Section). The second-order rate constants for this step k^2 obtained are summarized in Table 4 together with the activation parameters calculated. On the other hand, the rate of the decomposition of **3e** (R=Bu^t) was independent of the concentration of the added tetraethylammonium iodide, and the use of the tetrafluoroborate salt of 10-methylacridinium **2b** in place of the iodide salt **2a** did not alter the rate of the decomposition of **3e**. These observations show that this reaction proceeds through the S$_N$1 mechanism, precluding the possibility that **3e** decomposes from the ion pair composed of the phosphonium cation **3e** and iodide anion to give first-order kinetics experimentally.[8,27)] The first-order rate constants for the decomposition of **3e** as well as the activation parameters for the reaction of **3e** are listed in Table 5. Thus, the mechanism changes from S$_N$2 when R=Me, Et, Bu^n, and Pr^i to S$_N$1 when

Table 4. Kinetic Parameters of the Decomposition of **3a**—**d** to **4** in Acetonitrile[a)]

	$k^2\times10^3$/dm^3 mol^{-1} s^{-1}			
Temp/°C	**3a**	**3b**	**3c**	**3d**
5	110	0.911	0.631	0.724
20	534	4.89	2.53	1.33
36	1590	17.6	11.7	5.56
51	—	85.3	46.8	11.2
$\Delta H_2{}^{\ddagger}$ (kJ mol^{-1})	59.4±2.5	70.2±1.7	68.2±1.5	44.5±3.2
$\Delta S_2{}^{\ddagger}$ (J K^{-1} mol^{-1})	−48.4±15.6	−49.9±10.3	−61.5±9.3	−145.5±19.7
$\Delta G_2{}^{\ddagger}{}_{300}$ (kJ mol^{-1})	73.9±2.2	85.2±1.4	86.5±1.3	88.2±2.7

a) In the dark.

Table 5. Kinetic Parameters of the Decomposition of **3e** to **4** in Acetonitrile[a)]

	$k^2\times10^2$/s^{-1}	
Temp/°C	X=I	X=BF$_4$
5.0	1.58	—
20.0	5.30 (5.26)[b)]	5.43
35.0	17.9	—
$\Delta H_2{}^{\ddagger}$ (kJ mol^{-1})	55.1±1.6	—
$\Delta S_2{}^{\ddagger}$ (J K^{-1} mol^{-1})	−80.9±10.2	—
$\Delta G_2{}^{\ddagger}{}_{300}$ (kJ mol^{-1})	79.3±1.4	

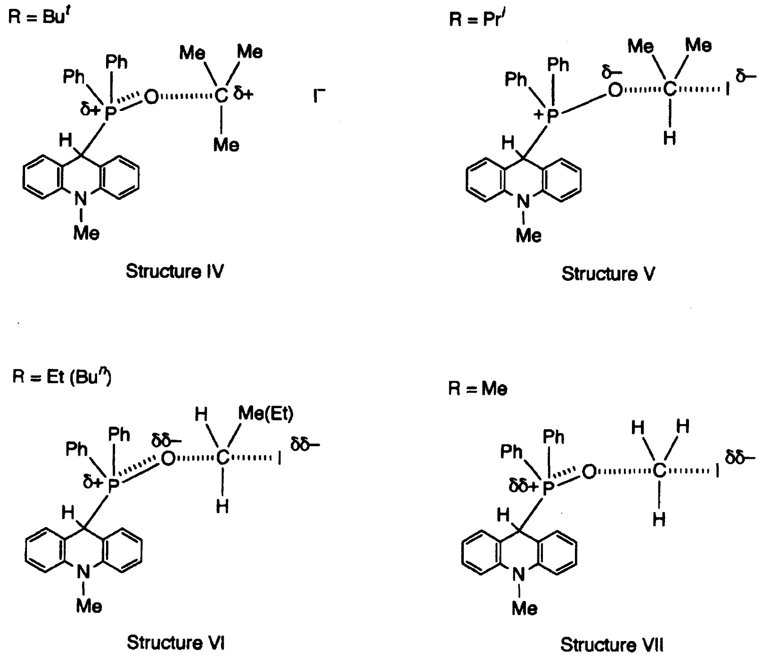
a) In the dark. b) 80 equiv of Et$_4$NI was added.

R=Bu^t. Iodide ion can not give rise to E2 reaction due to its extremely low basicity. In fact, **4** was obtained in a quantitative yield from each experiment.

