

### REDUCTION OF ACID PERMANGANATE BY METHANOL AND ETHANOL

THE kinetics of the oxidation of alcohols by various oxidants were studied by different workers. Bawn and White<sup>1</sup> studied the oxidation of methanol by Co(III) ion whereas the oxidation of methanol and ethanol by Ce(IV) ion was investigated systematically by Rao *et al.*<sup>2</sup> and Ardon<sup>3</sup> respectively. A search for literature showed that the reduction of permanganate by some alcohols<sup>4,5</sup> was also studied with a view to developing their new methods of estimations but their kinetics were not studied. The purpose of the present work was, therefore, to study the kinetics of the oxidation of alcohols by acid permanganate and some results have been recorded in this communication.

The materials employed were of the highest possible purity. Potassium permanganate was of E. Merck's grade and the solution was estimated by the iodometric method. The alcohols (L.R. variety) were purified by distillations.

followed the first order law with respect to the oxidant concentration.

In connection with their oxidations it might be mentioned that the reactions were studied up to aldehydic stage, i.e., consumption of 0.4 moles of the oxidant per mole of the substrate. The formation of HCHO and CH<sub>3</sub>CHO in the cases of the oxidation of methanol and ethanol was tested. It was found that Mn(II) ion eliminated the induction period whereas fluoride ion greatly prolonged it. On the other hand, when trivalent manganese ion, i.e., Mn(III) was added, the oxidation of alcohols commenced immediately. It was, therefore, assumed that the trivalent manganese ion was the reacting species and the reaction may be explained on the basis of the mechanism proposed by Levesley and Waters.<sup>6</sup> It may be assumed that an initial activated complex was rapidly formed between the Mn(III) ion and the alcohol. The complex then disproportionated slowly and by the rate-determining step produced the alkoxy radicals.

TABLE I

No.	[Alcohol]	[KMnO <sub>4</sub> ]	pH	$\mu$	Temp. °C.	K (min. <sup>-1</sup> )
1	$3.974 \times 10^{-2}$ M	$12.31 \times 10^{-3}$ M	1.63	0.132	20	$2.763 \times 10^{-2}$
2	"	"	2.12	"	"	$2.073 \times 10^{-2}$
3	$2.208 \times 10^{-2}$ M	$10.25 \times 10^{-3}$ M	"	0.136	"	$1.151 \times 10^{-2}$
4	"	"	"	0.152	"	$0.6909 \times 10^{-2}$
5	"	"	"	0.168	"	$0.4606 \times 10^{-2}$
6	$3.974 \times 10^{-2}$ M	$12.31 \times 10^{-3}$ M	1.22	0.132	31	$6.448 \times 10^{-2}$
7	"	"	"	"	25	$4.824 \times 10^{-2}$
8	"	"	"	"	20	$2.994 \times 10^{-2}$
9	$4.352 \times 10^{-3}$ M	$8.210 \times 10^{-3}$ M	1.42	0.108	"	$5.984 \times 10^{-3}$
10	"	"	1.98	"	"	$5.501 \times 10^{-3}$
11	"	"	3.82	"	"	$3.684 \times 10^{-3}$
12	$8.704 \times 10^{-3}$ M	"	1.72	0.124	"	$4.606 \times 10^{-3}$
13	"	"	"	0.140	"	$4.030 \times 10^{-3}$
14	"	"	"	0.156	"	$2.878 \times 10^{-3}$
15	$4.352 \times 10^{-3}$ M	$2.121 \times 10^{-3}$ M	2.89	0.108	5	$1.842 \times 10^{-3}$
16	"	"	"	"	10	$2.187 \times 10^{-3}$

Experiments 1-8 and 9-16 denote the oxidation of Methanol and Ethanol respectively.

The reactions were carried out in a thermostat regulated to  $\pm 0.5^\circ$ . The ionic strengths of the solutions were maintained constant by the addition of requisite amounts of potassium sulphate to the solutions. The pH of the solution was adjusted by the addition of dilute sulphuric acid to the reaction mixture. In order to study the kinetics, alcohols and acid permanganate solutions were brought to the temperature of the thermostat and then rapidly mixed. Aliquot parts were withdrawn at suitable intervals of time and analysed for residual permanganate ion by the method mentioned previously. There was a period of disturbance in each case at the beginning of the reaction after which the rate

The alkoxy radical further reacted with Mn(III) and by very fast steps produced aldehydes.

The reactions were studied at different H<sup>+</sup> and Mn(II) ion concentrations. As the concentration of H<sup>+</sup> ion was increased, the rate of reaction also increased but Mn(II) retarded the rate of reaction. The activation energies were calculated from the plots of Log K vs. 1/T. The values were found to be  $9.2 \pm 0.5$  and  $11.5 \pm 0.7$  k. cal in the cases of the oxidation of methanol and ethanol respectively.

