KINETICS OF CHROMIC ACID OXIDATION OF METHYL ALCOHOL: EFFECT OF PHOSPHORIC ACID AND OXALIC ACID

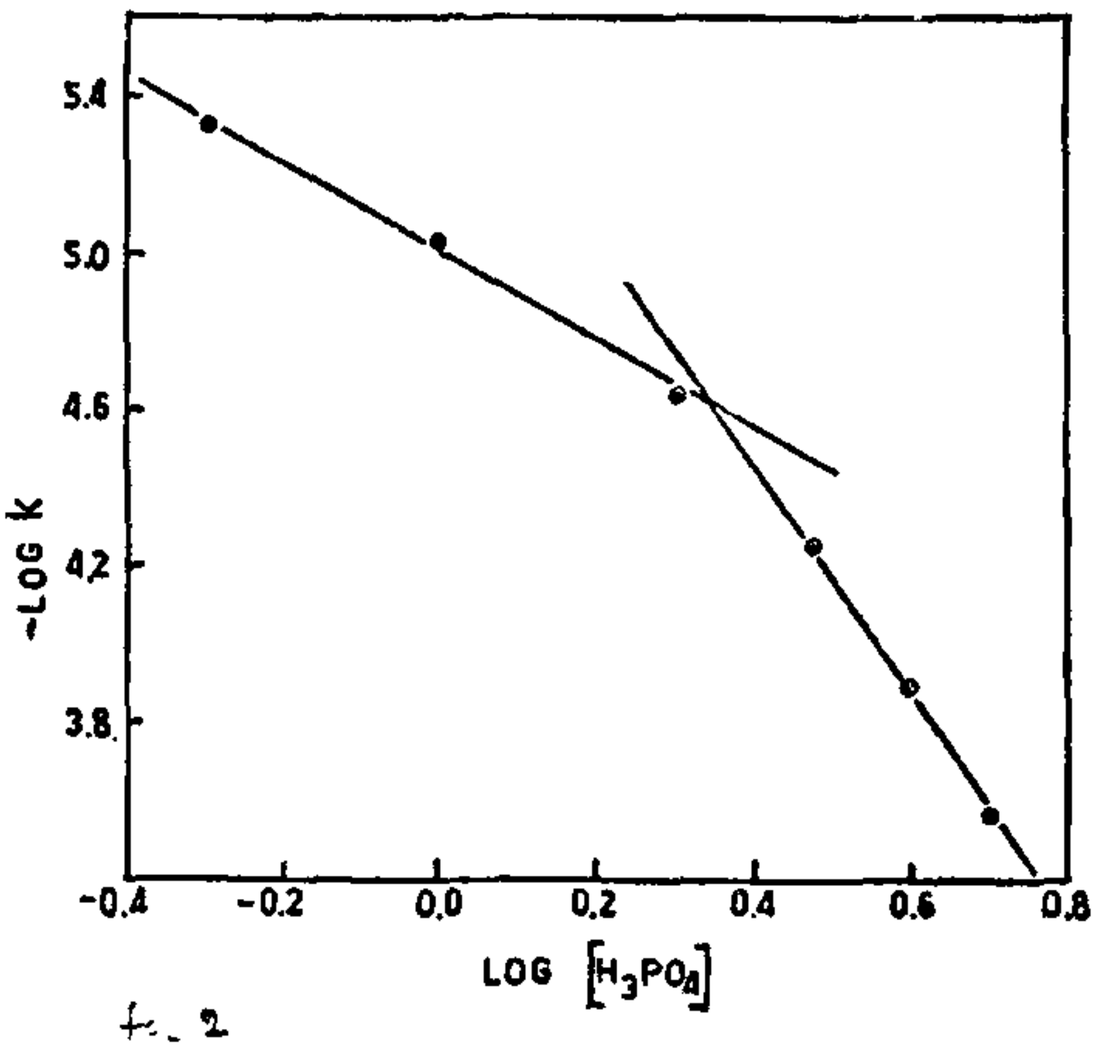
It was reported by Rao, G. G. *et al.*[1] that the oxidising ability of chromium(VI) increased greatly in the presence of moderately high concentrations of phosphoric acid. Further it is reported by Rocek[2] that a bidentate substrate such as oxalic acid exhibits a catalytic activity on the oxidation reactions by chromic acid. A survey of the literature showed that no attention has been paid to the oxidation kinetics of methyl alcohol by chromic acid in presence of moderately concentrated acids in general and phosphoric acid in particular. The authors have therefore investigated the oxidation kinetics of methanol in phosphoric acid medium (0·5–5·0 M) and also the catalytic effect of oxalic acid on the reaction at 1·0 MH_3PO_4 and the results are communicated here. La l *et al.*[3] studied the oxidation kinetics of methyl alcohol in low concentrations of perchloric acid (0·05–0·43 M) and reported that the C–H bond rather than the cleavage of the molecule is involved in the oxidation process. Anantakrishnan and Varadarajan[4] investigated the oxidation of aliphatic primary alcohols (except CH_3OH) in acetic acid-water mixtures and reported that the activation energy decreased with an increase in the chain length.

