

The kinetics and mechanism of the reaction of trimethyl phosphite with benzylideneacetophenones



Imre Petneházy,^a György Clementis,^a Zsuzsa M. Jászay,^b László Töke^a and C. Dennis Hall^c

^a Department of Organic Chemical Technology, Technical University of Budapest, H-1521 Budapest, Hungary

^b Research Group of Organic Chemical Technology of Hungarian Academy of Sciences, H-1521 Budapest, Hungary

^c Department of Chemistry, School of Physical Sciences and Engineering, King's College, University of London, Strand, London, UK WC2R 2LS

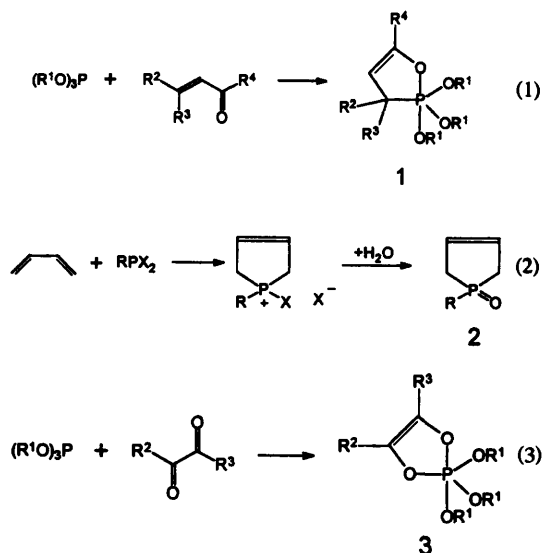
The kinetics and mechanism of the equilibrium reaction of benzylideneacetophenones **4** with trimethyl phosphite (TMP) to yield, 2,2,2-trimethoxy-2,3-dihydro-1,2λ⁵-oxaphospholes **5** are reported. The second-order rate constants for the formation of **5** were determined using a polarographic method and the rate constants for the decomposition reaction were calculated from the equilibrium constants. The linear Hammett plots in some cases and the curved ones in others indicate that the rate-determining step depends on the character of the ring substituents in **4** and **5**. A thermodynamic study of the forward reaction showed a relatively small enthalpy and a large negative entropy of activation in agreement with the existence of a strongly polarised and/or crowded structure in the transition state. The proposed mechanism, in cases where electron-donating substituents (Y) or hydrogen are on the aromatic ring next to the carbonyl carbon or where electron-donating substituents (X) are on the aromatic ring next to the double bond, involves nucleophilic attack of phosphite on the carbonyl carbon atom in the rate-limiting step to form intermediate **I**₁, followed by a ring closure to an oxaphosphirane **I**₂, and ring enlargement to the oxaphospholene **5**. The use of electron-withdrawing substituents (both for X and Y) results in a change in the reaction pathway in which phosphite attacks the carbon atom β to the carbonyl group in the rate-limiting step followed by a fast ring closure of **I**₁ to oxaphospholene **5**.

Introduction

The α,β-unsaturated carbonyl group is one of the most versatile and useful entities in organic synthesis. A nucleophilic reagent may attack enones at either the carbonyl carbon atom to give 1,2-addition or at the β position, the so-called 'conjugate addition', to give a 1,4-adduct. In fact, attack occurs preferentially and sometimes exclusively at the carbonyl carbon atom although conjugate (Michael) addition is also encountered. For example, dialkyl phosphite anion attacks both centres in the Pudovik reaction resulting in formation of hydroxy- or keto-phosphonates.^{1,2}

It is well known from the work of Ramirez,³ Arbusov⁴ and others⁵ that trialkyl phosphites react with enones to form 2,2,2-trialkoxy-2,3-dihydro-1,2λ⁵-oxaphospholes **1** but the kinetics have not yet been studied. The analogous addition reactions of trivalent phosphorus compounds to 1,3-dienes and 1,2-diketones have, however, been studied in detail. Thus, the reaction between dienes and trivalent phosphorus compounds, such as phosphonous dihalides and phosphinous halides or sometimes simple trialkyl phosphites (the McCormack reaction),⁶ yields phospholenes **2** and the mechanism proposed for the reaction involves a 1,4-cycloaddition process.⁷

In the reaction of trialkyl phosphites and α-diketones, dioxaphospholenes **3** are formed and the kinetics and mechanism of the reaction have been studied by Ogata and Yamashita.⁸ The rate-limiting step was found to be nucleophilic attack of the trialkyl phosphite on the carbonyl carbon atom of the diketone and the subsequent steps consist of a fast rearrangement of the dipolar ion, leading to ring closure. On the other hand EPR measurements by Boekstein and co-workers⁹ and also Ogata¹⁰ indicated that in some cases reactions between trivalent phosphorus compounds and activated ketones resulted in complete



electron-transfer and involved radical ions as intermediates in the reaction.

