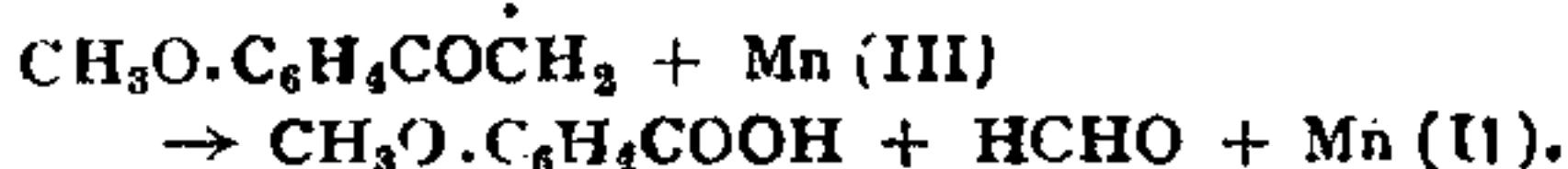
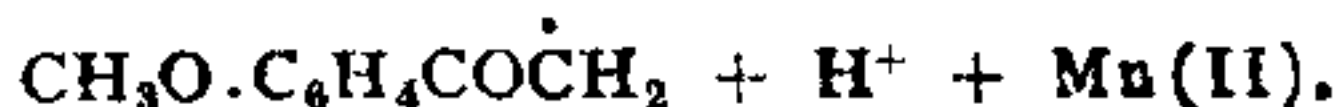
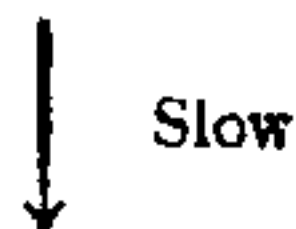
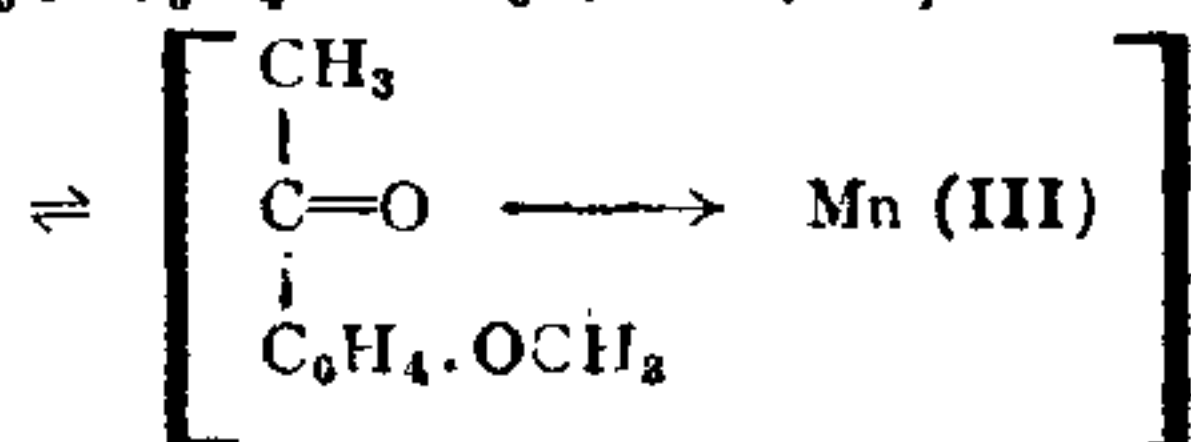


(20-60%) and by addition of Mn(II). The reaction was studied at different temperatures from 30°-45° C. and thermodynamic parameters calculated.

The enolisation rate of *p*-methoxyacetophenone was measured by bromination method and is of first order with respect to the ketone and hydrogen ion individually, and of zero order to bromine. The higher concentration of acetic acid (20-80%) results in increased enolisation rate at 35° C. ( $k_2 = 2.63 \times 10^{-4} - 7.76 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>).

