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Kinetics of the Photochemically Generated *t*-Butoxy Radical Reactions with Phosphine(PH₃)*

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The gas phase reactions of the photochemically generated *t*-butoxy radicals with phosphine (PH₃) were studied in the temperature range of 35–80°C. We found the significant differences between high temperature thermal reactions and low temperature photo reactions. In comparison with the reactions of *t*-butoxy radicals with other hydrogen donors, some possible mechanistic suggestions were made for the explanation of the results.

Introduction

In the last two decades our knowledge of phosphorus compounds has expanded so rapidly that it now constitutes a major branch of chemistry.¹

In many ways phosphorus rivals carbon in its structural versatility, the general variety of its compounds, and its biochemical importance.

The presence of unoccupied low energy d-orbitals makes them participate in bonding and form hybridized orbitals which have special spatial orientations. The ready availability of d-orbitals in the phosphorus accounts for many of their differences in chemistry compared to nitrogen.

Phosphorus usually forms either three, four, or five covalent linkages to other atoms and a handful of one, two, and six-connected compounds are also known. In a few special cases, the phosphorus atom may form some kind of direct chemical linkage with as many as ten neighbors.¹

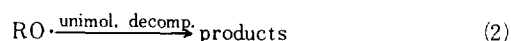
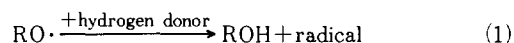
The intimate involvement of phosphorus compounds in living processes is now well recognized and modern biochemistry is dominated by phosphate esters such as ATP and DNA.

Phosphorus compounds have also been detected as minor constituents of the atmospheres of Jupiter and Saturn.² It has been proposed that the Great Red Spot on Jupiter may be due to red phosphorus formed as a final product of the photodissociation of phosphine by Prinn and Lewis.

Thus, to supply some informations for this interesting chemistry of phosphorus compounds, we have studied the reactions of phosphine with *t*-butoxy radicals in the gas phase.

Among alkoxy radicals, *t*-butoxy radical reactions have been the most extensively studied. Alkoxy radicals themselves are also known to be one of the most important intermediates in biological systems, atmospheric reactions, and etc.

Most of the alkoxy radical reactions have been studied by competition methods.^{3,14} In the presence of hydrogen donors, alkoxy radicals may have two competitive pathways; the hydrogen abstraction reaction and self-decomposition.



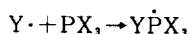
Consequently, the distribution of final products are determined by the relative rate constants for two reaction routes.

In the liquid and gas phase, the relative rate constants for

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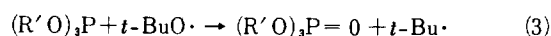
reactions (1) and (2) with different alkoxy radicals and hydrogen donors were studied by many research groups.^{4,15,16}

A phosphorus (III) compound can react with a free radical to increase the coordination number to four and give a phosphoranyl radical with nine valence electrons.

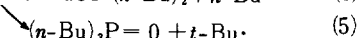
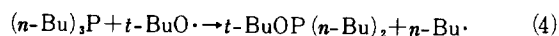


The reactions of alkoxy radicals play an important role in the transfer of kinetic chains in the autoxidation of phosphites and phosphines.

Trialkyl phosphites ((R'O)₃P) readily interacts with *t*-butoxy radicals, forming the corresponding derivatives containing the phosphoryl group $\equiv P=O$:^{5,13}



In case of alkyl phosphines (R'P), both the oxygen transfer and substitution reaction were observed by Buckler.^{6,13}



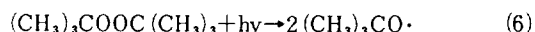
Thus there seems to be a definite kinetic control of the relative amounts of the products of addition to phosphines; its possible causes may be different distributions of unpaired electron density in the P-O and P-C bonds of phosphoranyl radical and also the differences between the energies of the bonds undergoing dissociation.

No report has yet been published on the alkoxy radical reactions with P-H bonded compound in the gas phase. We, therefore, decided to use PH₃ as hydrogen donor in the above-mentioned reaction schemes (reaction (1) and (2)) to examine the *t*-butoxy radical reactions with P-H bonded compounds.

The results were compared with those of known reactions in which other hydrogen donors were used.

Experimental

t-Butoxy radicals were generated by ultraviolet photolysis of *di-tert*-butyl peroxide (DTBP).¹⁰



In the presence of phosphine (PH₃), we assumed at first that *t*-butoxy radicals react through the following two major routes.



The relative rate constants for the reactions (7) and (11) were determined by quantitative analyses of major products, acetone and *t*-butyl alcohol, with gas chromatography.

