

Solvent effects on the oxidation rates of 2,6-diphenylpiperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one by Mn(VII) in acetic acid media

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Abstract-

In this paper the oxidation of 2,6-diphenyl-piperidine -4-one and 3-methyl-2,6-diphenylpiperidine-4-one by acid permanganate, Mn(VII) has been studied. The rate of oxidation is slowest in those solvents that contained high proportions of water and increasing proportions of acetic acid increase the rate considerably.

There are only two possibilities when the nature and type of reactants undergoing the reactions under investigations are considered. The reaction should be classified as either ion-dipole type or dipole-dipole type.

Keyword: 2,6-diphenyl-piperidine-4-one, 3-methyl-2,6-diphenylpiperidine-4-one, Mn(VII), solvents, acetic acid

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I. Introduction

Transition metal ions are broadly used as oxidants in synthetic organic chemistry as well as in analytical chemistry. These metal ions are simply and economically prepared and their reactions can be properly controlled by the reaction conditions in the presence of right oxidants. Stemming from the pioneering work of Westheimer and later studies made by Waters, Wells and McAuley, there have been much interest shown in kinetic and mechanistic features of the oxidation reactions of organic substrates with transition metal ions. This area under discussion has been reviewed several times and articles have published in books (1-6). Solvent variations may affect the kinetics and the energy of the electron transfer processes, particularly in mixed solvent media, in a complex manner as the physicochemical properties of mixed solvent media are often quite different from those of the pure solvents or of their ideal mixtures. [7]. Although the separation of solvent effects into various solvent-solvent-solute interactions mechanisms is purely formal, the multi-parameter approach to solvent effects has been shown to work well [8]. The investigation of reaction kinetics in chemical reactions is the most important in deciding the reaction mechanisms. The kinetics deal with the study of change in concentrations of the components of the reaction system with the passage of time and the results are summarized in the form of rate expressions [9].

II. Material and Method

2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one, both were prepared in distilled water according to V. Balaish [10]. KMnO₄, H₂SO₄ and Na₂SO₄ were used without further purification. All other chemicals like acids and solvents used in this research work were of analytical grade. For the preparation of 0.05 M solution of Mn(IV) and Mn(VII) [11] approximately 7.8 g of potassium permanganate was mixed in 9.0 Molar H₂SO₄ with energetic stirring by a magnetic stirrer for a period of 7-8 hours. The solution was left for 10-12 hours and made up to 1 litre with 9 M H₂SO₄. Titrimetrically method was used to determine manganese (IV) solution with the help of Ferric sulphate solution. For the determination of end point Ferrion indicator was used. Stoichiometries were determined by estimating the concentration of manganese (VII) in reaction samples by titration [12].

IV. Result and Discussion

Heterolytic cleavages are explained by significant electrical transferences in the reactant substances. Reactions involving anionic reactants are also disposed to solvent influences. In the present study, the solvent should be playing an important role. That the oxidation reactions under consideration are definitely influenced by solvent systems is well brought about by the rate as Table 1.

Table 1: Rate constants $k_0 \times 10^4 \text{ sec}^{-1}$ for the oxidation of 2,6-diphenylpiperidine-4-one by [Mn(VII)] in acetic acid media

CH ₃ COOH % (V/V)	Temperature °C		
	35	45	55
10	9.03	18.80	45.00
20	9.60	19.95	48.70
30	11.72	23.60	52.00
40	12.60	24.56	56.80
50	14.07	30.70	58.70

The computed values for various compositions of the solvent system are given in the Table 2. It is seen that the plot of $\log_{10} k$ against the reciprocal of the dielectric constant gives a good linear relationship showing the reactant to be an ionic one and not a dipole. The slope of the line also gives an indication of charge on this ion. A complete explanation of the role of solvent in chemical reactions cannot be offered on the basis of the dielectric constants of media alone. Although certain macroscopic properties of the solvent, like the dielectric constant, are of importance in determining the effect of solvent changes on reaction rate, such macroscopic properties are quite inadequate for a complete explanation of solvent effects.