Recently, we investigated the reactivity of a series of α,β-unsaturated carbonyl compounds with trialkyl phosphites and found that although the majority of enones do react to give oxaphospholenes **1**, a number of other enones do not. We also proved that the occurrence of the reaction could be monitored by measuring the polarographic halfwave potential of the enones.¹¹ The present paper reports a kinetic study of the reaction of trimethyl phosphite (TMP) with benzylideneacetophenones **4** and the decomposition of the oxaphospholene **5** in the equilibrium process shown in Scheme 1.

Table 1 Equilibrium constants ($K/10^{-2} \text{ dm}^3 \text{ mol}^{-1}$) and second-order rate constants ($k_f/10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for the reaction of **4** with trimethyl phosphite at 55.1–90.1 °C

Substituents in 4 ^a		55.1 °C	63.2 °C	71.2 °C	80.2 °C	90.1 °C
X	Y	k_f	k_f K	k_f K	k_f K	k_f
4-MeO	H		3.8 4.1	4.6 2.4	7.4 1.4	31.1
4-Me	H		5.0 6.7	6.3 2.6	9.0 2.8	14.6
H	H	3.4	6.4 14.9	10.5 10.7	22.5 6.4	40.0
4-Cl	H	4.3	7.8 18.5	12.4 12.4	23.8 9.2	
3,4-di-Cl	H	5.4	9.6 30.3	13.8 19.8	20.0 12.6	
H	4-MeO		2.6 4.0	4.1 2.6	9.9 1.6	16.3
H	4-Me		3.4 5.8	5.8 4.3	11.4 3.3	20.0
H	4-Cl	8.4	16.3 21.9	23.8 14.2	58.8 1.2	
H	3,4-di-Cl	21.0	38.8 37.3	70.0 25.6	124 1.7	
H	4-NO ₂	51.2	91.3 50.6	163.1 35.9	338 2.9	

^a In case of X = *p*-NO₂ the solubility of **4** was low in trimethyl phosphite; this measurement was omitted.

Experimental

Materials

The preparation of benzylideneacetophenones **4** has been described previously.¹² TMP was purified by distillation from metallic Na under N₂.¹³ Physical and spectroscopic data for 2,2,2-trimethoxy-3,5-triaryl-2,3-dihydro-1,2λ³-oxaphospholones **5** have been published.¹¹

Polarographic measurements

The concentrations of benzylideneacetophenones **4** and oxaphospholones **5** were determined by differential-pulse polarography using equations derived from the calibration data.¹⁴

Equilibrium experiments

Reactions were carried out at 63.2, 71.2 and 80.2 °C (± 0.2 °C). A sample of TMP (2.5 cm³) was thermostatted and 0.25 mmol of benzylideneacetophenone **4** was transferred into the flask. After complete dissolution of the benzylideneacetophenone (3–5 s) a 300 μl sample was injected into an acidic polarographic stock electrolyte. The supporting electrolyte was 0.1 M sulfuric acid containing ethanol (65% v/v) and 0.001% TritonX-100.¹⁴ Further samples were taken over 10–12 h, and concentrations of enone **4** and oxaphospholene **5** were determined polarographically¹⁴ to allow calculation of the K values (Table 1) from eqn. (1).

$$K = \frac{[\mathbf{5}]}{[\mathbf{4}][\text{TMP}]} / \text{dm}^3 \text{ mol}^{-1} \quad (1)$$

Kinetic experiments

Kinetic measurements were carried out at 55.5, 63.2, 71.2, 80.2 and 90.1 °C (± 0.2 °C). TMP (10 cm³) which was used as solvent and reactant was thermostatted in a 20 cm³ double-surface Erlenmeyer flask and benzylideneacetophenone (**4**, 1.0 mmol) was transferred into the flask. Samples of (300 μl) were taken at intervals of 5 or 10 min between 5 and 150 min and each sample was diluted to 25.0 cm³ with the polarographic supporting electrolyte. The concentrations of enone were determined by differential-pulse polarography.¹⁴ Fig. 1 shows a typical example of the data obtained for **4** (Y = X = H) at 63.2 °C. The initial straight section of concentration of enone vs. time diagram was plotted as ln [enone] vs. time to provide pseudo-first-order rate constants. The second-order rate constants were calculated by dividing the first-order rate constant by the concentration of TMP (8.4 M, Table 1). The second-order rate constant for the same reaction was also calculated using the standard equation for a reversible second-order reaction ($A + B \rightleftharpoons C$)¹⁵ which gave an excellent linear correlation (Fig. 2) and $k_f = 6.6 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in comparison to $k_f = 6.4 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by the initial slope method. The data in Table 1 are therefore derived by the latter method.