The oxidation of ketones by Mn(III) pyrophosphate was postulated *via* enolisation.<sup>1</sup> The kinetics of the oxidation and enolisation of *p*-methoxyacetophenone are different and enol form is not likely to be involved in the oxidation process. At 35° C. and in 20% acetic acid solution the enolisation rate is  $2.63 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> while the oxidation rate under similar condition is  $26.5 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. Thus the oxidation is faster than enolisation and the oxidation involved the attack on the keto-form by Mn(III), which also supports the observation of Littler.<sup>2</sup>

The following mechanism may be suggested:



The energy of activation and entropy of activation as calculated from results at different temperatures are 17.5 kcal mole<sup>-1</sup> and -14.2 e.u. respectively.

Formaldehyde was mainly the identified product and its estimation by chromotropic acid<sup>3</sup> suggested a 4:1 stoichiometry for  $\Delta \text{Mn(III)} / \Delta$  *p*-methoxyacetophenone.

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## OXIDIMETRIC DETERMINATION OF THALLIUM (I)

BISHOP AND JENNINGS<sup>1</sup> have reported that thallium (I) can be determined accurately by potentiometric titration with chloramine-T in 3-4 M hydrochloric acid in presence of iodine monochloride as reaction intermediate. It has been found in the present studies that aqueous chloramine-T solution is unstable in 3-4 M hydrochloric acid medium. Hence, it is always desirable to work at lower acidities in the range 0.1-0.2 M hydrochloric acid as chloramine-T solution is quite stable under these conditions. But the oxidation of thallium (I) with chloramine-T in 0.1-0.2 M hydrochloric acid medium is very slow. An alternative method would be to oxidise thallium (I) with chloramine-T in 2-4 M hydrochloric acid medium, destroying the unused chloramine-T and then determining thallium (III) iodometrically. We found that chloramine-T can be completely destroyed by excess dimethylsulphoxide in 1-2 M hydrochloric acid medium. Dimethylsulphoxide and its oxidised product dimethylsulphone are inert to thallium(III), potassium iodide and iodine under these conditions.

The chloramine-T-thallium (I) reaction was studied under diverse conditions to find out the optimum conditions for achieving quantitative oxidation of thallium (I). For this purpose, solutions containing 0.5-1 m. mole of thallium (I) were conditioned variously and then excess chloramine-T or chlorine water (20 ml. of 0.1 N) was added. The reaction mixture was set aside for definite length of time. Then excess dimethylsulphoxide (20 ml. of 0.2 M) was added and the overall acidity was adjusted to 1 M by adding concentrated hydrochloric acid. This destroyed the excess of the chlorine oxidants. Then 15 ml. of 10% potassium iodide was added and the iodine liberated due to thallium (III) reduction was titrated with standard thiosulphate solution after the addition of 10 ml. of 2% starch solution.

The results presented in Table I indicate that oxidation of thallium (I) with chloramine-T is very slow in sulphuric acid and in sodium hydroxide media. At pH 4.7, the rate of the oxidation is very much higher but still not sufficient to produce quantitative oxidation within 15 minutes. However, in presence of excess chloride ions (overall concentration > 0.5 N) the oxidation was favoured not only at pH 4.7 but also at higher acidities to such an extent that quantitative oxidation resulted

1. Drummond, A. Y. and Waters, W. A., *J. Chem. Soc. (London)*, 1953, p. 435.
2. Littler, J. S., *Ibid.*, 1962, p. 832.
3. Mitchell, J. Jr., *Organic Analysis*, Interscience Publishers, New York, 1953, 1, 288.

within 5-10 minutes. Based on this the following procedure is recommended for the accurate determination of thallium (I).

TABLE I  
Oxidation of thallium (I) with chloramine-T and chlorine water (m. equivalents of chloramine-T or chlorine added = 2.500 ; overall volume = 100 ml.

