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THERMODYNAMIC AND RELATED STUDIES OF THE OXIDATION OF *p*-AMINOBENZOIC ACID, SULPHANILIC ACID AND ANTHRANILIC ACID BY PERIODATE

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ABSTRACT

Thermodynamic parameters for the oxidation of *p*-aminobenzoic acid, sulphanilic acid and anthranilic acid by periodate ion are reported and discussed. All the reactions obey the Arrhenius equation; the plot of log k_2 vs. $1/T$ is linear in each case. The validity of the isokinetic relationship and other related equations is tested. An attempt is made to correlate these findings with the nature of the transition state formed in the oxidation of the acids by the periodate ion.

INTRODUCTION

In order to investigate the nature of mechanisms of reactions in solution it is important to study the effect of temperature on the rate of the reaction and to determine various thermodynamic parameters. The isokinetic relationship [1] and Exner's equation [2] are useful in deciding whether a similar interaction mechanism is followed for a reaction series. The isokinetic parameter β is used to decide whether a system is entropy controlled or enthalpy controlled. Occasionally, differences in activation energies have been used as evidence of a change in reaction mechanism.

A review of the literature on oxidation by the periodate ion [3] has revealed that no attempt has been made to study the effect of various thermodynamic parameters on the mechanism of the non-malaparadian oxidation [4–6] by periodate. Therefore, we investigated some non-malaparadian oxidations by periodate and determined the nature of the mechanism. We carried out a systematic study of various thermodynamic parameters for the oxidation of anthranilic acid, *p*-aminobenzoic acid and sulphanilic acid by periodate ion to determine the mechanism. The validity of the Arrhenius equation, the isokinetic relationship and other related equations was tested. Results of these studies are presented and discussed in this paper.

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EXPERIMENTAL

Sodium metaperiodate was of AnalaR grade (May and Baker). Anthranilic acid (Sarabhai Merck), *p*-aminobenzoic acid and sulphanilic acid (AnalaR, BDH) were used after recrystallization. All other chemicals used were of analytical grade. All reactions were studied in aqueous medium.

The progress of the reaction was followed by estimating the unreacted periodate iodometrically at various intervals of time. The following procedure was adopted. An aliquot (5 ml) of the reaction mixture was pipetted into a mixture of 10% KI (5 ml) + saturated $NaHCO_3$ solution (5 ml) + arsenious oxide of appropriate concentration (10 ml). The excess arsenious oxide was titrated against a standardized I_2 solution.

All the reactions followed second-order kinetics overall: first order in periodate and first order in each acid [4–6]. Hence the reactions were studied at equimolar concentrations of the reactants and the second-order rate constants k_2 were evaluated graphically by plotting $1/(a-x)$ vs. t, where a is the initial concentration of periodate ion and x is the concentration after time t. The second-order rate constants k_2 obtained were then used to determine various thermodynamic parameters and for other studies.

RESULTS AND DISCUSSION

Thermodynamic parameters

The kinetic studies of the reactions were performed at various temperatures and at equimolar concentrations of the reactants to evaluate the thermodynamic parameters, i.e. activation energy E_a, frequency factor A, entropy of activation $\Delta S^{\ominus}$, enthalpy of activation $\Delta H^{\ominus}$ and free energy of activation $\Delta F^{\ominus}$. The second-order rate constants k_2 evaluated at various temperatures are recorded in Table 1. The Arrhenius equation relating temperature and rate constant

$$\log k_2 = -\frac{E_a}{2.303RT} + \text{constant} \tag{1}$$

TABLE 1

Second-order rate constants at various temperatures

Acid	$k_2 \times 10^3$ (dm^3 mol^{-1} s^{-1})					
	303 K	308 K	313 K	318 K	323 K	328 K
Anthranilic acid	7.13	9.86	11.92	16.2	19.70	–
p-Aminobenzoic acid	–	2.13	2.72	3.44	4.64	5.58
Sulphanilic acid	–	3.71	5.63	8.10	10.67	17.0

