

Kinetics of Oxidation of Triphenylarsine and Triphenylstibine by Hydrogen Peroxide

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The kinetics of oxidation of triphenylarsine and triphenylstibine (Ph_3M ; $\text{M} = \text{As}, \text{Sb}$) have been studied in 70% (v/v) and 95% (v/v) aqueous ethanol respectively. The reaction exhibits second-order kinetics, first-order each in Ph_3M and hydrogen peroxide. A mechanism analogous to the one proposed for the oxidation of triphenylphosphine has been suggested.

INTRODUCTION

Earlier we have reported the kinetics and mechanism of oxidation of triphenylphosphine (TPP) by hydrogen peroxide¹. Herein we present the kinetics of oxidation of Ph_3M ($\text{M} = \text{As}, \text{Sb}$) by hydrogen peroxide.

EXPERIMENTAL

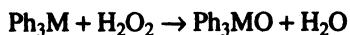
Triphenylarsine (TPA) (Fluka AG) was recrystallized from ethanol. Triphenylstibine (TPS) was prepared by literature method². Hydrogen peroxide (s.d. Fine-Chem Pvt. Ltd.) was estimated by using a standard potassium permanganate solution. Ethanol was purified by the usual method. All the other chemicals used were of AR grade.

The kinetic studies were carried out under pseudo first-order conditions ($[\text{H}_2\text{O}_2] \gg [\text{Ph}_3\text{M}]$) by monitoring the disappearance of the ultraviolet absorption characteristics of TPA ($\lambda_{\text{max}} = 248 \text{ nm}$) and TPS ($\lambda_{\text{max}} = 255 \text{ nm}$). The pseudo first-order rate constant (k_1) in each kinetic run was evaluated from the slope of linear plot of $\log (\text{O.D.})$ versus time (correlation coefficient, $r > 0.995$), by the method of least-squares. The second-order rate constants (k_2) were obtained from $k_2 = k_1/[\text{H}_2\text{O}_2]$. The precision of k values is given in terms of 95% confidence limit of the 'Student t '.

In TPA oxidation, TLC of the reaction mixture of an actual kinetic run showed the formation of a single product which has identified to be triphenylarsine oxide from UV and IR studies³⁻⁵ ($\bar{\nu}_{\text{As=O}} = 880 \text{ cm}^{-1}$). In TPS oxidation, the reaction product was found to be a crystalline polymeric antimony product⁶⁻⁸ which did not melt even after 280°C and which liberated free iodine from potassium iodide

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in glacial acetic acid. The stoichiometry of the reaction was found to be 1 : 1 and the reaction can be represented as



RESULTS AND DISCUSSION

Rate coefficients for different concentrations of Ph_3M at constant $[\text{H}_2\text{O}_2]$ and vice versa (Table 1) show that the reaction is first-order in Ph_3M and first-order in H_2O_2 . Further a plot of k_1 versus $[\text{H}_2\text{O}_2]$ is a straight line passing through the origin (TPA : $r = 0.999$, TPS : $r = 0.998$). These results show that the reaction is overall second-order.

TABLE I
DEPENDENCE OF RATE ON $[\text{Ph}_3\text{M}]$ and $[\text{H}_2\text{O}_2]$

$10^5 [\text{Ph}_3\text{M}]$ (mol dm ⁻³)	$10^3 [\text{H}_2\text{O}_2]$ (mol dm ⁻³)	$10^4 k_1^a$ (s ⁻¹)	$10 k_2^a$ (dm ³ mol ⁻¹ s ⁻¹)
TPA ^b			
7.50	3.00	4.14 ± 0.05	1.38 ± 0.02
8.00	3.00	4.18 ± 0.05	1.39 ± 0.02
8.50	3.00	4.09 ± 0.09	1.36 ± 0.03
9.00	3.00	4.05 ± 0.06	1.35 ± 0.02
9.50	3.00	4.11 ± 0.05	1.37 ± 0.02
10.00	3.00	4.02 ± 0.09	1.34 ± 0.03
9.00	1.00	1.39 ± 0.02	1.39 ± 0.02
9.00	1.50	2.00 ± 0.05	1.33 ± 0.04
9.00	2.00	2.78 ± 0.03	1.39 ± 0.02
9.00	2.50	3.36 ± 0.05	1.34 ± 0.02
9.00	3.50	4.91 ± 0.06	1.40 ± 0.02
9.00	4.00	5.44 ± 0.12	1.36 ± 0.03
TPS ^c			
9.0	2.00	13.1 ± 0.4	6.55 ± 0.20
10.0	2.00	13.4 ± 0.2	6.70 ± 0.11
12.5	2.00	12.9 ± 0.1	6.47 ± 0.05
15.0	2.00	13.6 ± 0.2	6.79 ± 0.11
17.5	2.00	12.9 ± 0.1	6.44 ± 0.06
20.0	2.00	12.8 ± 0.2	6.42 ± 0.01
15.0	1.50	9.90 ± 0.3	6.63 ± 0.21
15.0	2.50	16.1 ± 0.2	6.46 ± 0.07
15.0	3.00	16.9 ± 0.6	6.64 ± 0.20
15.0	3.50	22.4 ± 0.2	6.40 ± 0.07
15.0	4.50	29.7 ± 0.8	6.61 ± 0.19

^aThe error quoted in k is the 95% confidence limit of the 'Student t '.