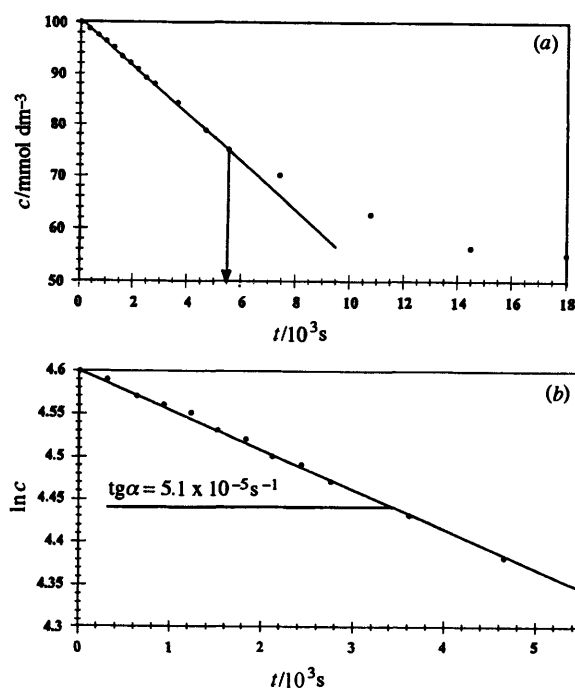


Fig. 1 A typical example of data for the calculation of the rate constant for the reaction of (**4**, X = Y = H at 63.2 °C). The initial straight section is represented in the concentration of enone vs. time plot (above) and $\text{tg} \alpha =$ first-order rate constant from $\ln c$ vs. time (below).

Calculation of charge densities within the oxaphospholones **5** were performed using the SPARTAN III program and the results are shown in Table 2.

Results and discussion

The reactions of TMP with benzylideneacetophenones **4**, containing methyl, methoxy, chloro or nitro substituents in the *para* position either on the aromatic ring next to the carbonyl group or on the aromatic ring next to the double bond usually gave oxaphospholones as oils, or crystalline solids. In several cases, however, the products were only detected in the reaction mixture by ³¹P NMR. The pure oxaphospholones decomposed to TMP and the corresponding enone by heating in an aprotic solvent, and the same type of decomposition was observed on prolonged storage at room temperature.

The equilibrium constants (K) of the reactions were determined by measuring the concentration of benzylideneacetophenones **4** and the oxaphospholones **5** and the resultant equilibrium constants at 63.2, 71.2 and 80.2 °C are reported in Table 1. A plot of $\log K$ values vs. the Hammett σ values for X and Y resulted in two lines (Fig. 3) broken at X or Y = H. As

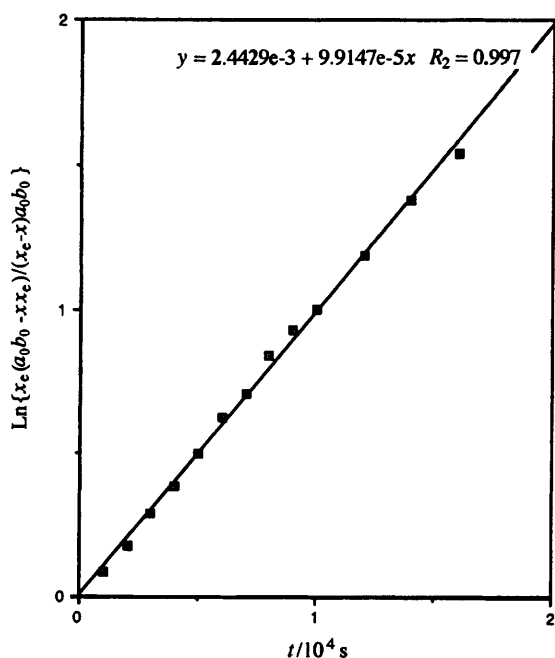


Fig. 2 Second-order plot for the reaction to equilibrium between $(\text{MeO})_3\text{P}$ and $(4, X, Y = \text{H})$ at 63.2°C . Data taken from Fig. 1 and based on $K = 0.149$ and x_e (the concentration of **5** at equilibrium) = 0.055 M .