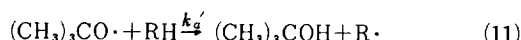
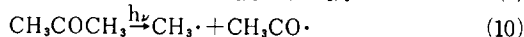
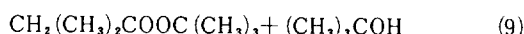
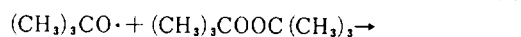
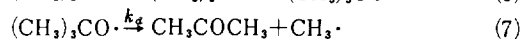
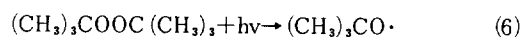
The schematic diagram of the reaction system is shown in Figure 1. The detailed description of the reaction system and procedures were reported recently¹⁰. 2.4m HALL M-18-OL column was used to separate reactants and products in our system. Reaction products were identified with the GC retention times of standard samples. Quantitative analyses were carried out with the calibration curves obtained with known concentrations of standard samples.

Phosphine(PH₃) was purchased from Matheson Gas Co., and used without further purification after confirming its purity by

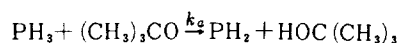
Gas Chromatography.

Results and Discussion

It is well known that the following reactions are important in the photolysis of *di-tert*-butyl peroxide (DTBP) in the presence of hydrogen donors.⁷



As mentioned earlier, at this stage we have once assumed that hydrogen abstraction is the only available reaction path for the interaction of *tert*-butoxy radicals with phosphine (PH₃).



Since we are only interested in the formation of acetone and *t*-butyl alcohol in our kinetic analyses for the present, reaction (8) can be excluded in our considerations. Reaction (12) is unim-

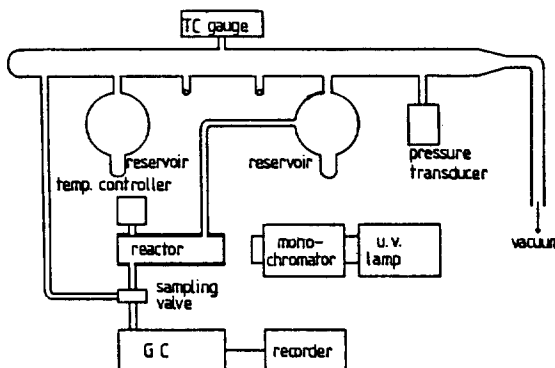


Figure 1. Schematic diagram of the reaction system.

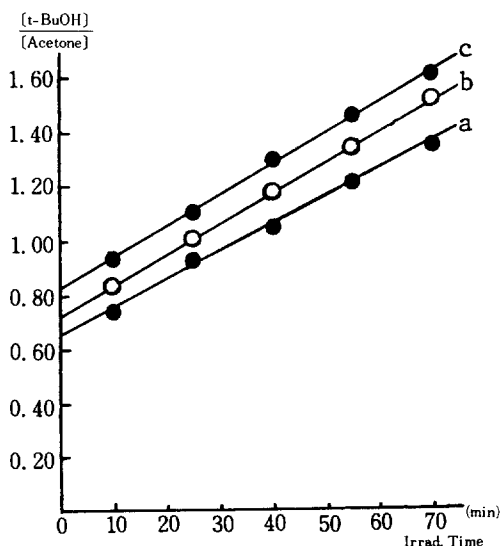


Figure 2. [t-BuOH]/[Acetone] ratios at various reaction times at 65°C. a; [PH₃] = 2.73 × 10⁻³ mole/l. b; [PH₃] = 3.81 × 10⁻³ mole/l. c; [PH₃] = 5.21 × 10⁻³ mole/l.

portant since excess amounts of PH_3 are present in the reaction system at all times. Reaction (9) is also unimportant; With the usual concentration of DTBP about 1 ± 0.3 torr, we can conclude that k_9 , DTBP is several orders of magnitude smaller than k_7 , from the experimental results of Hendry group and the accepted Arrhenius parameters for k_7 ($\log A = 14.1 \text{ s}^{-1}$, $E_a = 15.3 \text{ kcal/mol}$).⁹ Hendry *et al.* estimated Arrhenius parameters for the reactions $(\text{CH}_3)_3\text{CO} \cdot (\text{CH}_3)_3\text{COC}(\text{CH}_3)_3 \rightarrow (\text{CH}_3)_3\text{COH} + \text{CH}_2(\text{CH}_3)_2\text{COC}(\text{CH}_3)_3$ ($\log A = 9.0 \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$, $E_a = 7.93 \text{ kcal/mol}$).⁸ We expect negligible difference in Arrhenius parameters between this reaction and reaction (9).

