Reaction of Tetramethyl-1,2-dioxetane with Triphenylphosphine: Activation Parameters for the Formation of 2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxaphospholane

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The reaction of tetramethyl-1,2-dioxetane (**1**) and triphenylphosphine (**2**) in benzene-d_6 produced 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxaphospholane (**3**) in ~90% yield over the temperature range of 6-60°. Pinacolone and triphenylphosphine oxide (**4**) were the major side products [additionally acetone (from thermolysis of **1**) and tetramethyloxirane (**5**) were noted at the higher temperatures]. Thermal decomposition of **3** produced only **4** and **5**. Kinetic studies were carried out by the chemiluminescence method. The rate of phosphorane was found to be first order with respect to each reagent. The activation parameters for the reaction of **1** and **2** were: Ea ≅ 9.8 ± 0.6 kcal/mole; $\Delta S^{\neq}$ = -28 eu; $k_{30°}$ = 1.8 $m^{-1}sec^{-1}$ (range = 10-60°). Preliminary results for the reaction of **1** and tris (*p*-chlorophenyl)phosphine were: Ea ~ 11 kcal/mole, $\Delta S^{\neq}$ = -24 eu, $k_{30°}$ = 1.3 $M^{-1}sec^{-1}$ while those for the reaction of **1** and tris(*p*-anisyl)phosphine were: Ea ~ 8.6 kcal/mole, $\Delta S^{\neq}$ = -29 eu, $k_{30°}$ = 4.9 M^{-1} sec^{-1}.

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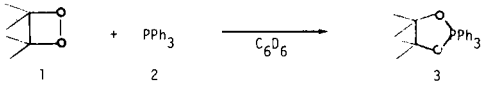
1,2-Dioxetanes have been extensively studied (1) because of their unique chemiluminescent thermal decomposition to two carbonyl fragments. Dioxetanes also undergo a number of interesting reactions in which no excited products are formed. Phosphorus compounds have been shown (2,3) to undergo insertion into the peroxy bond of dioxetanes. The reaction of triphenylphosphine with tetramethyl-1,2-dioxetane was shown (2) to produce a stable phosphorane in high yield. Subsequent work has shown that insertion reactions are of synthetic utility for the preparation of: phosphoranes (3), sulfuranes (4), arsenic V and antimony V compounds (5). Recent work has shown (6) that the reaction of triarylphosphines with tetramethyl-1,2-dioxetane occurs *via* a concerted (biphilic) insertion of the phosphorus atom into the peroxy bond of the dioxetane. In the present study, the activation parameters for phosphorane formation in the reaction of triphenylphosphine with tetramethyl-1,2-dioxetane are reported.

Results and Discussion.

The reaction of triphenylphosphine (**2**) with tetramethyl-1,2-dioxetane, **1**, to yield 2,2-dihydro-4,4,5,5,-tetramethyl-2,2,2-triphenyl-1,3,2-dioxaphospholane (**3**), was carried out as previously reported (6). The yield of the phosphorane (**3**) was 90% or better over a temperature range of 6-60°.



1 2 3

The thermal decomposition of phosphorane, **3**, produced tetramethyloxirane and triphenylphosphine oxide. Analogous results (6) were obtained for the reaction of **1** with tris(*p*-chlorophenyl)phosphine and tris(*p*-anisyl)phosphine. Kinetic studies were carried out by the chemiluminescence method. A ten-fold or greater excess of phosphine in xylenes was added to a solution of **1** in xylenes at the desired temperature and the decay of luminiscence intensity monitored with time. The thermal decomposition of **1** is extremely slow compared to the reaction of **1** with phosphine. The intensity of luminescence serves as a measure of dioxetane concentration. Figure 1 shows the results of a typical experiment in which phosphine is added to the reaction mixture. The insert in Figure 1 shows the pseudo-first order plot of the data. The reaction is of