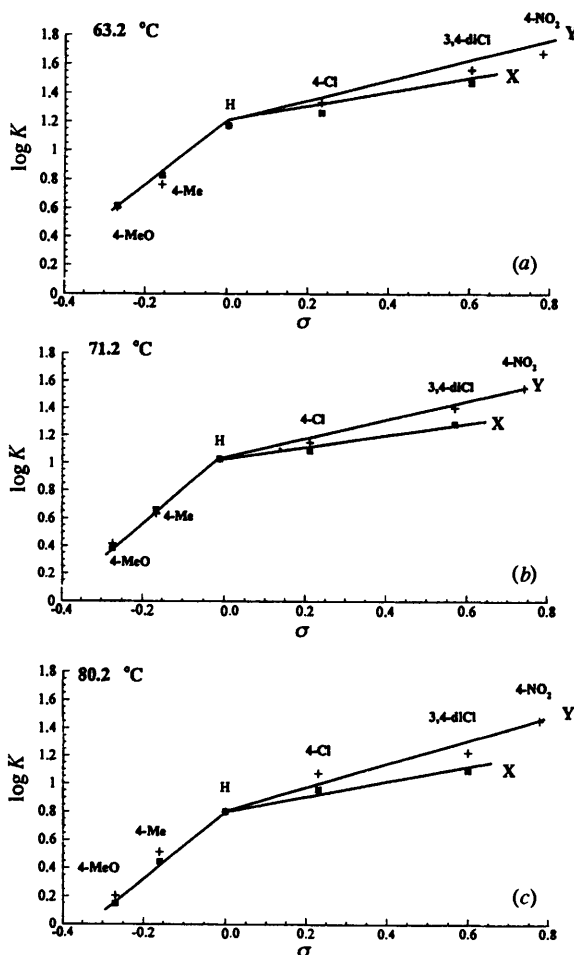


Fig. 3 Plots of the log equilibrium constants ($\log K$) vs. Hammett σ values for the reaction of $\text{XC}_6\text{H}_4\text{CH}=\text{CHCOC}_6\text{H}_4\text{Y}_4$ with $(\text{MeO})_3\text{P}$: (+) $X = \text{H}$; $Y = 4\text{-MeO}, 4\text{-Me}, \text{H}, 4\text{-Cl}, 3,4\text{-diCl}$ and 4-NO_2 ; (■) $Y = \text{H}$; $X = 4\text{-MeO}, 4\text{-Me}, \text{H}, 4\text{-Cl}$ and $3,4\text{-diCl}$

Table 2 Calculated electron densities of oxaphospholenes (**5**)

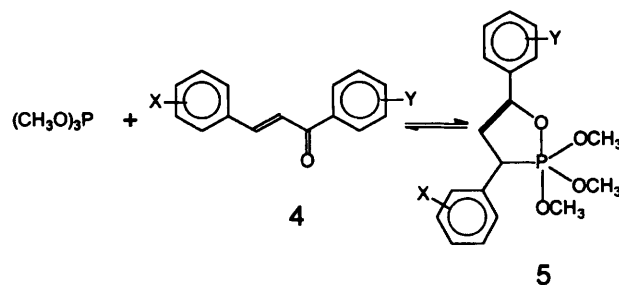
X	Y	P	O	C-3	C-4	C-5
H	H	2.29996	-0.6534	0.2359	-0.2616	-0.3275
H	4-Cl	2.2852	-0.6541	0.2196	-0.2819	-0.2819
H	4-MeO	2.2809	-0.6563	0.2274	-0.2983	-0.2405
4-Cl	H	2.2986	-0.6505	0.2017	-0.2716	-0.2879
4-MeO	H	2.3084	-0.6619	0.2369	-0.2826	-0.2818

Table 3 Activation parameters for the reaction of **4** with TMP (r values were calculated by the least-squares treatment)

Substituents in 4		ΔH^\ddagger / kJ mol^{-1}	r	ΔS^\ddagger at 298 K/ $\text{J mol}^{-1} \text{K}^{-1}$	r
4-MeO	H	59	0.966	-192	0.999
4-Me	H	47	0.968	-177	0.976
H	H	70	0.967	-144	0.950
4-Cl	H	66	0.974	-157	0.990
3,4-di-Cl	H	57	0.946	-182	0.991
H	4-MeO	71	0.969	-150	0.968
H	4-Me	68	0.973	-158	0.957
H	4-Cl	73	0.979	-131	0.968
H	3,4-di-Cl	69	0.957	-134	0.991
H	4-NO ₂	73	0.977	-166	0.984

expected, the equilibrium constants are largest for electron-withdrawing substituents in both aromatic rings.

The dependence of reaction rates on the ring substituents was studied recently by a gas chromatographic method¹⁶ which showed that electron-withdrawing substituents on the aromatic ring next to the carbonyl group ($Y = \text{Cl}$) increased the rate whereas electron-releasing substituents ($Y = \text{Me}$) decreased the rate. The effect was not observed, however, if the electron-withdrawing substituent was on the aromatic ring next to the double bond (e.g. $X = \text{Cl}$). These results suggested that the reaction presented in Scheme 1 was more complex than a simple



Scheme 1

rate-limiting nucleophilic attack on the carbonyl carbon by trialkyl phosphite followed by fast phosphoryl migration and ring closure.

