

precipitated by ammonia in the presence of ammonium salts is not due to the formation of barium carbonate by absorption of carbon dioxide.

2. The loss of barium ion when hydrous aluminum, chromic and ferric oxides are precipitated by ammonia in the presence of ammonium salts is probably due partly to surface adsorption.

3. Ammonium ion replaces barium in the adsorption, yet all the barium ion is not recovered even in a saturated solution of ammonium salts.

4. All three hydrous oxides cause the loss during precipitation of some barium ion by occlusion.

5. Hydrous aluminum and chromic oxides also cause the loss of some barium ion by postprecipitation.

6. When large amounts of hydrous oxides are precipitated, the surfaces do not become saturated with barium ion.

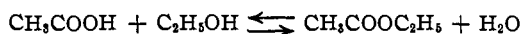
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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

Equilibrium in an Esterification Reaction with Perchloric Acid as Catalyst

BY H. M. TRIMBLE AND EARL L. RICHARDSON

Many workers have found that the equilibrium concentrations in reversible homogeneous reactions change when a catalyst is introduced, and that the degree of change varies with the concentration of the catalyst. Few, however, have investigated the phenomenon with other than small concentrations of the catalyst. This paper reports the results of a study of the reaction



in the presence of perchloric acid over a wide range of concentration. The efficiency of this substance in promoting simple esterification has not been examined previously, so far as the authors have been able to determine.

Experimental

Reagent grade perchloric acid, 70%, conforming to A. C. S. specifications was redistilled. It was diluted as needed to give aqueous solutions varying from 0.37 to 71.2% perchloric acid by weight which were used in making up the different reaction mixtures. Reagent grade glacial acetic acid was redistilled, saving the middle 75%. Repeated analyses showed it to be 99.8% pure. Ethyl alcohol was freed from aldehydes by treating it with silver oxide as described by Dunlap¹ and distilling. Its density was determined at 30° several times during the course of the work and found to remain constant at 0.80056 ± 0.00004. Reference to the tables by Osborne² shows that it contained 93.2% C₂H₅OH. The base used in all the titrations was approximately half normal sodium hydroxide. It contained a small excess of barium chloride, and it was protected at all times with soda lime tubes to ensure the absence of carbonate. It was standardized by means of reagent grade potassium hydrogen phthalate with phenolphthalein as indicator.

(1) Dunlap, *This Journal*, **28**, 397 (1906).

(2) Osborne, *Bull. Bureau Standards*, **9**, 424-425 (1913).

The experiments were run at 30.00 ± 0.05°. The reaction vessels were 100- or 250-ml. bottles with well-fitting ground-glass stoppers. In experiments 1 to 7, 10-ml. portions of perchloric acid solution and 2-ml. portions each of acetic acid and ethyl alcohol, all measured at 30° by means of precision pipets, were taken in making up the reaction mixtures; in the other experiments half these quantities were used. The stoppers were sealed externally with paraffin wax and the bottles were immersed in the bath for three days or longer to allow the reaction to proceed to equilibrium. Titrations of the total acid present at equilibrium were carried out rapidly in the reaction vessels after adding ice water. Each experiment was run in triplicate, and repeated if the results failed to check satisfactorily. Portions of the perchloric acid solution used for each experiment were weighed and titrated at the same time as the mixture itself. The quantities of the organic substances delivered were checked by weighing, and found

TABLE I
EQUILIBRIUM DATA AND RESULTS

Expt.	HClO ₄ soln., m	HClO ₄	H ₂ O	EtOAc	M Mole % HClO ₄	K ^o ap- parent
1	0.038	0.00038	0.5636	0.00476	0.06	3.32
2	.066	.00066	.5634	.00492	.11	3.47
3	.097	.00096	.5612	.00498	.15	3.51
4	.144	.00142	.5608	.00513	.23	3.65
5	.342	.00335	.5561	.00530	.54	3.79
6	.733	.00707	.5482	.00576	1.15	4.19
7	.92	.00876	.5438	.00600	1.57	4.41
8	1.37	.00647	.2695	.00329	2.11	5.00
9	2.26	.01033	.2615	.00364	3.43	5.67
10	3.04	.01347	.2533	.00407	4.55	6.57
11	3.77	.01628	.2480	.00436	5.55	7.22
12	4.29	.01822	.2440	.00458	6.26	7.74
13	4.73	.01946	.2370	.00485	6.83	8.33
14	6.15	.02432	.2284	.00528	8.66	9.42
15	8.02	.02989	.2165	.00583	10.92	10.88
16	9.26	.03288	.2067	.00610	12.32	11.45
17	12.79	.04090	.1890	.00664	15.94	12.67
18	15.93	.04706	.1745	.00693	18.98	12.95
19	19.01	.05201	.1627	.00718	21.60	13.19
20	24.61	.05924	.1448	.00760	25.79	13.51