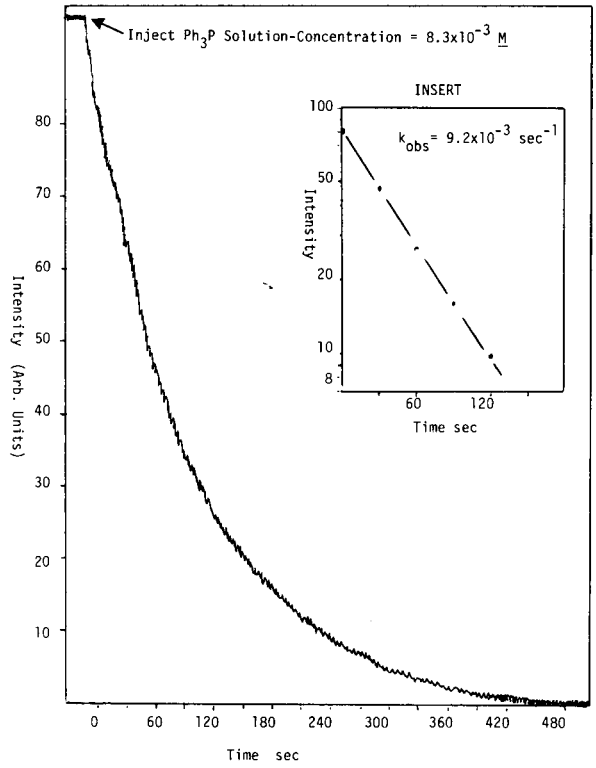


Figure 1. Trace of the Decay of Luminescence Intensity for the Reaction of Triphenylphosphine and Tetramethyl-1,2-dioxetane in Xylenes at 20°. Insert: Semi-log Plot of Relative Dioxetane Concentration vs Time (k_2= 1.1 $M^{-1}sec^{-1}$).

the first order with respect to dioxetane. Variation of the ratio of phosphine to dioxetane as well as the linear dependence of k_{obs} on phosphine concentration (Figure 2) showed the reaction to be of the first order with respect to

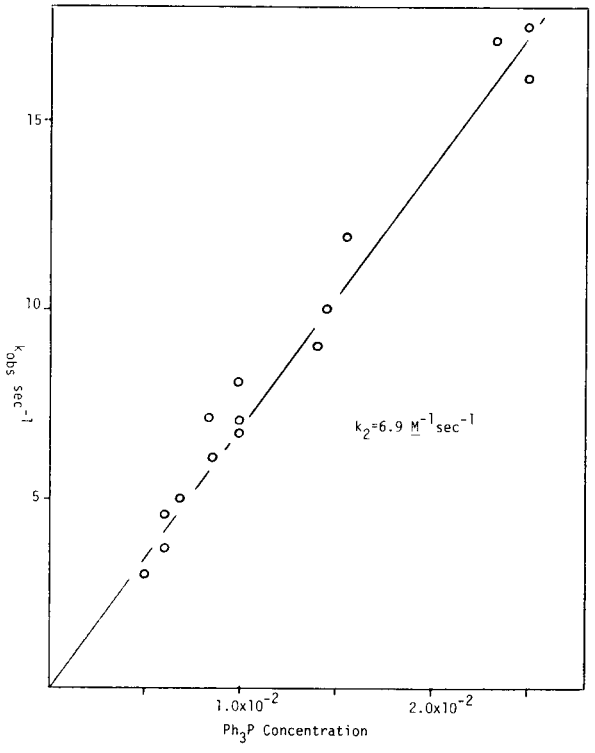


Figure 2. Plot of k_{obs} vs Triphenylphosphine Concentration for the Reaction of 1 and 2 at 55° in Xylenes.

phosphine as well. Plots of the calculated second order rate constants *vs* 1000/T°K are shown in Figure 3. The activation parameters calculated from the data are listed in Table 1.

Table 1

Activation Parameters for the Formation of Phosphoranes in the Reaction of Triarylphosphines with Tetramethyl-1,2-dioxetane in Xylenes

Ar-	Ea (kcal/mole)	$\Delta S^{\neq}$	$k_2 M^{-1}sec^{-1}$ (30°)
Ph	9.8 ± 0.6	-28	1.8
p-anisyl	8.6 ± 0.5	-29	4.9
p-chlorophenyl	~11	-24	1.3

Historically, the reaction of dialkyl peroxides with trivalent phosophrus compounds has been regarded (7) to proceed *via* nucleophilic attack on oxygen by phosphorus. Denney showed (8) that the results for the reaction of diethyl peroxide with trivalent phosphorus compounds were consistent with a biphilic process in which the phosphorus atom was bonding with both oxygen atoms in the transition state. Based on relative rates and the lack of a polar solvent effect (3a), the mechanism for the reaction of trivalent phosphorus compounds with tetramethyl-1,2-dioxetane was considered to be a concerted process.

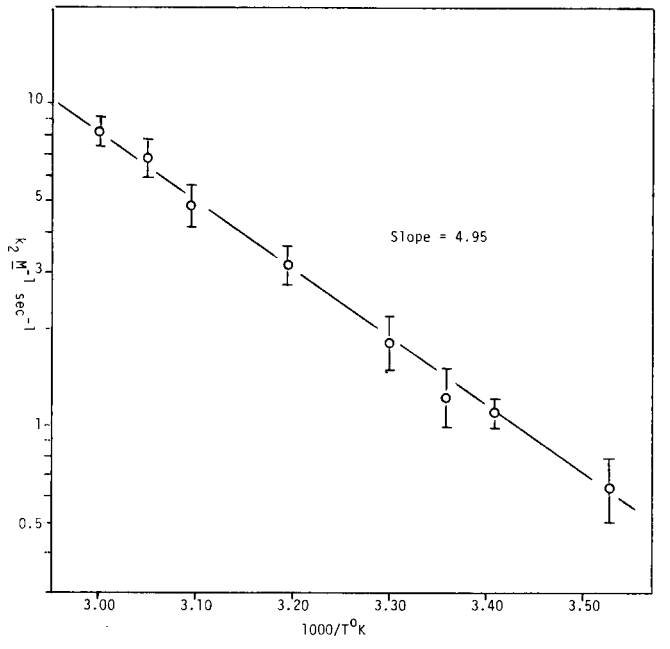
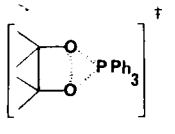


Figure 3. Arrhenius Plot of k_2 for the Reaction of 1 and 2 in Xylenes.