For a detailed and accurate study of the reaction a new analytical procedure¹⁴ was devised to determine the concentration of the reactants and products. Using this method the kinetics of the reaction were studied at $55.1\text{--}90.1^\circ\text{C}$ in the presence of a large excess of TMP as reactant and solvent and the second-order rate constants of the oxaphospholene forming reaction (k_f) were calculated from the results (Table 1). By measuring the rate of reaction at several temperatures activation parameters were calculated using the Arrhenius and Eyring equations (Table 3).

The enthalpies of activation ΔH^\ddagger which vary from 47 to 73 kJ mol^{-1} , correspond to nucleophilic attack by trialkyl phosphite in agreement with the results of Ogata and Yamashita⁸ for the reaction of α,β -diketones with trialkyl phosphite. Large negative values of the entropy of activation ($\Delta S^\ddagger = -131$ to $-192 \text{ J mol}^{-1} \text{K}^{-1}$) were obtained which is generally characteristic of an associative mechanism and in particular reactions of

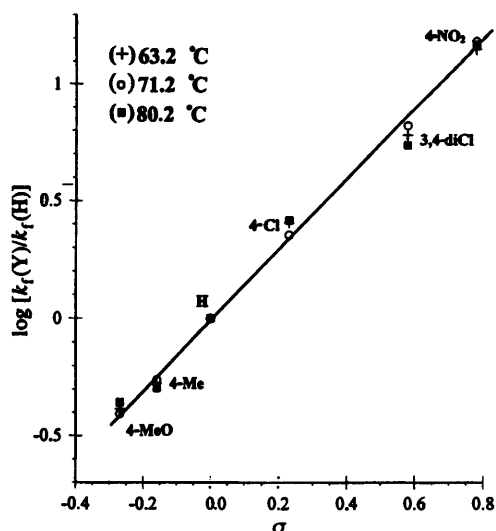


Fig. 4 The Hammett σ plots for the reaction of $C_6H_5CH=CHCOC_6H_4Y$ with $P(OCH_3)_3$ ($Y = 4\text{-MeO}, 4\text{-Me}, H, 4\text{-Cl}, 3,4\text{-diCl}$ and 4-NO_2) at different temperatures [$\rho = 1.48$]

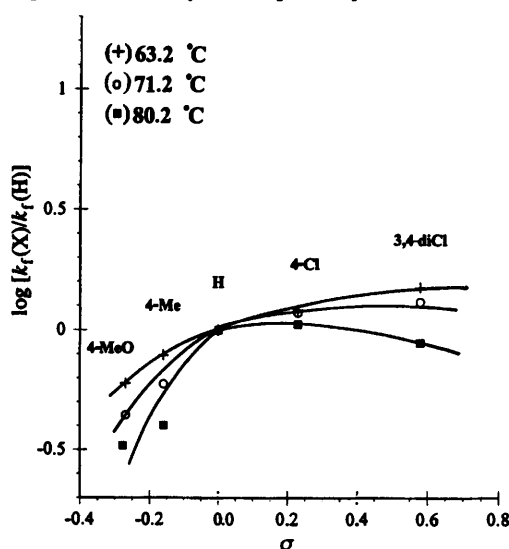


Fig. 5 The Hammett σ plots for the reaction of $XC_6H_4CH=CHCOC_6H_5$ with $P(OCH_3)_3$ ($X = 4\text{-MeO}, 4\text{-Me}, H, 4\text{-Cl}$ and $3,4\text{-diCl}$) at different temperatures [ρ (+) = 0.81 and 0.31; ρ (o) = 1.32 and 0.21; ρ (■) = 1.84 and -0.07]

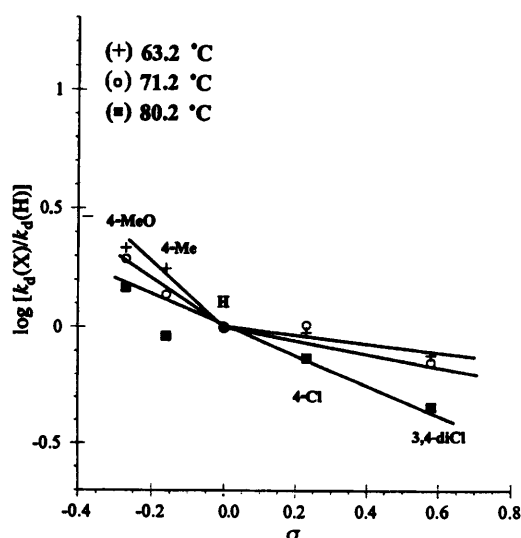


Fig. 6 The Hammett σ plots for the decomposition reaction of oxaphospholene **5** ($X = 4\text{-MeO}, 4\text{-Me}, H, 4\text{-Cl}$ and $3,4\text{-diCl}$; $Y = H$) at different temperatures [ρ (+) = -1.30 and -0.19; ρ (o) = 1.02 and -0.23; ρ (■) = -0.65 and -0.58]

