

SOLVENT EFFECTS IN THE OXIDATION OF TRIPHENYLPHOSPHINE

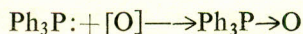
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Abstract. Oxidation of triphenylphosphine with peroxybenzoic acid has been studied kinetically in various polar solvents. It has been observed that this reaction follows second order kinetics and its rate constant is directly proportional to the dielectric constant of the solvent employed. Activation energies and entropies of activation of this reaction have also been calculated.

It has previously been reported that peroxybenzoic acid oxidations of sulphoxides and cyclic olefins to the corresponding sulphones and epoxides respectively, are influenced by the nature of the solvent.^{1,2} It was pointed out there that the rates of the oxidations were indirectly proportional to the dielectric constants of the solvents in which the reactions were carried out and that in these oxidations the electrostatic interactions were more important compared to the nonelectrostatic ones. In order, therefore, to probe more into such a trend, oxidation of triphenylphosphine with peroxybenzoic acid was considered kinetically. A literature survey, however, revealed that this reaction has not so far been kinetically studied although the formation of triphenylphosphine oxide from the phosphine by various oxidising reagents has been known for a long time.³



Present study, therefore, deals with the kinetics of the oxidation of triphenylphosphine with peroxybenzoic acid to triphenylphosphine oxide in the following solvents, arranged in their ascending order of dielectric constants: tetrahydrofuran, 2-methoxyethanol, acetone, ethanol, methanol, dimethylformamide and acetonitrile. The selection of these solvents was motivated firstly because of the ready solubility of the reactants in them and secondly for their appreciable differences in the dielectric constants.

Results and Discussion

The rate constants for the oxidation of triphenylphosphine with peroxybenzoic acid were determined in tetrahydrofuran, 2-methoxyethanol, acetone, ethanol, dimethylformamide and acetonitrile at 30°C ($\pm 0.5^\circ\text{C}$) and in methanol at 40.0, 45.0 and 50.0 ($\pm 0.5^\circ\text{C}$). It was observed that the reaction is bimolecular and follows second order kinetics. The activation energy was calculated from the Arrhenius plots as shown in Fig. 1 and the entropy of activation was worked out with the help of the following equation.⁴

$$\Delta S^\ddagger/4.576 = \log K - 10.753 - \log T + E/4.576 T$$

All the data, as obtained in these studies are recorded in Tables 1 and 2.

It is obvious from these results that there is a relationship between the rate constants and the dielectric constant of the solvents. A plot of the rate constants vs the dielectric constants of the solvents employed gives a straight-line (Fig. 2). It is seen from this plot that the rate of this oxidation reaction increases with the increase of the dielectric constant of the solvent medium. In other words the rate constant in a particular solvent is directly proportional to its dielectric constant. It is, therefore, inferred that the electrostatic and not the nonelectrostatic interactions are more important in this reaction.

The effects of solvents on the kinetics of the reaction between triphenylphosphine and *cis*-2-butene episulphide and *trans*-2-butene episulphide have been reported by Denny and Boskin.⁵ These workers noted that this reaction is relatively insensitive to large variations in the dielectric constant of the medium and proceeds by a nucleophilic attack of the phosphine on the sulphur to give the phosphine sulphide and olefin in one step.

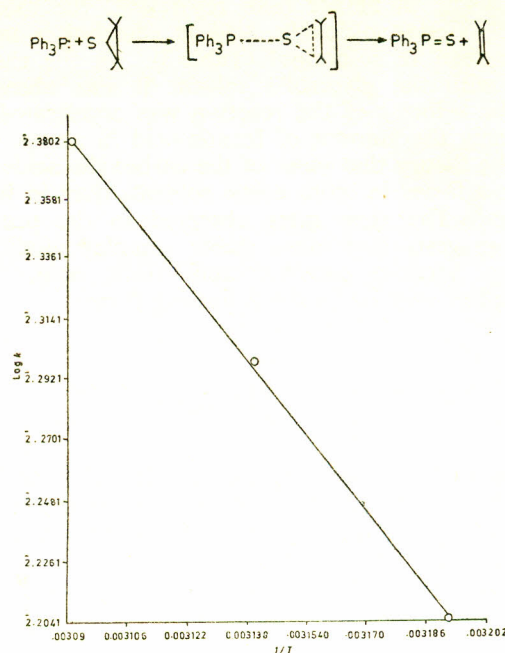


Fig. 1. Arrhenius plot for peroxy benzoic acid oxidation of triphenylphosphine in methanol.

TABLE 1. ARRHENIUS PLOT FOR PEROXYBENZOIC ACID OXIDATION OF TRIPHENYLPHOSPHINE IN METHANOL.

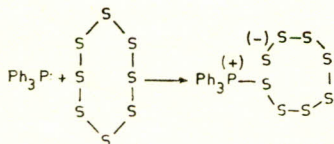
Temperature (°C)	Reciprocal of temperature	Rate constants (k l, mole ⁻¹ sec ⁻¹)	Log k	E (kcal mole ⁻¹)	ΔS^\ddagger (deg ⁻¹ cal mole ⁻¹)
40+273	0.00329	0.016	$\bar{2}.2041$		
45+273	0.00314	0.0199	$\bar{2}.2989$	8.108	-68.64
50+273	0.00309	0.024	$\bar{2}.3802$		

TABLE 2. SOLVENT EFFECTS IN THE OXIDATION OF TRIPHENYLPHOSPHINE WITH PEROXYBENZOIC ACID AT 30°C.