This change in kinetic order agrees well with the concept established for the hydrolyses of alkyl halides,[28)] and is well-accounted for in terms of different stabilization of the transition state by the alkyl substituent R.[29)] That is, the occurrence of the S$_\text{N}$1 mechanism for the decomposition of **3e** (R=Bu^t) results from stabilization of the positive charge developed in the transition state by three methyl groups attached to the reaction center (α-carbon in the substituent R) (Structure IV in Scheme 4). The lack of such stabilization for the decomposition of **3a**—**d** requires the assistance of iodide ion, resulting in the S$_\text{N}$2 mechanism. The highly crowded structure of *t*-butyl group is also responsible for the S$_\text{N}$1 mechanism for the decomposition of **3e**.

Since the positive charge on **3** is eventually neutralized during this step, one may expect positive values for the entropies of activation for this step $\Delta S_2^{\ddagger}$ based on general concept of kinetics.[24)] This is not the case as seen in Table 4, which instead shows negative $\Delta S_2^{\ddagger}$ values. It has been reported that benzyl(*p*-methoxy- and *p*-methylphenyl)dimethyllammonium iodides decompose to the corresponding amines with $\Delta S^{\ddagger}=-28$ J K^{-1} mol^{-1} and -7.5 J K^{-1} mol^{-1}, respectively, and these values have been claimed to indicate the reactant-like transition state with a part of positive charge remaining on the nitrogen.[30)] Nevertheless, the observed entropies of activation for the phosphorus counterpart in the present study is much more negative, which means that the positive charge remains on the phosphorus in the transition state of the decomposition of **3** to a quite large extent. This is rationalized by the idea that the breaking of the carbon–oxygen bond precedes the formation of the oxygen–phosphorus double bond. Thus, the large negative value of $\Delta S_2^{\ddagger}$ observed for **3d** (R=Pr^i) demonstrates that the phosphorus–oxygen double bond is hardly formed in the transition state of the decomposition of **3d**, leaving the positive charge on the phosphorus almost intact (Structure V in Scheme 4). This might result from the steric bulk of the isopropyl group which would prevent iodide ion from close approach to the reaction center. Sterically less hindered substituent in **3b** (R=Et) of **3c** (R=Bu^n), on the other hand, would allow iodide ion to approach the reaction center. Less negative value of $\Delta S_2^{\ddagger}$ for each of them indeed represents that the nucleophile partly neutralizes the positive charge on the phosphorus in the transition state. This also means that the double-bond character between the phosphorus and the oxygen is developed to a small extent (Structure VI in Scheme 4). Moreover, the least negative value of $\Delta S_2^{\ddagger}$ for **3a** (R=Me) indicates that the smallest substituent in **3a** provides the tightest association between **3a** and iodide ion in the transition state giving the smallest extent of the positive charge on the phosphorus atom. The double-bond character would significantly be developed in this case (Structure VII in Scheme 4).

Concluding Remarks. We presented the results of the kinetic study upon both the formation and the decomposition of the phosphonium intermediate along the single Arbuzov-type reaction. It was elucidated that the structure of the transition state for the phosphonium-forming step (the first step) is determined mainly by the bulkiness of the substituent R; the smaller substituent makes the association between the phosphinite and the acridinium ion in the transition state tighter facilitating the reaction enthalpically. The effect of the substituent, however, is compensated by the entropy term, which eventually causes a small change in the reaction rates with the change of the substituent R.



Scheme 4.

The phosphonium-decomposing step (the second step) is also governed by the steric factor; the bulkier the substituent on the phosphonium, the earlier the transition state of its decomposition. Thus, the phsphonium with a bulky substituent such as the isopropyl derivative has the transition state in which the breaking of the carbon–oxygen bond predominates over the formation of the phosphorus–oxygen double bond. The phosphonium with *t*-butyl group decomposes according to the S_N1 mechanism without assistance of a nucleophile.

Experimental

Instruments. ^{1}H and ^{31}P NMR spectra were recorded on a JEOL Model GSX270 NMR spectrometer operating at 270 MHz and a Varian XL200 NMR spectrometer operating at 81 MHz, respectively. UV-vis spectra were obtained on a Hitachi 124 UV-vis spectrophotometer. Stopped-flow spectrophotometry was performed with a Union Giken RA-401 rapid reaction analyzer equipped with a Union Giken K2R temperature controller and a Union Giken System 77 or an NEC PC-9801 personal computer system. Mass spectrum was obtained on a Shimadzu GCMS-QP2000A gas chromatograph mass spectrometer equipped with a Shimadzu GC-MSPAC 200S data processor using a direct sample introducer (Shimadzu DIRECT INLET DI20).