carbonyl compounds with nucleophiles.¹⁷ For the formation of **3** a value of $\Delta S^\ddagger = -200 \text{ J mol}^{-1} \text{ K}^{-1}$ was found⁸ and the large negative values of ΔS^\ddagger observed in the reaction under study substantiate a strongly polarised and/or crowded structure in the transition state. A typical concerted reaction such as the Diels-Alder addition generally exhibits ΔS^\ddagger values in the region $-120 \text{ J mol}^{-1} \text{ K}^{-1}$ and hence the concerted, one-step cycloaddition of benzylideneacetophenone with TMP seems less likely.¹⁸

To obtain a better insight into the reaction, however, Hammett plots were derived from the second-order rate constants using the appropriate σ values.¹⁹ A good straight line was obtained for the reaction of TMP with **4** having the substituents (Y) on the aromatic ring next to the carbonyl carbon (Fig. 4). The magnitude and positive sign of the ρ value for this reaction ($\rho = 1.48, r = 0.9980$) are also in agreement with nucleophilic attack of the phosphite in the rate-determining step and indicate an ionic component to the transition state.²⁰

On the other hand, the Hammett plot for the reaction of TMP with **4** having the substituents (X) on the aromatic ring next to the $C=C$ double bond gives a 'curved plot' (two intersecting lines) at all temperatures (Fig. 5). In the region of electron-releasing substituents ($X = p\text{-MeO}$ and $p\text{-Me}$) and including the case of unsubstituted benzylideneacetophenone ($X = H$) the value of ρ was approximately 1.4 ± 0.4 but for the electron-withdrawing groups ($X = p\text{-Cl}$ and $X = 3,4\text{-diCl}$) the value of ρ was *ca.* 0. The rate constants for the decomposition (k_d) of **5** to **4** were calculated from the equilibrium constants (K) and from the rate constants of the oxaphospholene forming reaction (k_f) using eqn. (2).

$$K = \frac{k_f}{k_d} \quad (2)$$

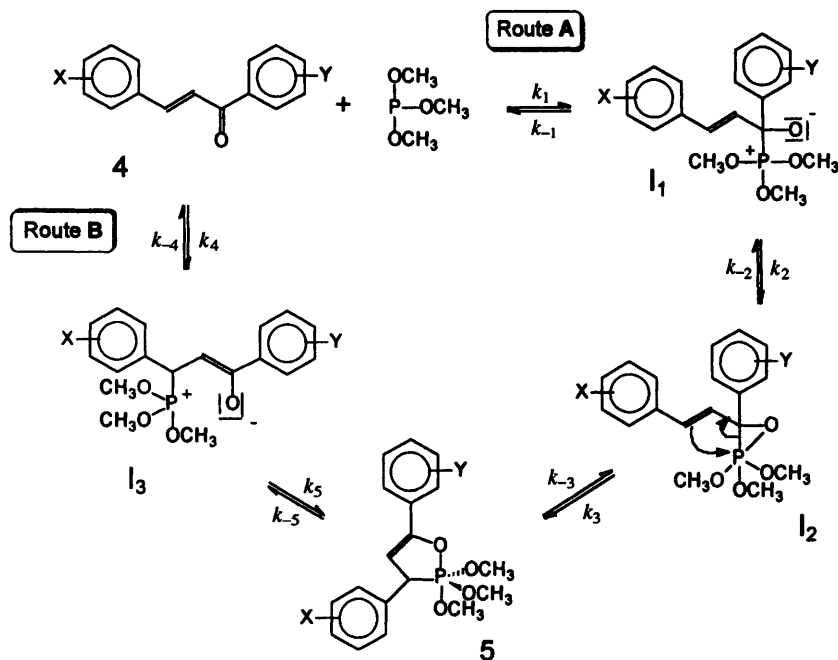
The activation parameters for the decomposition were also calculated (Table 4). The large negative values of ΔS^\ddagger are again consistent with a mechanism which involves transition states with bipolar structures. The calculated rate constants (k_d) showed a sensitivity to the substituents (X and Y) of both aromatic rings and they were also plotted as a function of the Hammett σ constants.