Reaction (10) is very difficult to eliminate totally in our experimental system. A blank experiment with acetone has indicated a small amount of acetone decomposition at a prolonged irradiation with a UV lamp.

Thus the product ratios have been extrapolated to zero reaction time from the plot of the product ratios vs. irradiation times to correct the effect due to the possible secondary reactions of acetone and *t*-butyl alcohol, especially due to the acetone decomposition. Such a plot is shown in Figure 2.

Under the conditions that $[\text{PH}_3] \gg [\text{DTBP}]$ and at early reaction times, we thus may only consider reactions (7) (11) as the major reactions for *tert*-butoxy radicals. From eq (7) and (11) we obtain

$$\frac{[t\text{-BuOH}]_{t=0}}{[\text{acetone}]_{t=0}} = \frac{R(t\text{-BuOH})}{R(\text{acetone})} = \frac{k_a}{k_d} [\text{PH}_3] + C \quad (13)$$

where C is the small and nearly constant term that is related to the fact that some *t*-butyl alcohol was formed even when no PH_3 was present in the system.¹⁰

Under our experimental pressure (*i.e.*, total pressure of 30 torr or more), *t*-butoxy radical decomposition, reaction (7), was found to be in high-pressure limit. A total pressure change from 30 torr to 1 atm with addition of Ar as an inert third body did not change the $[t\text{-BuOH}]/[\text{acetone}]$ ratios. (Figure 3)

Table 1 shows the experimental results of the change of $[t\text{-BuOH}]/[\text{acetone}]$ ratios (extrapolated to zero reaction times) with different PH_3 concentrations at different reaction temperatures.

In Figure 4, $[t\text{-BuOH}]_{t=0}/[\text{acetone}]_{t=0}$ ratios were plotted against PH_3 concentrations. From the slope of the figure the absolute rate constant ratios (reference eq. (13)) at different temperatures were obtained.

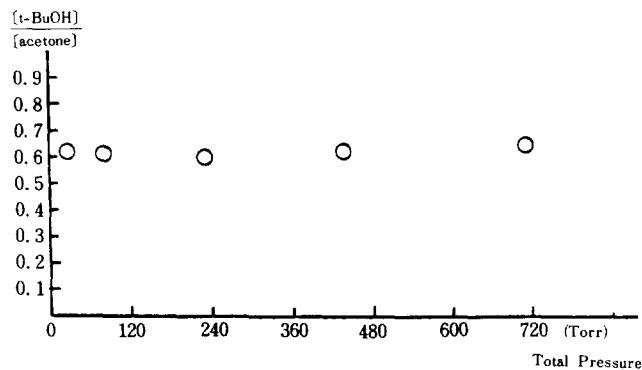


Figure 3. $[t\text{-BuOH}]/[\text{Acetone}]$ ratios vs. total pressures at 65°C , PH_3 , 30 torr; DTBP, 1 torr; Ar was used as third body.

The Arrhenius plot for the rate constant ratios is shown in Figure 5.

Since the estimation of activation energy and A factor from the rate constants in the narrow temperature range is inaccurate, we have assumed A factor of $10^{9.0} \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$ for the reaction (11); A factors can be predicted with relatively small errors from the known related reactions. A factor for the reaction $(\text{CH}_3)_3\text{CO} \cdot + \text{HSi}(\text{CH}_3)_3 \rightarrow (\text{CH}_3)_3\text{COH} + \cdot\text{Si}(\text{CH}_3)_3$ has been known to be $10^{8.5} \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$, and we have only corrected the difference between the reaction path degeneracies for PH_3 .

By using the most reasonable Arrhenius parameters for k_d ($\log A_d = 14.1 \text{ s}^{-1}$, $E_{ad} = 15.3 \text{ kcal/mol}$), we obtained $\log A_a = 9.0 \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$ and $E_{aa} = 5.0 \text{ kcal/mol}$ for hydrogen abstraction reaction of *t*-butoxy radicals with PH_3 (eq (11)).