Results with triphenylarsine and triphenylantimony and tetramethyl-1,2-dioxetane were interpreted to be consistent (5) with a concerted or biphilic mechanism. The results of the recent study (6) of the kinetics of phosphorane formation and decomposition have ruled out a nucleophilic mechanism for the reaction of triarylphosphines with tetramethyl-1,2-dioxetane. The correlation of k_2 for the reaction of **1** with triarylphosphines with σ^+ values was interpreted (6) to be consistent with a biphilic mechanism of insertion in which both the nucleophilicity and electrophilicity of the phosphorus are involved in the transition state (Scheme 1).

SCHEME 1



The activation parameters for the reaction of **1** and **2** are consistent with a bimolecular process (9). The data show that phosphines with electron-donating substituents yield a lower activation energy while phosphines with electron-withdrawing substituents yielded the opposite results. Little or no effect is noted in the entropy term. These effects suggest that the nucleophilic component in the biphilic process is more important than the electrophilic component in agreement with the previous observations (6). The activation parameter data can not prove a biphilic process. The present results further characterize the well-established biphilic mechanism.

The activation parameters for the reaction of **1** and **2**

are very similar to those reported (10) for the reaction of triphenylphosphine with alkyl hydroperoxides in ethanol [activation parameters for the reaction of triphenylphosphine and *t*-butyl hydroperoxide were: Ea = 10.8; $\Delta S^{\neq}$ = -24 e.u.]. The results (10) were interpreted in relationship to a nucleophilic process, in which little or no weakening of the O-H bond was occurring in the transition state. However, the results of Shulman (11) for the reaction of *t*-butyl hydroperoxide and group 5A compounds suggest (6) the possibility of a biphilic-type process.

EXPERIMENTAL

All solvents were of reagent grade. Tetramethyl-1,2-dioxetane (**1**) was prepared according to published procedures (12) and recrystallized from *n*-pentane at -78°. The resulting pale-yellow needles were stored in mg quantities at -30° until use. ^{1}H nmr spectra were recorded on a Varian 360L spectrometer. Triarylphosphines (Alfa-Ventron) were used without further purification.

Phosphorane Product Studies.

2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxaphospholane, 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-tri(*p*-anisyl)-1,3,2-dioxaphospholane, and 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-tri(*p*-chlorophenyl)-1,2,3-dioxaphospholane were prepared as previously reported (6). The reactions of triarlyphosphines and **1** in benzene-d_6 were carried out at various temperatures (up to 60°), followed by rapid cooling on ice after several minutes. The products of the reactions at the various temperatures were determined by nmr spectroscopy. At 60°, the yields of the phosphoranes were high (~90%) and only slightly lower than the results reported (6) for the low temperature preparations. In addition to the normal (6) side product, pinacolone, small amounts of acetone and tetramethyloxirane were noted in the high temperature preparations. The acetone apparently resulted from the normal thermal decomposition of **1** before addition of phosphine. The formation of tetramethyloxirane was apparently due to some thermal decomposition of the newly-formed phosphoranes at the higher temperatures. Thermal decomposition of the phosphoranes produced only tetramethyloxirane and the corresponding phosphine oxide (6).

Kinetic Studies.

The chemiluminescence apparatus was modified from that previously employed (6). The jacketed cell was enlarged to hold a total capacity of 2 ml and to allow rapid mixing of reagents by magnetic stirring. Microsyringes with 9 inch needles were used to inject a concentrated phosphine solution directly into the dioxetane solution without opening the chemiluminescence apparatus. With these modifications, the value of k_2 (1.1 $M^{-1}sec^{-1}$) for the formation of **3** from the reaction of **1** and **2** at 20° was found to again agree with the easiest reported value, 1.0 $M^{-1}sec^{-1}$ (2). Although the results reported (6) using the unmodified apparatus were reproducible, the values of k_2 were systematically high due to the lack of efficient mixing of reagents in a narrow sample cell. However, the present data show that previous values (6) were consistent relative to each other. The following procedure was employed. A tenfold or greater excess of triarylphosphine in 50 $\mu\propto$ of xylenes was added rapidly (*via* syringe) to a solution of **1** (2×10^{-4} to $8 \times 10^{-4}M$) in a known volume of xylenes containing $8 \times 10^{-3}M$ 9,10-dibromoanthracene in a jacketed cell (temperature controlled to ±0.1°). The decay of luminescence was monitored *vs* time on a strip-chart recorder.

Acknowledgment.

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