In the series varying the substituents (X) in **5** the Hammett equation gave broken lines with $\rho = -0.3 \pm 0.3$ for the electron-withdrawing groups and $\rho = -1.0 \pm 0.3$ for the electron-donating groups (Fig. 6). In the series, varying the substituents (Y) in **5** the Hammett equation gave two lines having opposite slopes (Fig. 7) at all temperatures with $\rho = +0.8 \pm 0.2$ for electron withdrawal by Y and $\rho = -0.8 \pm 0.2$ for electron-donating groups. The discontinuity in the Hammett plots provides strong evidence for either a change in the rate-limiting step of the reaction or a change in the mechanistic pathway.²¹ Moreover, the data suggest that the change occurs at the same point in both the forward and backward reactions, thus satisfying the law of microscopic reversibility. Interestingly, the equilibrium constants also show a break in the Hammett plots for X and Y at the same point ($X, Y = H$) which suggests that there are two different equilibria involved. The two possible pathways involve nucleophilic attack by TMP either on carbonyl carbon (route A) or on the β carbon of the enone (route B, Scheme 2). In route A the trialkyl phosphite nucleophile attacks the carbonyl carbon atom in the rate-limiting step. We assume that zwitterionic intermediate (**I**₁) transforms into the adduct having an oxaphosphirane ring²² (**I**₂) at a rate which is characteristic for the interaction of ions (*i.e.* k_2 is very fast) and exists exclusively in this form before rearranging in a concerted process to give the end product **5** with a rate k_3 so that $k_1 \ll k_2, k_3$. Route B represents the attack of the TMP on the β carbon resulting in a bipolar adduct (**I**₃) in the rate-limiting step, which is followed by fast ring closure to give the product **5**.

Although the data are somewhat limited a tentative explanation for the Hammett plots is as follows. First consider two reasonable free energy profiles for routes A and B (Fig. 8). For

Table 4 Calculated rate constants at different temperatures ($k_d/10^{-4} \text{ s}^{-1}$) and activation parameters (r values were calculated using the least-square treatment) for the decomposition reaction (**5** \rightarrow **4**)

Substituents in 5		$k_d/10^{-4} \text{ s}^{-1}$			$\Delta H^\ddagger/$	r	ΔS^\ddagger at 298 K/	r
X	Y	63.2 °C	71.2 °C	80.2 °C	kJ mol^{-1}		$\text{J mol}^{-1} \text{ K}^{-1}$	
4-MeO	H	0.9	1.9	5.1	101	0.978	-141	0.973
4-Me	H	0.8	1.3	3.2	84	0.990	-172	0.988
H	H	0.4	0.9	3.5	123	0.971	-104	0.954
4-Cl	H	0.4	1.0	2.6	108	0.969	-136	0.993
3,4-di-Cl	H	0.3	0.7	1.6	91	0.968	-166	0.947
H	4-MeO	0.6	1.6	6.1	130	0.989	-86	0.972
H	4-Me	0.6	1.4	3.5	105	0.987	-138	0.954
H	4-Cl	0.7	1.7	5.0	112	0.977	-123	0.980
H	3,4-di-Cl	1.0	2.7	6.9	112	0.969	-122	0.950
H	4-NO ₂	1.8	4.5	11.1	108	0.969	-125	0.972



Scheme 2

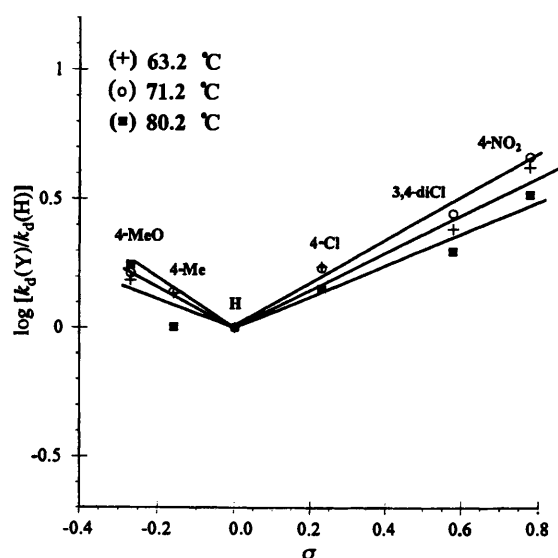


Fig. 7 The Hammett σ plots for the decomposition reaction of oxaphospholene **5** ($Y = 4\text{-MeO}$, 4-Me , H , 4-Cl , $3,4\text{-di-Cl}$ and 4-NO_2 ; $X = \text{H}$) at different temperatures [ρ (+) = -0.71 and $+0.76$; ρ (o) = -0.80 and $+0.82$; ρ (■) = -0.73 and $+0.61$]