Medium	TI (I) taken mM	Standing time min.	Iodometric titre value m. equiv.	4/2
0.2N H <sub>2</sub> SO <sub>4</sub>	0.9543	60	0.287	0.3008
0.2N NaOH	0.9543	60	0.146	0.1531
2M HCl	0.7157	5	1.432	2.001
3M HCl	0.7157	5	1.429	1.997
pH 4-7	0.9543	10	1.708	1.790 <sup>a</sup>
	0.9543	60	1.927	1.915 <sup>a</sup>
	0.9543	5	1.819	1.908 <sup>b</sup>
	0.9543	15	1.903	1.995 <sup>b</sup>
	0.9543	5	1.907	1.999 <sup>c</sup>
	0.9543	5	1.905	1.998 <sup>d</sup>

(<sup>a</sup>) No chloride was added Overall concentration of sodium chloride was 0.5N in (<sup>b</sup>), 1.0N in (<sup>c</sup>), and 2.0N in (<sup>d</sup>).

To 80 ml. of the solution containing 0.5-1 m. mole of thallium (I) and 2M hydrochloric acid, excess chloramine-T or chlorine water (20 ml. of 0.1N) is added. After about 5 minutes 20 ml. of 0.2M dimethylsulphoxide is added. Then 15 ml. of 10% potassium iodide is added and the iodine liberated by the thallium (III) is determined with thiosulphate. The results obtained were accurate to within 0.3%. Instead of chloramine-T, chlorine water of comparable strength can also be used in the above procedure.

Dept. of Chemistry, Indian Institute of Tech., Madras-36, January 15, 1970.  
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1. Bishop, E. and Jennings, V. J., *Talanta*, 1962, 9, 679.

### MAGNETIC AND INFRA-RED SPECTRAL STUDIES ON DITHIOCYANATO-*o*-PHENANTHROLINE-VANADIUM (IV) COMPLEX

It has been earlier reported that vanadium(IV) forms a mixed ligand complex with *o*-phenanthroline and thiocyanate.<sup>1</sup> The solid complex separates from the aqueous medium at pH 2. This gets extracted into *n*-butanol, and spectrophotometric and solvent extraction studies showed the composition of the complex to be

[VO(ROH)(Phen.)<sub>2</sub>(SCN)<sub>2</sub>]. We are now reporting the infra-red absorption and the magnetic moment of the solid complex that was isolated.

The infra-red spectrum was recorded on Nujol mull using Unicam SP200 Spectrophotometer with rock-salt optics. The main features of the spectrum are as follows: (1) There is no characteristic band attributable to co-ordinated water in the region 3400 cm.<sup>-1</sup>; this signifies that co-ordinated water molecule is definitely absent in the complex. (2) The sharp band at 2040 cm.<sup>-1</sup> due to C-N stretching frequency indicates the presence of terminal (and not bridging) thiocyanate groups bonded through nitrogen.<sup>2,3</sup> (3) The sharp band at 960 cm.<sup>-1</sup> indicates definitely the presence of V=O bonding in the complex.<sup>4</sup> (4) The sharp bands at 715 cm.<sup>-1</sup> and 845 cm.<sup>-1</sup> are due to the bonded ligand, *o*-phenanthroline.<sup>5</sup>

The magnetic susceptibility measurement was made on a solid sample at room temperature using Guoy method and the  $\mu_{eff}$  value was found to be 1.91 B.M., on the basis that its formula is VO(Phen.)<sub>2</sub>(SCN)<sub>2</sub>. This clearly indicates the presence of one unpaired electron which is in conformity with the presence of quadri-valent vanadium in the complex.

It is therefore concluded that in the solid state, the complex is probably a penta co-ordinated monomer having the composition [VO(Phen.)<sub>2</sub>(SCN)<sub>2</sub>] and when dissolved in *n*-butanol, a solvent molecule is co-ordinated in the sixth position of the octahedron as was generally assumed by Clark.<sup>6</sup>

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