^bSolvent = 70% (v/v) aqueous ethanol, temp. = 35°C

^cSolvent = 95% (v/v) aqueous ethanol, temp. = 25°C

Effect of added H⁺ ions and solvent composition on the rate of oxidation are shown in Table 2. Addition of H⁺ ions has no effect on the rate of oxidation. The rate of the reaction increases with increase in the dielectric constant, *i.e.*, nucleophilicity (water content) of the reaction medium. Kinetic studies with vinyl monomer acrylonitrile has no effect on the rate of oxidation and no polymerization occurred. The rate constants at five different temperatures and the activation parameters are given in Table 3.

TABLE 2
EFFECT OF [H⁺], SOLVENT COMPOSITION ON THE RATE OF OXIDATION

$10^3 [H^+]$ (mol dm ⁻³)	$10 k_2^{a,c}$ (dm ³ mol ⁻¹ s ⁻¹)	$10 k_2^{b,d}$ (dm ³ mol ⁻¹ s ⁻¹)	C ₂ H ₅ OH-H ₂ O (% v/v)	$10^2 k_2^a$ (dm ³ mol ⁻¹ s ⁻¹)	$10 k_2^b$ (dm ³ mol ⁻¹ s ⁻¹)
0.00	1.35 ± 0.02	6.63 ± 0.21	95-5	—	6.63 ± 0.21
2.00	1.35 ± 0.02	6.71 ± 0.10	90-10	7.74 ± 0.12	7.23 ± 0.26
4.00	1.32 ± 0.04	6.45 ± 0.07	80-20	9.09 ± 0.17	7.97 ± 0.40
6.00	1.34 ± 0.02	6.45 ± 0.07	75-25	9.65 ± 0.22	8.33 ± 0.20
8.00	1.34 ± 0.03	6.45 ± 0.07	70-30	13.5 ± 0.2	—
10.00	1.35 ± 0.02	6.75 ± 0.11	65-35	20.0 ± 0.3	9.66 ± 0.37
15.00	1.34 ± 0.02	6.66 ± 0.19	60-40	22.8 ± 0.6	11.5 ± 0.2

^a10⁵ [TPA] = 9.0 mol dm⁻³, 10³ [H₂O₂] = 3.0 mol dm⁻³, temp. = 35°C

^b10⁴ [TPS] = 1.5 mol dm⁻³, 10³ [H₂O₂] = 1.5 mol dm⁻³, temp. = 25°C

^cSolvent = 70% (v/v) aqueous ethanol

^dSolvent = 95% (v/v) aqueous ethanol

TABLE 3
EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION

Temp. (°C)	10 k ₂ (dm ³ mol ⁻¹ s ⁻¹)	
	TPA ^a	TPS ^b
25	0.649 ± 0.009	6.63 ± 0.21
30	0.848 ± 0.007	7.63 ± 0.09
35	1.35 ± 0.02	8.49 ± 0.16
40	1.52 ± 0.02	9.63 ± 0.26
45	2.02 ± 0.02	10.3 ± 0.1
ΔH [‡] (K J mol ⁻¹)	42.5	15.0
ΔS [‡] (J K ⁻¹ mol ⁻¹)	-125	-198

^a10⁵ [TPA] = 9.0 mol dm⁻³, 10³ [H₂O₂] = 3.0 mol dm⁻³, solvent = 70% (v/v) aqueous ethanol.

^b10⁴ [TPS] = 1.5 mol dm⁻³, 10³ [H₂O₂] = 1.5 mol dm⁻³, solvent = 95% (v/v) aqueous ethanol.

The foregoing experimental observations with TPA and TPS are exactly analogous to those reported for the oxidation of TPP by hydrogen peroxide¹. Hence the mechanism proposed for TPP oxidation is applicable in the present study also. In TPP oxidation by hydrogen peroxide¹, a mechanism involving a

biomolecular nucleophilic displacement of Ph_3P on the peroxide molecule in the rate-determining step has been proposed.

The reactivity of TPA and TPS is compared with that of TPP^1 . The rate constant for the reaction of TPA with hydrogen peroxide was measured in 95% (v/v) aqueous ethanol at 25°C to compare the reactivity under identical conditions. The second-order rate constants for the oxidation of TPP^1 , TPS and TPA in 95% (v/v) aqueous ethanol at 25°C are $155 \pm 3 \times 10^{-2}$, $66.3 \pm 2.1 \times 10^{-2}$ and $2.93 \pm 0.04 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. The relative order of reactivity is found to be $\text{TPP} > \text{TPS} > \text{TPA}$. This observed order of reactivity is interesting because of the transposition of TPA and TPS. The same order of reactivity has been observed in the reaction of *tert*-butylhydroperoxide with Ph_3M^9 , peroxodisulphate (PS) with $\text{Ph}_3\text{M}^{7,10}$ and peroxodiphosphate (PP) with Ph_3M^8 . Hiatt *et al.*⁹ attribute this order to two conflicting trends, availability of d orbitals for π -bonding with peroxide oxygen and the Group V element to oxygen bond strength. The reactivity order in PS oxidation⁷ and PP oxidation⁸ have been attributed to the above two conflicting trends. The reactivity order observed in the present investigation can also be accounted for by the two conflicting trends proposed by Hiatt *et al.*⁹.

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