the forward reaction, $k_{\text{obs}} = k_f = k_1$ for route A and $k_f = k_4$ for route B. Increasing electron withdrawal in Y would produce an increase in k_1 and k_4 thus generating positive ρ values. If the ρ value is approximately (and accidentally) the same for each pathway, the Hammett plot would generate a straight line as observed in Fig. 4 with $\rho = 1.5$. It is reasonable to propose that the ρ values for paths A and B associated with variations in Y would be similar since the negative charge generated on oxygen in intermediates I_1 and I_3 is the same distance from Y in each case. For the effect of variations in X on k_f one would predict a similar ρ value (ca. 1.5) for route A since X is conjugated with the double bond in I_1 but a lower ρ value for route B since X is isolated from the double bond in I_3 and further from the oxyanion. Since ρ (X) is ca. +1.5 for *p*-MeO, *p*-Me and H, but 0 ± 0.2 for H, *p*-Cl and 3,4-di-Cl (Fig. 5) it seems likely that route A is followed for the former (electron-donating) and route B for the latter (electron-withdrawing) group of substituents.

If we now consider the reverse reaction, the principle of microscopic reversibility dictates that the reactions follow the same mechanistic pathways as the forward process. For the reverse of pathway A, $k_{\text{obs}} = k_d = K_{-3}K_{-2}k_{-1}$ with predicted ρ (Y) values of 0 for K_{-3} (no charge developed) positive for K_{-2} (negative charge developed) and negative for k_{-1} with a resultant which is negative for *p*-MeO, *p*-Me and H (Fig. 7). For the reverse of route B, however, $k_{\text{obs}} = k_d = K_{-5}k_{-4}$ which for variations of Y would have a positive ρ for K_{-5} (negative charge

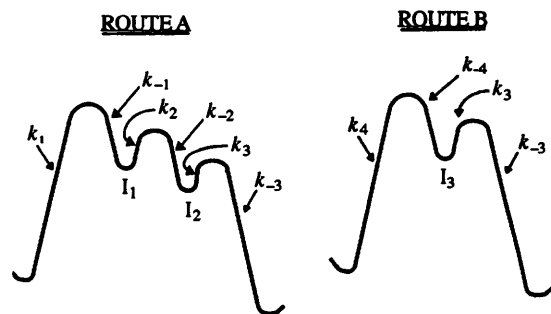


Fig. 8 Energy profile for routes A and B

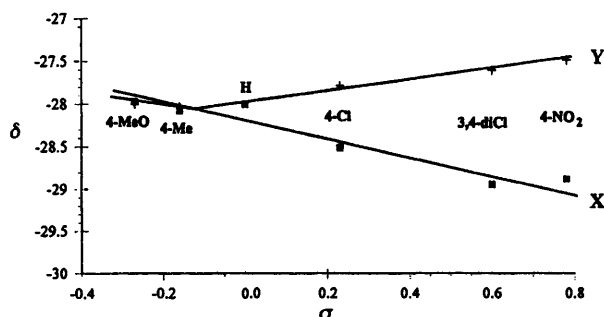


Fig. 9 Plots of the ^{31}P NMR chemical shift of oxaphosphenolene **5** vs. Hammett σ in the series (+) X = H; Y = 4-MeO, 4-Me, H, 4-Cl, 3,4-di-Cl, 4-NO₂ and in the series (■) Y = H; X = 4-MeO, 4-Me, H, 4-Cl, 3,4-di-Cl and 4-NO₂

developed) but a negative ρ for k_{-4} with a resultant positive ρ value which appears to be the case for Y = H \cdots *p*-NO₂ (Fig. 7). For the effect of variations in X on the reverse reaction, the same mechanistic pathways and analysis must be followed which gives resultant moderate negative ρ value for X = H \cdots *p*-MeO (route A) but a low negative ρ value for X = H \cdots *p*-NO₂ via route B (Fig. 6). The alternative explanation of a change in the rate-limiting step is hard to sustain in view of the fact that variations in Y give a straight line in the forward direction but two lines of opposing slopes in the reverse direction.

Similar tendencies were observed for both series (X and Y) when the ^{31}P NMR chemical shifts of oxaphosphenolene (which reflect shielding at the phosphorus atom) were plotted against Hammett σ values (Fig. 9). Variations in X gave a monotonous line with negative slope but variations in Y gave two lines, one with negative ($\sigma_y < 0$) and the other with positive slopes ($\sigma_y > 0$).

The proposed reaction mechanism (Scheme 2) involves both P-C and P-O bond fission within the oxaphosphenolene, a concept which is supported by the calculated charge densities around the skeleton atom of the five-membered ring (Table 2). The large difference between the polarity of the P and O atoms suggests a favourable bond fission according to route B. We assume, however, that in some cases route A is preferred because it involves not only the P-C-5 bond fission but the formation of a new P-C-3 bond.

Acknowledgements

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