A Kinetic Study of the Redox System Containing Citric Acid and Manganic Acetate

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Waters and his co-workers[1] have studied the oxidation of some carboxylic acids and other organic compounds by using manganese-(III) in the form of pyrophosphate. Manganic acetate has been employed for the oxidation of organic compounds by Zonis and his co-workers.[2] In the present study, manganic acetate has been used as an oxidant for citric acid.

1) W. A. Waters et al., *J. Chem. Soc.*, **1953**, 2836; **1954**, 2456.

2) S. A. Zonis et al., *J. Gen. Chem.* (*U. S. S. R.*), **20**, 1301 (1950); **24**, 815 (1954); *Zhur., Obschei Khim.*, **24**, 814, (1954).

Experimental

All the chemicals used were of B.D.H., A.R. quality, and fresh solutions of citric acid were prepared in boiled distilled water. Manganic acetate was prepared by the oxidation of manganous nitrate under suitable conditions. It was stored in blackened Pyrex bottles at a low temperature to prevent disproportioning ($2Mn^{3+} \rightleftarrows Mn^{2+} + Mn^{4+}$). Calculated amounts of the reactants (i. e., citric acid and manganic acetate) were placed separately in a thermostat maintained at $(t\pm0.05)$°C, where t is the desired temperature. Reaction was started by thoroughly mixing the two reactants in a solvent containing 90 per cent glacial acetic acid and 10 per cent water. Five milliliters of the reaction mixture were pipetted out at different intervals, and the concentration of manganese(III) was estimated colorimetrically by using Unicam Photoelectric colorimeter with a Filter No. 303. Lambert-Beer's law was found to hold for the concentration ranges employed in the experiment. The kinetics of the reaction has been followed by varying the concentration of the reactants and the temperature.

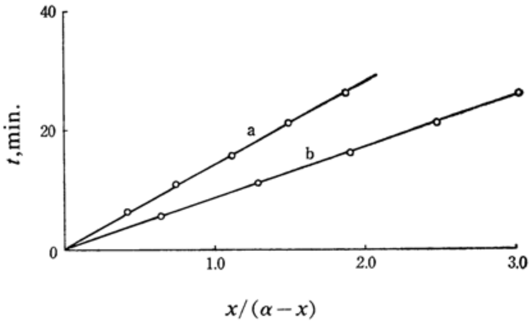

Fig. 1.

Results and Discussion

It has been found that one molecule of citric acid requires 9.5 equivalents of manganic acetate in order to be oxidized in the temperature range from 20 to 30°C. The rate constants have been determined graphically. k_1 and k_2 represent the rate constants for the first and second order reactions respectively. Some of the data are reproduced in Tables I, II and III.

TABLE I

Reactant	Temp. °C	Rate constant	Figure
Citric acid : 0.005 N Mn(III) : 0.005 N	20	$k_2=0.08012$	1(a)
Citric acid : 0.005 N Mn(III) : 0.005 N	30	$k_2=0.1354$	1(b)
Citric acid : 0.005 N Mn(III) : 0.0005 N	20	$k_1=0.1497$	2(a)
Citric acid : 0.02 N Mn(III) : 0.0025 N	20	$k_1=0.2917$	2(b)

TABLE II

Reactant	$t_{1/2}$, min.	k'
Citric acid : 0.005 N Mn(III) : 0.005 N	15.2	0.07429
Citric acid : 0.005 N Mn(III) : 0.0025 N	12.1	0.07293
Citric acid : 0.005 N Mn(III) : 0.0016 N	9.4	0.07361

TABLE III

Temp., : 20°C

Reactant	$k_2\times10^{-4}$
Citric acid : 0.005 N ; Mn(III) : 0.005 N	801
Citric acid : 0.005 N ; Mn(III) : 0.0016 N	835
Citric acid : 0.005 N ; Mn(III) : 0.00125 N	909
Citric acid : 0.0025 N ; Mn(III) : 0.0025 N	674
Citric acid : 0.005 N ; Mn(III) : 0.0025 N	752
Citric acid : 0.01 N ; Mn(III) : 0.0025 N	806

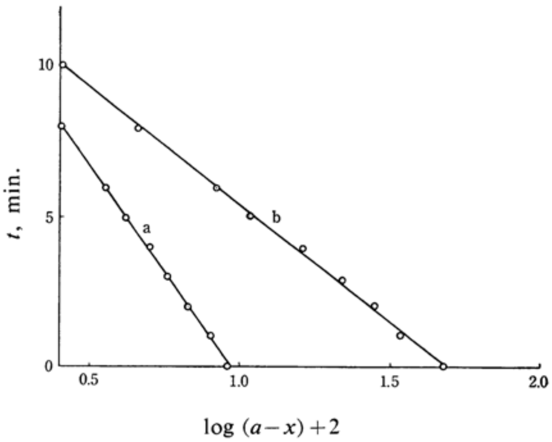

Fig. 2.

It has been noted that if the concentrations of the reactants are approximately equal, the total order of the reaction is two—one with respect to each reactant separately. There is a slight increase in the total value of the rate constant as the concentration of manganese(III) is decreased. It appears that a complex is formed between manganese(III) and citrate which slowly decomposes, giving the reaction product. The temperature coefficient for a 10°C rise in temperature is slightly less than two.

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