Materials. 10-Methylacridinium iodide (**2a**) was obtained as reddish-brown needles according to the procedure described in the literature.[31] 10-Methylacridinium tetrafluoroborate (**2b**) was obtained as follows; the iodide salt **2a** was reacted with a 5-equivalent amount of silver tetrafluoroborate in acetonitrile, and silver iodide formed was filtered off. The filtrate was washed with a small portion of ether to give **2b** as yellow crystals in 37% yield. The material was purified through repeated recrystallization from acetonitrile–ether. Alkyl diphenylphosphinites (**1**) were prepared according to the procedure described in the literature.[32] **1a**, bp 76—77 °C (0.01 mmHg, 1 mmHg=133.322 Pa), 52%. **1b**, bp 86—87 °C (0.01 mmHg), 40%. **1c**, bp 99—100 °C (0.01 mmHg), 21%. **1d**, bp 90—91 °C (0.01 mmHg), 54%. **1e** was purified by column chromatography (Wako Gel C-100; ethyl acetate as the eluent).

Reaction of 1 with 2. Compound **1a** (58.5 mg, 0.21 mmol) was allowed to react with **2** (66.1 mg, 0.21 mmol) in 5 ml of acetonitrile at room temperature in the dark for 30 min. The crystalline product precipitated was collected by filtration. After purification through repeated washing with methanol, the product was analyzed by ^{1}H, ^{31}P, and ^{13}C NMR and mass spectroscopy as well as elemental analysis to be identified as (9,10-dihydro-10-methyl-9-acridinyl)-diphenylphosphine oxide (**4**) (isolated yield, 89%).

The reactions of **1b**—**e** with **2** also gave **4** in nearly quantitative yields. Mp 257—258 °C (decomp). ^{1}H NMR ($CDCl_3$ δ in ppm from TMS) δ=2.74 (3H, s), 5.12 (1H, d; $^2J_{P-9-H}$=16.2 Hz), 6.58—7.59 (18H, m). ^{13}C NMR (proton decoupled, $CDCl_3$ δ in ppm from TMS) δ=32.5 (s), 50.2 (d, $^1J_{P-9-C}$=63.6 Hz), 112.2 (d, J_{P-C}=2.9 Hz), 118.6 (d, J_{P-C}=3.9 Hz), 120.5 (d, J_{P-C}=2.0 Hz), 127.6 (d, J_{P-C}=11.7 Hz), 128.1 (d, J_{P-C}=2.9 Hz), 130.2 (d, J_{P-C}=3.9 Hz), 130.3 (d, $^1J_{P-1'-C}$=93.9 Hz), 131.5 (d, J_{P-C}=2.9 Hz), 132.4 (d, J_{P-C}=8.8 Hz), 143.0 (d, J_{P-C}=3.9 Hz). MS *m/z* 201, 194, 179. Anal. Found: C, 78.43; H, 5.55; N, 3.34%. Calcd for $C_{26}H_{22}NOP$: C, 78.99; H, 5.57; N, 3.54%.

NMR Spectroscopy. In an NMR tube equipped with a septum was placed 2.2×10^{-2} mmol of **2**, and the solution of 2.2×10^{-2} mmol of **1** in 0.5 ml of CD_3CN was added to the tube through a syringe under N_2 to resolve the material **2**. The NMR measurement was then performed immediately.

Kinetics. Pseudo-first-order rate constants for the first step were determined as follows: A solution of **2** and a solution of an excess amount of **1** in acetonitrile were mixed in a reaction vessel of a stopped-flow spectrophotometer (the concentrations of **1** and **2** in the vessel; (1.0—3.0)$\times10^{-2}$

$\mathrm{mol\,dm^{-3}}$ and 1.0×10^{-4} $\mathrm{mol\,dm^{-3}}$, respectively) and rapid decrease in the absorbance at 360 nm was followed spectrophotometrically at an appropriate temperature. The measurements were performed at various concentrations of **1**, and the second-order rate constant was obtained from the plot of the pseudo-first-order rate constants against the concentrations of **1** (correlation coefficient; >0.999). In order to determine the rate constants for the second step, a 100-μl solution of **1** (1.60×10^{-2} $\mathrm{mol\,dm^{-3}}$) in acetonitrile was added through a syringe into a 3.9-ml solution of acetonitrile containing **2a** (4.10×10^{-4} $\mathrm{mol\,dm^{-3}}$) and various concentrations of tetraethylammonium iodide ($(0.820—3.28)\times10^{-2}$ $\mathrm{mol\,dm^{-3}}$) in an UV-cell equipped with a septum, and after the completion of the first-step reaction (within 0.02—1 s depending on the substrate) the increase in the absorbance at 320 nm from **4** was followed spectrophotometrically at an appropriate temperature. The plot of the pseudo-first-order rate constants against the total concentrations of iodide ion (correlation coefficient; >0.999) gave the second-order rate constants. All kinetic runs for both the first and the second steps were repeated at least twice or five times in most cases. The reproducibility was satisfactory. The Arrhenius plots for the first and second steps for each substrate afforded the activation parameters with satisfactory reliability (correlation coefficient; 0.99—0.999).