The authors express their deep sense of gratitude to Prof. B. N. Ghosh for laboratory facilities.



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### LIQUID SCINTILLATION COUNTING OF $^{35}\text{S}$ LABELLED HYDROGEN SULPHIDE

DURING a study of the radiation chemistry of some inorganic sulphur compounds, it was observed that micro-quantities of hydrogen sulphide are produced, when gamma irradiated alkali thiosulphate<sup>1</sup> or tetrathionate<sup>2</sup> was dissolved in water. The gas was estimated by the methylene blue spectrophotometric method.<sup>3</sup> In an attempt to elucidate the mechanism of decomposition of the salts under radiation the 'outer' sulphur in these compounds was labelled with  $^{35}\text{S}$ . Upon solution of the irradiated labelled compounds, the  $\text{H}_2\text{S}$  produced was found to be radioactive. The radio isotope  $^{35}\text{S}$  is a soft  $\beta$  emitter of energy 0.167 Mev, with a half life of 87.1 days. A liquid scintillation technique was therefore followed to determine the amount of the radioactive gas produced.

#### MATERIALS

(i) *Labelled Compounds.*—Approximately 5 millicurie sample (in about a weight of 100 mg.) of 'outer' labelled sodium thiosulphate ( $\text{Na}_2\overset{*}{\text{S}}\text{SO}_3$ ) was obtained from the Atomic Energy Commission of Canada Ltd. Assuming a 20% counting efficiency of the counter used, approximately 5 mg. of the active material was mixed with about 400 gm. of inactive  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  to give about  $10^6$  counts per min. per gram, and was recrystallised from aqueous solution.

Anhydrous  $\text{Na}_2\overset{*}{\text{S}}\text{SO}_3$  was prepared from the pentahydrate, as described elsewhere.<sup>4</sup>

Sodium tetrathionate  $\text{Na}_2\overset{*}{\text{S}}\text{SSSO}_6 \cdot 2\text{H}_2\text{O}$  was prepared by the method given in Abegg's *Handbuch der Anorganischen Chemie*.<sup>5</sup>

(ii) Hyamine hydroxide [*p*-(diisobutyl-cressoxyethoxyethyl benzylammonium hydroxide)] used for absorbing the radioactive  $\text{H}_2\text{S}$  was obtained from Packard Instrument Co. Inc., Illinois, U.S.A.

Irradiation of the solid samples was carried out at room temperature ( $25 \pm 5^\circ \text{C}$ .) in the Gamma cell 220  $\text{CO}^{60}$  Irradiation Unit' manufactured by the Atomic Energy Commission of Canada Ltd.

The counting of labelled samples was accomplished with a liquid scintillation counter supplied by Tracer Lab., Inc., Richmond, California, U.S.A. The scintillator was a solution of 5.3334 gm. of 2, 5-diphenyl oxazole (PPO) and 0.1333 gm. of 1, 4-bis-2-[(5-phenyl oxazolyl)] benzene (POPOP) in a litre of re-distilled toluene.

To determine the initial activities of the labelled  $\text{Na}_2\overset{*}{\text{S}}\text{SO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SSO}_3$  and  $\text{Na}_2\text{SSSSO}_6 \cdot 2\text{H}_2\text{O}$ , about 10 mg. of each sample was accurately weighed and placed in a 20 ml. counting bottle of low potassium content. The bottle could be fitted with a bakelite screw cap. The solid was dissolved in 0.2 ml. of deaerated triple distilled water and the final counting solution made up to 20 ml. had the following composition by volume (Table I).

TABLE I

Component	Sodium thiosulphates	Sodium tetrathionate
Scintillator solution	75%	80%
95% ethanol	10%	..
Hyamine hydroxide	10%	10%
Re-distilled toluene	4%	9%
Water	1%	1%

The amount of alcohol, water and hyamine in the counting solution were kept constant, since they are known to quench the scintillations. Reproducible results could be obtained only when the solutions were cooled to  $-10^\circ \text{C}$  before counting. Solutions were counted to get approximately a total of 10,000 counts,<sup>6</sup> to reduce the statistical deviation to  $\pm 1\%$ .

The apparatus used for generating  $\text{H}_2\text{S}$  from the irradiated compounds was similar to that of Budd and Bewick.<sup>7</sup> A known weight of the gamma irradiated salt was dissolved in de-aerated triple distilled water in a reaction vessel, in an atmosphere of nitrogen. Pure and dry nitrogen was bubbled into the solution for 3-4 hours. The  $\text{H}_2\text{S}$  carried in the nitrogen stream was dried over calcium chloride and was absorbed in 2 ml. of hyamine hydroxide placed