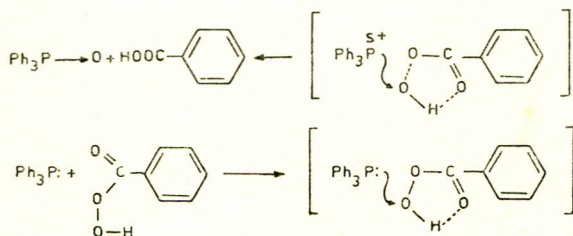
Solvent	Dielectric constant	Concn (m-mole/litre)		Rate constants (k l, mole ⁻¹ sec ⁻¹)
		Triphenyl phosphine	Peroxybenzoic acid	
Tetrahydrofuran	7.6	5.00	10.00	0.00130
		7.00	15.00	0.00129
		10.00	27.00	0.00128
Methoxyethanol	15.0	2.5	5.00	0.00225
		4.9	10.00	0.00221
		9.5	20.00	0.00225
Acetone	21.4	5.00	10.00	0.0037
		10.00	19.00	0.0035
		2.5	5.00	0.0035
Ethanol	24.3	10.00	18.00	0.00410
		5.00	8.5	0.00411
		2.5	5.00	0.00411
Methanol	32.6	10.00	19.00	0.0056
		5.00	10.00	0.0054
		9.00	17.00	0.0054
Dimethylformamide	37.0	9.00	17.00	0.00589
		4.9	9.8	0.00587
		2.5	5.00	0.00586
Acetonitrile	38.8	10.00	20.00	0.00615
		5.00	8.40	0.00610
		5.00	8.40	0.00610
		5.00	9.00	0.00618

However, Meguerian and Bartlett have described the reaction between elemental sulphur and triphenylphosphine using various solvents and reported that the rate of this second order reaction is considerably influenced by the change of the dielectric constant of the medium.⁶

In fact a several hundred-fold increase of the rate with a small increase of the dielectric constant of the medium was observed and it was attributed to the separation of charge in the rate-controlling step as shown below:



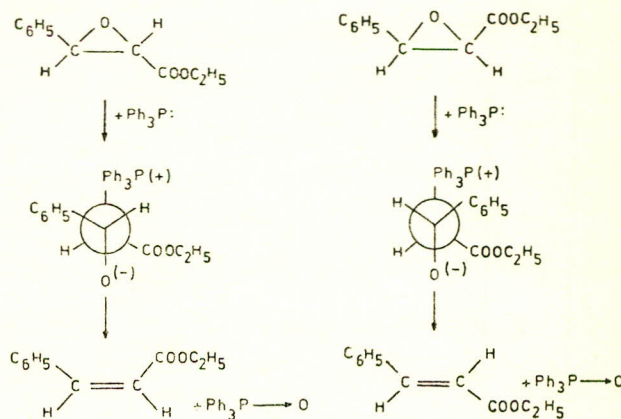
The results of the present study can, therefore, be explained on the basis of a transition state which is highly polar in character as depicted below:



In this scheme there is a nucleophilic attack of the triphenylphosphine on the more electronegative peroxy-oxygen of the peroxybenzoic acid. The observed rate increase with increasing solvent polarity is consistent with this mechanism because of the formation of a charged transition state.

It will be seen from a study of Table 2 that changing the dielectric constant of the solvent from 7.5 to 38.7 changes the rate by a factor of 7 only, indicating that there is little charge separation in the rate determining step. It can, therefore, safely be concluded that the reaction is concerted and proceeds without the intervention of any ions.

Similar conclusions have been drawn by Speziale and Bissing in their studies relating to the kinetics and mechanism of Witting reaction,⁷ particularly the reaction between triphenylphosphine and *cis*- and *trans*-ethylphenyl glycidates giving the triphenylphosphine oxide and the *trans*- and *cis*-ethyl cinamates respectively.⁷



It is of interest to mention here that the reaction between aryl peroxides and triphenylphosphine has also similarly been explained.⁸

Experimental

All solvents were purified by standard procedures. Triphenylphosphine (BDH) was recrystallised from ethanol, m.p. 79.5°C (lit. m.p. 80°C).⁹ Triphenylphosphine oxide, m.p. 154–156°C, was isolated from every oxidation experiment carried out in the solvents mentioned here. Peroxybenzoic acid was prepared by Kolthoff, Lee and Mair's¹⁰ method from benzoyl peroxide just before use in the kinetic runs, dissolved in the desired solvent and kept in a refrigerator (0°C). It was iodometrically standardised and the solutions of different concentrations were then prepared by dilution for use in these studies.

Kinetic Measurements. Solutions (100 ml) of triphenylphosphine and peroxybenzoic acid, in the

same solvent, were separately taken in two volumetric flasks and kept at the desired constant temperature provided by a thermostatically controlled-bath. The triphenylphosphine and peroxybenzoic acid solutions were mixed together after they had attained the temperature of the bath. From this reaction mixture aliquots were withdrawn after suitable but fixed, time intervals and the oxygen uptake by the triphenylphosphine from the peroxybenzoic acid was followed by iodometric titrations. Second order rate constants were then calculated by the usual procedures.^{1,2}

References

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