Table 5.2: The Values of 1/D of acetic acid

CH ₃ COOH % (V/V)	Temperature °C		
	35	45	55
10	0.0147	0.015	0.016
20	0.016	0.017	0.018
30	0.018	0.019	0.020
40	0.021	0.022	0.023
50	0.025	0.026	0.028

The selective solvation and the greater electrostatic attraction of the solute for the more polar component of a mixed solvent may produce near the solute particle, a region of dielectric constant entirely different from the average or bulk dielectric constant. Ingold has shown that the polarity of a solvent increases with an increasing thickness of shielding of the dipole charges. The latter factor may become important indicating the solvent polarity, often overweighing the effect of dipole moment [13].

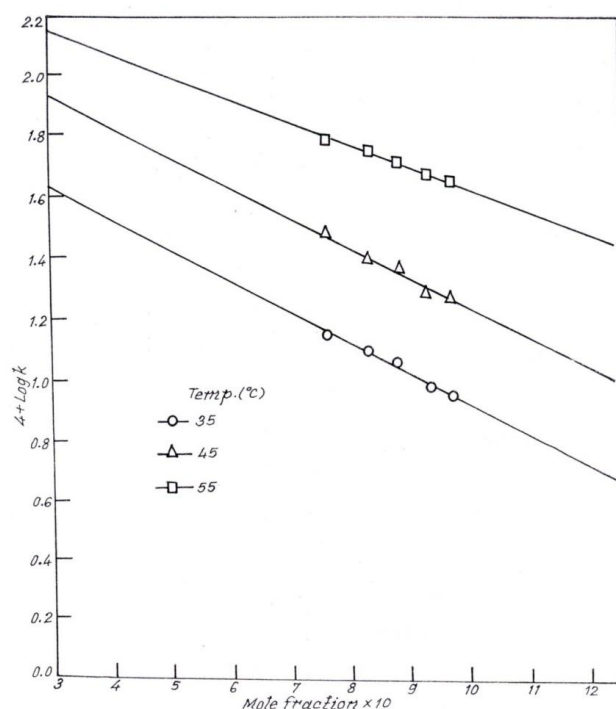


Fig. 1: Plots of $4 + \text{Log } k$ against mole fraction for 2,6-diphenyl piperidine-4-one oxidation by Mn(VII)

Although the reciprocal of the dielectric constant does show linearity with $\text{Log}_{10} k$, the mole fraction of water in solvent mixture has apparently got a good relationship also (Fig.1). A fair linearity with $\text{Log}_{10} k/\text{mole fraction}$ was observed, thus ensuring a wider range of applicability even though binary solvent mixtures of acetic acid and water are not definitely what one would call ideal mixtures. The deviations are possibly caused by the association of acetic acid molecules and also by the cumulative effect on the difference in solute and solvent-solvent interactions in an electrostatic field i.e., the dielectric constant of the medium. The oxidation rates of 2,6-diphenyl-4-piperidones with and without 3-alkyl substituent during the course of oxidations with Mn (VII) reveal that the rate of oxidation of the former is higher than that of the 3-alkyl substituted 2,6-diphenylpiperidones. Stabilization of a non-classical cation type proposed for the oxidation of Mn(VII) is much easier without an alkyl substituent for the participation of phenyl group at the 2-position. As such this is reflected in the rate differences between the piperidones (Table 3). Plots of $4+\text{Log} k$ against $1/D$ for 2,6-Diphenyl piperidine-4-one oxidation by Mn (VII) has been given in fig 2.

