

formation of a new bond to a water molecule is required.

Summary

1. Data on the rate of reaction in aqueous solutions between β -propiolactone and hydroxide ion at 0.07° and 6.90° are presented.

2. Data are given on the rate of reaction between water and β -propiolactone at 11.68, 25.00 and 37.28°. Between pH values of 0 and 7 this water reaction is the only one which occurs. A preliminary study of salt effects on this reaction has been made. Sodium perchlorate and silver or potassium nitrate at concentrations up to 0.1 molar cause little or no change in rate. A large apparent effect of sodium chloride is due to en-

trance of a reaction of the lactone with chloride ions.

3. An acid catalyzed hydrolysis of the lactone occurs in aqueous solutions of strong acids when the acid concentration is 2 molar or higher. This reaction has been studied at 25° in solutions of perchloric, sulfuric and nitric acids. The rate of hydrolysis is accurately proportional to H_0 , the Hammett acidity function, and not at all to molar concentration of strong acid. The result suggests that the mechanism of the acid catalyzed hydrolysis of the β -lactone differs from that of γ -lactones and most aliphatic esters and that the reaction goes through the A'-1 mechanism of Day and Ingold.

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NOTES

A Thermal Reaction in Neutron-Irradiated Permanganates

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An entirely new possibility for the study of chemical processes in crystal lattices has been demonstrated in a recent paper by Green and Maddock.¹ These authors activated potassium chromate with slow neutrons and determined the retention in the irradiated product both after subsequent heating and without. It is evident that this method furnishes data about thermal reactions between two types of atoms within a crystal lattice, the over-all structure of which is left intact during the process.

We have been interested in the same kind of reactions, and we considered that potassium permanganate, which is known to suffer thermal decomposition around 200°, should offer a fair chance for the observation of this type of process. Our results, listed in Table I, show that the thermal reaction is quite slow below about 90°.

TABLE I

THERMAL REACTION OF RADIOACTIVE MANGANESE IN NEUTRON-IRRADIATED POTASSIUM PERMANGANATE

Temp., °C.	Fraction of total activity in reduced state		
	Unheated (0.70)	Heated 20 min.	Heated 120 min.
From Libby's graph			
85	.79	..	0.64
	.78	..	.65
180	..	0.33	0.26
	.77	.30	.27
	.74	.35	.30

(1) J. H. Green and A. G. Maddock, *Nature*, **164**, 788 (1949).

Just as in the experiment of Green and Maddock the entire activity does not return to the original ion and more prolonged heating does not make much difference in this respect. It is evident that not all radioactive atoms are subject to the same reaction. It is worth noticing that in the case of potassium permanganate the fraction of the total activity associated with the reduced valency does not decrease below one-fourth of the total activity on heating, whereas it is reduced to about 5% in potassium chromate.

A thin layer of small crystals of potassium permanganate was exposed to slow neutrons from 100 mc. radium-beryllium. (If the material is ground to a fine powder before heating, the thermal reaction does not go as far as it does with whole crystals during the same time.) In most experiments two or three samples of the same irradiated batch were treated simultaneously. Some were heated to the required temperature as rapidly as possible and one was kept at room temperature and used as a blank. All were dissolved in 0.02 *N* sulfuric acid and mixed with a small quantity of dissolved manganese sulfate. The manganese dioxide was filtered through a small paper filter without suction. After this the permanganate solution was reduced and precipitated as the dioxide. A rough estimate of the accuracy of the separation may be obtained from the differences between the figures in the last column of Table I and from a comparison with experiments by Libby.² The distribution of radioactivity in unheated samples was also determined in ten other cases. The figures obtained ranged between 0.75 and 0.82, indicating a very satisfactory reproducibility.

It should be mentioned that in our preparation decomposition began just about 180°. A slight change of color could sometimes be detected in the surface, but the loss of weight was negligible.

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(2) W. F. Libby, *This Journal*, **62**, 1930 (1940).