

SOLVENT EFFECTS IN THE OXIDATION OF PYRIDINE TO PYRIDINE 1-OXIDE

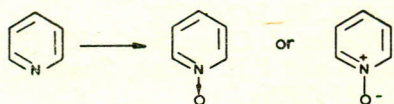
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(Received August 23, 1973)

Abstract. Kinetics of the oxidation of pyridine with peroxybenzoic acid to form pyridine 1-oxide have been studied in a number of polar and nonpolar solvents. It has been shown that this reaction follows second order kinetics and its rate constant is inversely proportional to the dielectric constant of the solvent medium. Activation parameters for this reaction have also been worked out.

Pyridine behaves towards per-acids in a manner characteristic of tertiary amines in general. The unshared pair of electrons of the nitrogen atom binds an oxygen atom in a coordinate linkage forming an amine oxide:



Pyridine 1-oxide was first obtained in 1926 when pyridine was oxidised with peroxybenzoic acid at room temperature.¹ More recently however, peroxyphthalic² and peroxyacetic acids³ have also successfully been used for the oxidation of pyridine to pyridine 1-oxide.

Effects of solvent on the kinetics of peroxybenzoic acid oxidation of some common nucleophiles such as aromatic sulfoxides, cyclic olefins and triphenyl phosphine have previously been reported.⁴⁻⁶ In continuation of our general interest in such reactions, we have now kinetically examined the system pyridine + peroxybenzoic acid \rightarrow pyridine 1-oxide + benzoic acid, in the solvents given in Table 2.

Some of these solvents have been used in the previously reported similar studies. These solvents not only represented a wide range of dielectric constants but were also easily available in pure form and hence their choice. This choice will, therefore, obviously be helpful in comparing the oxidative behaviour of different nucleophiles in similar environments.

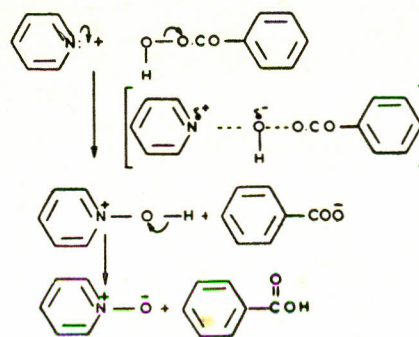
Results and Discussion

The rate constants for the oxidation of pyridine with peroxybenzoic acid were determined using hexane, cyclohexane, chloroform, chlorobenzene, butanol, n-propanol, acetone, ethanol and acetonitrile as the solvents, arranged in their ascending order of dielectric constants, at 30°C ($\pm 0.5^\circ\text{C}$) and in chloroform alone at 30.0, 40.0, 45.0 and 50.0°C ($\pm 0.5^\circ\text{C}$). The reaction was found to be second order with respect to both the reactants. The energy of activation was calculated from the Arrhenius plot and entropy of activation was worked out as reported previously.⁵ The rate data and other physical parameters for this reaction are recorded in Tables 1 and 2.

A graph of the rate constants versus the reciprocal of the dielectric constant of the solvents gave a straight

line. It was evident from the graph that the rate of oxidation of pyridine with peroxybenzoic acid decreases with the increase of dielectric constant of the medium; which means that the rate constant in a particular solvent is inversely proportional to its dielectric constant. A similar behaviour for the oxidation of cyclohexene and sulphoxide with peroxybenzoic acid has already been reported.^{4,6} However, in the peroxybenzoic acid oxidation of triphenyl phosphine it was observed that the rate constant is directly proportional to the dielectric constant of the solvent medium. The previously given explanation that electrostatic interactions are more important in the transition state of the reaction also holds for the present studies.

It is, however, pointed out that the observed difference in the peroxybenzoic acid oxidation of pyridine and triphenyl phosphine may be attributed to small difference in the localisation of charge in one as compared to the other. As a result of the present studies, therefore, it is proposed that pyridine 1-oxide is formed from pyridine by nucleophilic attack of its nitrogen on the peroxy oxygen of peroxybenzoic acid as depicted in the diagram below:



The oxidation of primary amines to nitroso and nitro compounds, of tertiary amines to amine oxides, of azo compounds to azoxy compounds and of nitrosamines to nitramines by the peroxy acid has similarly been explained.^{7,8}

Experimental

All the solvents were purified by standard procedures.⁹ Pyridine (B.D.H. reagent grade), b.p.

TABLE 1. ARRHENIUS PLOT FOR PEROXYBENZOIC ACID OXIDATION OF PYRIDINE IN CHLOROFORM.

Temperature (T)	Reciprocal of temperature (1/T)	Rate constant <i>k</i> (l/mole/sec)	Log <i>k</i>	<i>E</i> (kcal/mole)	ΔS^\ddagger (cal/mole/deg)
303	0.00300	0.000235	2.3711		
313	0.00319	0.000491	2.6911	13.02	-116.24
318	0.00314	0.000661	2.8202		
323	0.00304	0.000109	2.0374		

TABLE 2. SOLVENT EFFECTS IN THE OXIDATION OF PYRIDINE WITH PEROXYBENZOIC ACID AT 40°C.

Solvent	Di-electric constant	Concn (m-moles/litre)		Rate constants <i>k</i> (l/mole/sec)
		Pyridine	Peroxybenzoic acid	
Hexane	1.890	10.00	20.00	0.000651
		8.00	15.00	0.000650
		5.00	9.00	0.000650
Cyclohexane	2.05	10.00	21.00	0.00058
		7.00	16.00	0.000579
		5.00	9.00	0.00058
Chloroform	4.8	5.00	10.00	0.000420
		8.00	15.00	0.000421
		9.00	17.00	0.000419
Chlorobenzene	5.7	8.00	16.00	0.000175
		10.00	21.00	0.000176
		7.00	15.00	0.000174
Butanol	17.1	7.00	15.00	0.00010
		10.00	20.00	0.000101
		8.00	17.00	0.00012
n-Propanol	20.1	8.00	15.00	0.000109
		10.00	20.00	0.000108
		5.00	9.00	0.00011
Acetone	21.4	10.00	19.00	0.000094
		5.00	10.00	0.000095
		4.00	9.00	0.0000951
Ethanol	24.3	4.00	9.00	0.000082
		8.00	15.00	0.000083
		9.00	17.00	0.000084
Methanol	32.6	10.00	22.00	0.000069
		5.00	11.00	0.000070
		3.00	7.00	0.0000698
Acetonitrile	38.8	5.00	10.00	0.000049
		2.5	5.00	0.0000491
		4.00	9.00	0.0000490

115.3°, was distilled before use. Pyridine 1-oxide, m.p. 65°C (lit. ^{1,10} m.p. 66°), was isolated from every oxidation run carried out in the desired solvent. Peroxybenzoic acid was prepared by Kolthoff, Lee and Mair's method from benzoyl peroxide¹¹ just before use in the kinetic runs and kept in the refrigerator at 0°C. It was iodometrically standardized and the solutions of different concentrations were then prepared by dilution for use in these studies.

Kinetic Measurements. Solutions, 50 ml each of pyridine and peroxybenzoic acid in the same solvents, were separately taken in two volumetric flasks and kept at the desired constant temperature provided by a thermostatically controlled bath. The two reactants were mixed together after they had attained the temperature of the bath. From this reaction mixture aliquots were withdrawn after fixed time intervals and the oxygen uptake by pyridine was followed by iodometric titration. Second order rate constants were then calculated by the usual procedure.⁵

Acknowledgement. The authors are thankful to Mr. Nasir Ahmad of these Laboratories for practical assistance in the purification of solvents and preparation of peroxybenzoic acid.

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