Experimental

The reaction is monitored photometrically using ELICO Spectrocol Model CL-23 by following the unreacted Cr(VI) at 450 nm. Appropriate correction is made for the absorbance of Cr(III) at 450 nm. The pseudo first order rate constants (k) are obtained graphically from log Absorbance *vs* Time plots. The rate constants reported are the average values obtained in at least three runs. The values are reproducible within the usual experimental errors.

Results and Discussion

The rate constant (k) increased with the increase of phosphoric acid concentration and plot of log k *vs* log $[H_3PO_4]$ gave two linear plots (Fig. 1) with slopes 1 and 3 in the low (0·5 to 2·0 M) and high (> 2·0 M) phosphoric acid concentrations respectively. However log k varied linearly with $-H_0$ even though the slope is slightly greater than unity. The rate also increased with the increase of chromium(VI) and methyl alcohol concentrations. The order with respect to methyl alcohol (0·2 M to 0·7 M) and chromic acid ($1·67 \times 10^{-3}$ M to $2·7 \times 10^{-3}$ M) is one. The activation energy (ΔE^*) and entropy (ΔS^*) obtained from temperature effect are 13·0 K. cals mole^{-1} and $-27·7$ cal/° K respectively. The higher rate in H_3PO_4 solutions (> 2·0 M) can be ascribed to the formation of the powerful oxidant chromium(V). The formation of Cr(V) in higher concentration of H_3PO_4 in presence of the reductants was confirmed by ESR spectra[5].



FIGS. 1–2. Fig. 1. Plot of log k *vs* log $[H_3PO_4]$. Fig. 2. Plot of Rate Benefit *vs* [Oxalic acid].

The specific rate observed in 0·5 M H_3PO_4 is lower than that reported by Lal *et al.* in 0·43 M perchloric acid medium. This can be attributed to the complex formation between chromic acid and the anion of the acid. Perchlorate, being a more electron withdrawing anion, than phosphate ion leads to a larger dissociation of the complex[6] and hence the higher rate. It is observed that the rate increased with increase of oxalic acid concentration (Table I) and the rate of oxidation of oxalic acid alone under the experimental conditions is negligible. The rate benefit observed in presence of oxalic acid varied linearly with the concentration of oxalic acid (Fig. 2). Similar observation was made by Rocek *et al.* (*loc. cit.*) in their studies on the oxidation of isopropyl alcohol by chromium(VI) in presence of oxalic acid. The rate benefit in presence of oxalic

acid is attributed to the complex formation between oxalic acid and chromium(VI) which prevents the formation of energetically unfavourable chromium(IV) species (*loc. cit.*) and allows the direct one step reduction involving 3 electrons.

TABLE I

Dependence of rate constant (k) on [Oxalic acid]

$[MeOH] = 0\ 5\ M$
$[H_3PO_4] = 1\ M$
$[Cr(VI)] = 2{\cdot}33 \times 10^{-3}\ M$
Temp. = 40° C.

Oxalic acid $M \times 10^4$	Rate constant $k \times 10^6\ sec^{-1}$
..	9·8
1·0	10·9
2·0	12·0
4·0	14·3
6·0	15·5
8·0	18·7
10·0	20·5

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SYNTHESIS AND ANTIMICROBIAL SCREENING OF AMINO-1, 2-BENZISOXAZOLES AND SULPHANILAMIDO-1, 2 BENZISOXAZOLES

AMINO-1, 2-benzisoxazoles (II) have been synthesised by the reduction of nitro-1, 2-benzisoxazoles (I). Some of these amino-1, 2-benzisoxazoles have been converted into their sulphanilamido derivatives (IV). The antimicrobial activity of these compounds has been evaluated. Amino-1, 2-benzisoxazoles (II) have shown promising activity against *M. tuberculosis*, *in vitro*. The IR spectra of these compounds have been recorded. The mass spectrum of 5-amino-3-ethyl-7-methyl-1-, 2-benzisoxazole has also been represented.