References

1) B. P. Mundy and M. G. Ellerd, "Name Reactions and Reagents in Organic Synthesis," John Wiley & Sons, New York (1988).

2) S. F. Martin and J. A. Dodge, *Tetrahedron Lett.*, **32**, 3017 (1991).

3) A. Wagner, M. P. Heitz, and C. Mioskowski, *Tetrahedron Lett.*, **31**, 3141 (1990).

4) J. Nielsen and M. H. Caruthers, *J. Am. Chem. Soc.*, **110**, 6275 (1988).

5) M. Masui, Y. Mizuki, K. Sakai, C. Ueda, and H. Ohmori, *J. Chem. Soc., Chem. Commun.*, **1984**, 843.

6) T. Mukaiyama, R. Matsueda, and M. Suzuki, *Tetrahedron Lett.*, **1970**, 1901.

7) A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, **81**, 415 (1981), and references cited therein.

8) H. R. Hudson, R. G. Rees, and J. E. Weekes, *J. Chem. Soc., Chem. Commun.*, **1971**, 1297.

9) L. A. Jones, C. E. Sumner, Jr., B. Franzus, T. T. -S. Huang, and E. I. Snyder, *J. Org. Chem.*, **43**, 2821 (1978).

10) E. S. Lewis and D. Hamp, *J. Org. Chem.*, **48**, 2025 (1983).

11) G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, **18**, 38 (1964).

12) S. Yasui, K. Shioji, M. Yoshihara, T. Maeshima, and A. Ohno, *Tetrahedron Lett.*, **33**, 7189 (1992).

13) The stability of **1** is not enough to obtain well-resolved spectra of ^{31}P NMR under proton-coupled conditions.

14) "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis," ed by J. G. Verkade and L. D. Quin, VCH, Deerfield Beach, FL (1987), pp. 26—29 and 40—46.

15) K. S. Colle and E. S. Lewis, *J. Org. Chem.*, **43**, 571 (1978).

16) K. B. Dillon, M. P. Nisbet, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, **1982**, 465.

17) A. Skowrońska, J. Mikołajczak, and J. Michalski, *J. Chem. Soc., Chem. Commun.*, **1975**, 791

18) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," ed by M. S. Newman, John Wiley & Sons, New York (1956), Chap. 13.

19) As sometimes treated, Taft σ^*-values has been used in the form of $\mathrm{RCH_2}$ here, although the value for $\mathrm{R{=}Bu}^n$ is not availvable in this form. The use of σ^*-values themselves gave slightly more scattered plots. What is important here is that the ^{31}P NMR chemical shifts of both the neutral and the cationic species correlate with the values of certain σ-scale in a similar manner.

20) L. Z. Avila, P. A. Bisop, and J. W. Frost, *J. Am. Chem. Soc.*, **113**, 2242 (1991).

21) It has been argued that the stability of phosphonium salts increases with decreasing the number of oxyten atom(s) attached to the phosphorus: H. R. Hudson, A. T. C. Kow, and K. Henrick, "Phosphorus Chemistry, Proceedings of the 1981 International Conference," ed by L. D. Quin and J. G. Verkade, American Chemical Society, Washington, D. C. (1981), pp. 517—520.

22) K. Akiba, K. Ishikawa, and N. Inamoto, *Synthesis*, **1977**, 862.

23) P. van Eikeren and D. L. Grier, *J. Am. Chem. Soc.*, **98**, 4655 (1976).

24) N. S. Isaacs, "Physical Organic Chemistry," Longman Scientific & Technical, Essex (1987).

25) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

26) D. P. Evans, *J. Chem. Soc.*, **1944**, 422. Discussion is not based on the activation parameters in this article.

27) First-order kinetics was postulated for the decomposition of methoxyphosphonium salts in $\mathrm{CDCl_3}$ based on the assumption that the phosphonium exists almost wholly as an ion pair with iodide ion in this solvent; see Ref. 10.

28) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London (1969).

29) The $\mathrm{S_N1}$ mechanism has a priori been supposed for the attack of a nucleophile on *t*-butyl group in the second step of the conventional Arbuzov reactions: D. Cooper, S. Trippett, and C. White, *J. Chem. Res., Synop.*, **1983**, 234.

30) J. T. Burns and K. T. Leffek, *Can. J. Chem.*, **47**, 3725 (1969).

31) R. M. G. Roberts, D. Ostovic, and M. M. Kreevoy, *Faraday Discuss. Chem. Soc.*, **74**, 257 (1982).

32) R. S. Davidson, *Tetrahedron*, **25**, 3383 (1969).