Here, it should be remembered again that this result is based on the assumption that hydrogen abstraction is the only route

TABLE 1: $[t\text{-BuOH}]/[\text{acetone}]$ Ratios (Extrapolated to Zero Reaction Times) vs. $[\text{PH}_3]$ at Different Reaction Temperatures

35°C	PH_3 (mol/l) $\times 10^3$	2.00	2.78	3.88	4.42	5.40			
	$\frac{[t\text{-BuOH}]}{[\text{acetone}]}$	0.840	0.866	0.898	1.06	1.07			
50°C	PH_3 (mol/l) $\times 10^3$	1.92	2.67	3.72	5.19	7.79			
	$\frac{[t\text{-BuOH}]}{[\text{acetone}]}$	0.778	0.756	0.811	0.937	1.13			
65°C	PH_3 (mol/l) $\times 10^3$	1.41	1.96	2.73	3.81	5.08	5.31	8.16	10.8
	$\frac{[t\text{-BuOH}]}{[\text{acetone}]}$	0.581	0.627	0.652	0.720	0.732	0.820	0.889	1.14
80°C	PH_3 (mol/l) $\times 10^3$	1.94	2.48	2.71	3.77	4.21	5.25	6.16	9.40
	$\frac{[t\text{-BuOH}]}{[\text{acetone}]}$	0.533	0.529	0.530	0.581	0.567	0.750	0.657	0.770

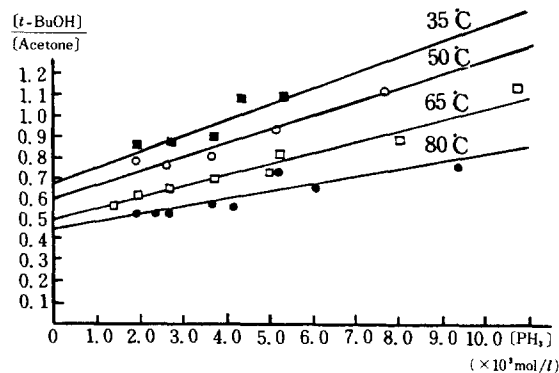


Figure 4. $[t\text{-BuOH}]/[\text{Acetone}]$ ratios (extrapolated to zero reaction times) vs. $[\text{PH}_3]$ at different reaction temperatures.

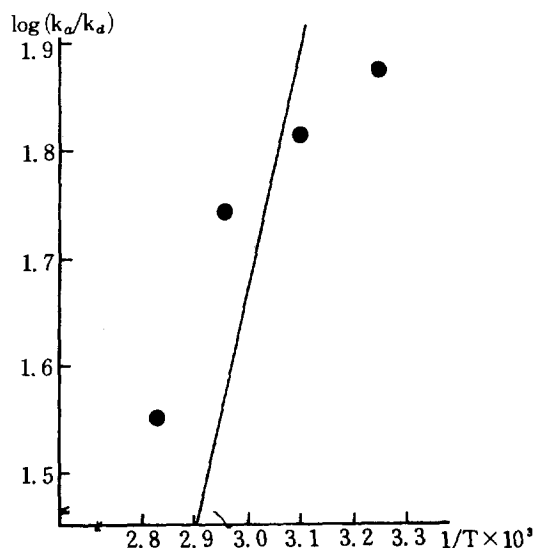
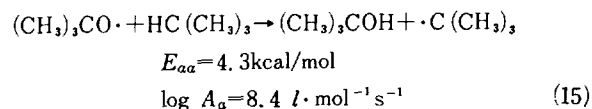
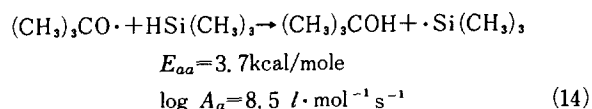


Figure 5. Arrhenius plot for the relative constant ratios; •, experimental value; solid line, the best fit linear line with $\log A_a (l \cdot \text{mol}^{-1} \text{sec}^{-1}) = 9.0$.

for the reaction of *t*-butoxy radicals with PH_3 .

These results are compared with those of other experiments in which different hydrogen donors are used.



Noticing that P-H bond dissociation energy of phosphine is 79 kcal/mol and Si-H and C-H bond dissociation energies of trimethylsilane and isobutane are 90,92 kcal/mol respectively, we have obtained absurdly large activation energy for PH_3 . Furthermore, as shown in Figure 5, the Arrhenius plot was not linear. In contrast, reasonable Arrhenius Parameters ($E_{aa} = 1.4$ kcal/mole, $\log A_a = 9.0 \text{ M}^{-1} \text{sec}^{-1}$) have been obtained in our laboratory for the thermally generated *t*BuO \cdot radical reactions with PH_3 at high temperatures (130–180°C).¹⁷

It is well known that alkoxy radicals can add to phosphorous

atoms at low temperatures.^{5,6,13} Although the Arrhenius parameters for the addition reactions are not known it is reasonable to assume that the stability of the addition adduct would increase as the temperature decreases.

We thus may only speculate that *t*BuO \cdot radical reactions with PH_3 at low temperatures proceed not only via H atom abstraction but also via addition to the phosphorous atom.

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