Table 3: Comparison of Bimolecular rate constants for the oxidation of 2,6-diphenyl-piperidine-4-one and 3-methyl-2,6-diphenylpiperidine-4-one by Mn(VII), Mn(IV) and Mn(III)

[piperidone]	[H ₂ SO ₄]M	Oxidant		
		Mn(III)	Mn(IV)	Mn(VII)
2,6-diphenylpiperidine-4-one	0.3	32.5	49.5	16.0
	0.4	50.0	57.5	25.5
	0.5	61.3	71.0	56.5
3-methyl-2,6-diphenylpiperidine-4-one	0.3	19.0	32.0	14.0
	0.4	32.0	39.0	29.0
	0.5	41.0	60.0	51.0

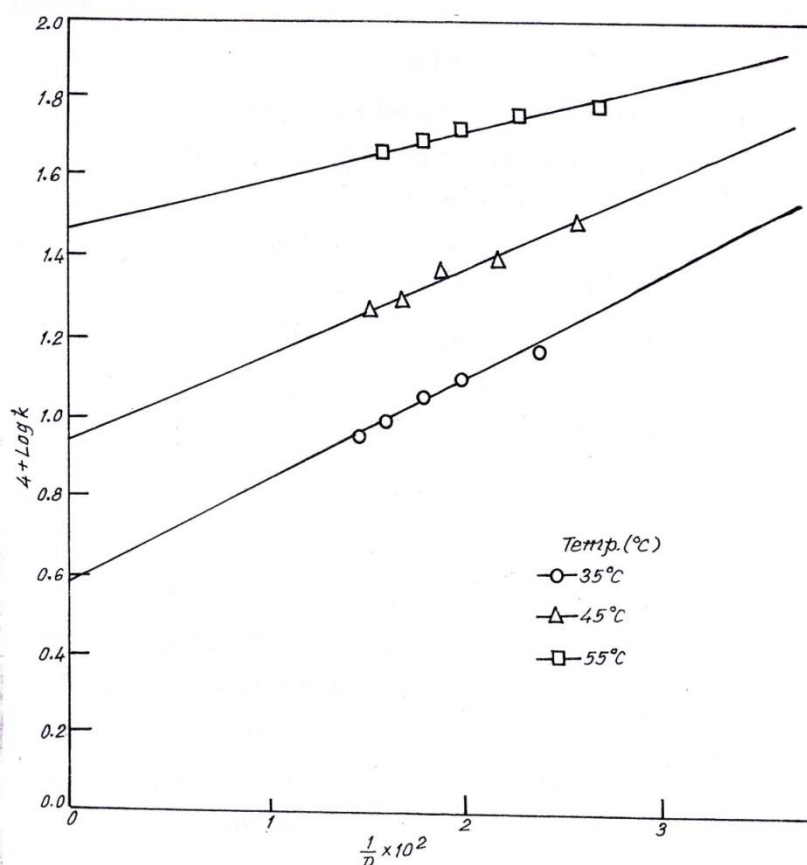


Fig. 2: Plots of $4+\text{Log} k$ against $1/D$ for 2,6-Diphenyl piperidine-4-one oxidation by Mn (VII).

A comparison of bimolecular rate constants of these oxidants with the piperidones reveals an interesting result. In case of these piperidones the rate of oxidation follows the trend Mn(IV) > Mn(III) > Mn(VII), such trend is not an unexpected one as it obviously supports the fact that the intermediate valency states of manganese are powerful oxidants than Mn(VII) itself.

V. Conclusion

We conclude that the rate of oxidation is slowest in those solvents that contained high proportions of water and increasing proportions of acetic acid increase the rate considerably. In this work related mechanisms have been postulated considering the reactivities of the substrates and the Mn(VII), Mn(IV) and Mn(III) species. But in all these reactions 'compensation' of energies has been maintained by actual balance between enthalpy and entropy changes. This demonstrates the similarities amongst these reactions. The linear relationship between the enthalpies and entropies of these reactions has led to the approximate constancy of free energies. The linear relationship between ΔH^* and ΔS^* should not be accounted for only by structural relations among these substrates. Since almost all the kinetic runs have been carried out near the isokinetic temperature, consideration of rates alone could lead to erroneous conclusion about the nature of reaction.

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