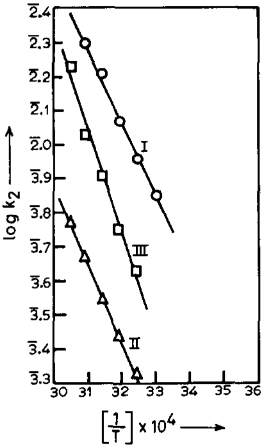


Fig. 1. Arrhenius plots for the oxidation of the acids: curve I, anthranilic acid; curve II, *p*-aminobenzoic acid; curve III, sulphanilic acid.

was followed; a plot of log k_2 vs. $1/T$ was linear in each case (Fig. 1). The activation energies for the reactions were evaluated from the slopes of the curves in Fig. 1. On the basis of these values of activation energy, the values of the various thermodynamic parameters were then calculated by the application of the equations

$$k_2 = A\ \mathrm{e}^{-E_a/RT} \tag{2}$$

$$\Delta S^{\ominus} = 19.147(\log k_2 - 10.753 - \log T) + \frac{E_a}{T} \tag{3}$$

$$\Delta H^{\ominus} = E_a - RT \tag{4}$$

$$\Delta F^{\ominus} = 19.147T(\log T + 10.319 - \log k_2) \tag{5}$$

The thermodynamic parameters thus calculated are given in Table 2. A perusal of the data in Table 2 shows that these reactions are characterized by a large negative entropy of activation $\Delta S^{\ominus}$. High negative entropy of activation values are mainly observed in solvents of low polarity and indicate that solvation effects are predominant in these reactions. This

TABLE 2

Thermodynamic parameters for the oxidation of the acids

Acids	E_a (kJ mol^{-1})	A (dm^3 mol^{-1} s^{-1})	$-\Delta S^{\ominus}$ (J K^{-1} mol^{-1})	$\Delta H^{\ominus}$ (kJ mol^{-1})	$\Delta F^{\ominus}$ (kJ mol^{-1})
p-Aminobenzoic acid	43.1	4.1×10^4	165.5	40.2	93.7
Sulphanilic acid	64.9	1.8×10^8	95.6	62.3	90.7
Anthranilic acid	40.8	4.8×10^4	170.3	38.1	88.32

suggests the formation of a charged and rigid transition state which is expected to be strongly solvated. Since the present reactions are ion-dipolar in nature [4–6], it is reasonable to expect that the entropy of the activated complex in all the reactions should be nearly the same. However, owing to the different polarities of the various acids, the extent of solvation should be different and hence may cause some variation in the observed $\Delta S^{\ominus}$ values [7].

The low energy of activation E_a observed for the reactions is characteristic of bimolecular reactions in solution. In addition, the free energy of activation $\Delta F^{\ominus}$ and the energy of activation E_a for all the reactions are comparable in magnitude, which suggests that the mechanisms of the oxidation processes are similar. The value of the frequency factor A is of the order of 10^4–10^8; this suggests that the reacting species are rather large in size. Furthermore, the almost constant values of $\Delta F^{\ominus}$ suggest that the site of attack is at the nitrogen of the amino group which is common in all the substrates. A slight variation in the rate for the different acids may be accounted for by a change in the basic strength of the acids and hence a change in the availability of the lone pair on the nitrogen of the amino group.

Validity of the isokinetic relationship and other related equations

The validity of the isokinetic relationship

$$\Delta H^{\ominus} = \beta \, \Delta S^{\ominus} \qquad (6)$$

where β is the isokinetic temperature, was tested by plotting a graph of $\Delta S^{\ominus}$ vs. $\Delta H^{\ominus}$ (Fig. 2). This was found to be linear (correlation coefficient, 0.998) showing that the isokinetic relationship is obeyed for these reactions. The validity of the isokinetic relationship suggests that the basic mechanisms for all the reactions are similar. The constant $\Delta F^{\ominus}$ values reported in Table 2 may be explained on the basis of the isokinetic relationship. In a series of compounds with slightly different structures which undergo a reaction by essentially the same mechanism, the $\Delta F^{\ominus}$ values may be more or less constant with relative changes in $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$, as pointed out by Leffler [1]. The value of the isokinetic temperature β, given by the slope of the curve in Fig. 2, is 343 K. Exner [2] has recommended an alternative method for checking the value of β. The rates of a series of reactions are measured at two temperatures and log k_2 (at T_2) is linearly related to log k_1 (at T_1) according to