In our recent publications[1–5] we have reported the synthesis and physiological activity of 1, 2-benzisoxazole derivatives. Some derivatives of 1, 2-benzisoxazole newly synthesised by us, showed antitubercular[2], antifungal[4,5] and antibacterial[5] activity. Amino and sylphanilamido derivatives are known for their physiological activity. Amino-1, 2-benzisoxazoles and their sulphanilamido derivatives are, therefore, synthesised and tested for their antimicrobial activity.

The nitro-1, 2-benzisoxazoles (I) prepared as reported by us earlier[3], on reduction with stannous chloride and HCl yielded amino-1, 2-benzisoxazoles (II). Sulphanilamido derivatives (IV, R=H) of some amino-1, 2-benzisoxazoles (II) were prepared by the condensation of amino compounds with *p*-acetamidobenzene sulphonyl chloride in presence of dry pyridine and subsequently hydrolysing N^4-acetyl-sulphanilamido-1, 2-benzisoxazoles (III, $R=COCH_3$) with 50% HCl. The physical data of these compounds are given in Table I.

Infrared spectra.—The infrared spectra of the compounds II, III and IV showed characteristic bands for primary amino group, N^4-acetylsulphanilamido group and sulphanilamido group respectively.

Mass spectra.—A mass spectrum of 5-amino-3-ethyl-7-methyl-1, 2-benziosxazole (IIe) is scanned as a representative of this series. The mass spectrum showed prominent peaks at *m/e* (M^+, 63%); 175 (*a*, 38%); 148 (*c*, 10%); 93 (*d*, 100%) and 65 (*e*, 32%). The fragmentation pattern of this compound is represented in Chart 1.

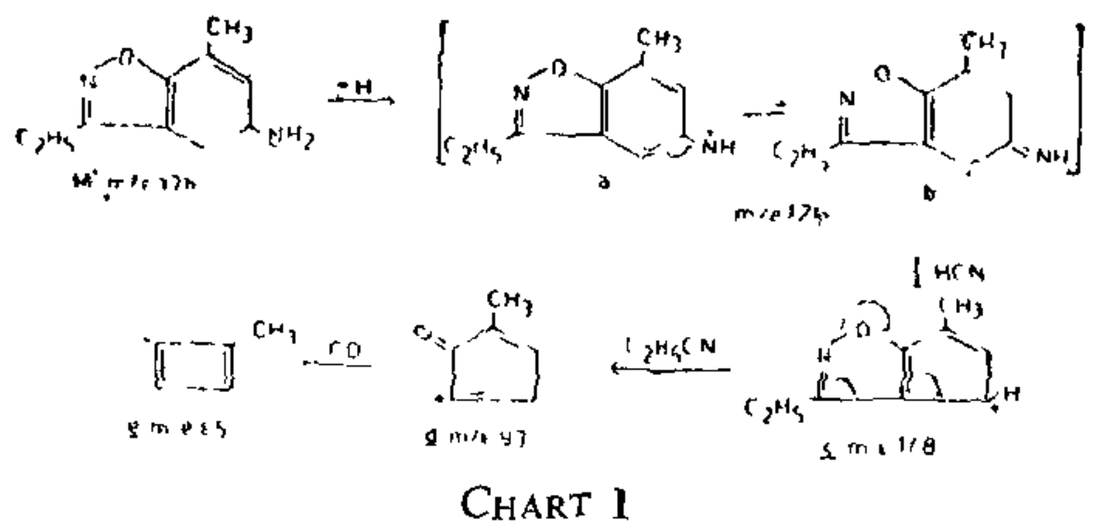

CHART 1

Antimicrobial activity

Antitubercular activity.—*In vitro* screening for antitubercular property of the compounds was carried out against human virulent "*Microbacterium tuberculosis*" (H_{37} Rv) by the method of Doub and Youmans[6]. The minimum concentration of the compounds (mentioned in μg/ml) which completely inhibited the growth of the test organism are recorded (Table I). For comparison the activity under similar conditions for Streptomycin is 1 μg/ml.