$$\log k_2 = a + b \log k_1 \qquad (7)$$

The value of the isokinetic temperature β can be calculated from the expression

$$\beta = \frac{T_1 T_2 (b-1)}{b T_2 - T_1} \qquad (8)$$

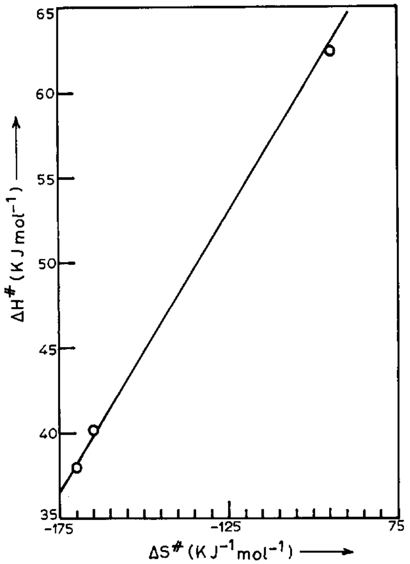


Fig. 2. Isokinetic plot.

In this study a plot of log k_2 (at 323 K) vs. log k_1 (at 313 K) (Fig. 3) was found to be linear, suggesting that Exner's equation, which correlates rate constants at two temperatures, is obeyed for these reactions. The value of β calculated by this method is 351 K, which is in good agreement with that evaluated from the isokinetic plot. Thus the value of β is well above the experimental temperatures employed in this study, suggesting that these reactions are enthalpy controlled [8]. This hypothesis is further supported by the observation that the reaction with the lowest energy of activation has the

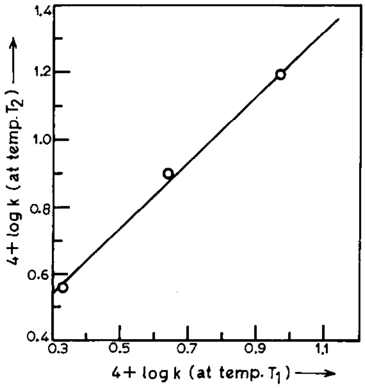
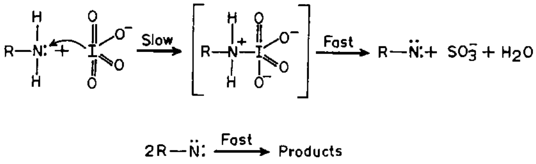


Fig. 3. Exner's plot (relationship between log k_2 (at T_2) and log k_1 (at T_1)) ($T_1 = 313$ K, $T_2 = 323$ K).



Scheme 1

highest rate, whereas that with the highest energy of activation has the lowest rate (Table 1).

MECHANISM

Before proposing a mechanism for the reactions under study, it is important to point out that the oxidation products in each case were identified as the corresponding azobenzene derivatives. Radical scavengers had no effect on the rate, thus excluding the possibility of a radical mechanism.

On the basis of these studies, it is proposed (Scheme 1 (where R is *o*- or *p*-$COOC_6H_4$ for anthranilic acid, *p*-aminobenzoic acid or *p*-HO_3S-C_6H_4 for sulphanilic acid)) that a general attack occurs by the periodate ion on the nitrogen of the amino group of the acid in the rate-determining step. The charged transition state thus formed may rearrange to give a nitrene molecule. Two nitrene molecules then couple to give the azobenzenes.

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