^oK_{apparent} = moles EtOAc × moles H₂O/moles AcOH × moles EtOH.

to be constant to within $\pm 0.1\%$. The alcohol contained 0.00360 mole of water per ml., and the water in the acetic acid was negligible. The essential data and results of the study are given in Table I. The graph shows the relation between the apparent equilibrium constant as calculated and the mole per cent. of perchloric acid present in the equilibrium mixtures. To save space the moles of ethyl alcohol and acetic acid at equilibrium have been omitted from the table. These values may be found for each experiment by subtracting the values of column 5 from 0.03190 for alcohol and 0.03456 for acetic acid in experiments 1 to 7, and from half these numbers for the others. These were the respective quantities of these substances introduced in making up the reaction mixtures.

A search of the literature indicates that perchloric acid will not oxidize any of the constituents of these mixtures, or react with alcohol to form an ester under the conditions of these experiments. This conclusion was borne out by suitable tests which were performed.

The relation of the apparent equilibrium constant to the mole per cent. of perchloric acid present is well expressed by the equation $K = 3.45 + 0.68 M$ up to about $M = 11$. Calculation shows that the variation of this constant with concentration of the catalyst cannot be explained as due to combination of a part of the water with it to form a definite hydrate, as has been proposed by Jones and Lapworth.³

(3) Jones and Lapworth, *J. Chem. Soc.*, **99**, 1427 (1911).

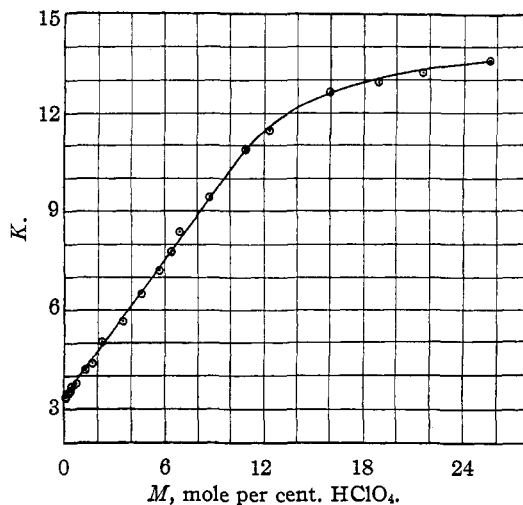
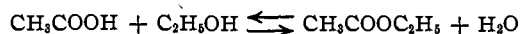


Fig. 1.—Relation of apparent equilibrium constant to mole per cent./HClO₄.

Summary

The results of a study of the apparent equilibrium constant for the reaction



in the presence of perchloric acid as catalyst, at concentrations up to 25.79 mole per cent., are presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Kinetics of Isotopic Exchange between Carbon Dioxide, Bicarbonate Ion, Carbonate Ion and Water¹

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Introduction

The important role of carbon dioxide in nature and in industry, as well as its intrinsically interesting properties, have made it the subject of intensive study.² These investigations have resulted in the belief that in aqueous solution less than 1% of the carbon dioxide present exists in combination with water. The rather strong metacarbonic acid so formed is highly ionized due to its small concentration. The first dissociation constant ordinarily determined is therefore not a true dissociation constant. Usually called the apparent dissociation constant it is nevertheless a real constant.

(1) Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University in the City of New York.

(2) Quinn and Jones, "Carbon Dioxide," The Reinhold Publishing Corp., New York, N. Y., 1936.

The differentiation between free and combined carbon dioxide has been possible through the circumstance, first noticed in 1912 by McBain,³ that carbon dioxide does not react instantaneously with water. The effect of various reagents on the rate of reaction has been studied in detail.⁴ The maximum amount of alkali instantaneously neutralized by a solution of carbon dioxide corresponds to the equilibrium amount of carbonic acid, ionized and un-ionized, if dissociation of carbonic acid is assumed to be very rapid. From conductivity data the ionized portion is known. The true first dissociation constant was therefore estimated to be 4×10^{-4} . The reaction also has

(3) McBain, *J. Chem. Soc.*, **101**, 814 (1912).

(4) Vorlander and Strube, *Ber.*, **46**, 172 (1913); Thiele, *Ber.*, **46**, 867 (1913); Thiele and Strohecker, *ibid.*, **47**, 1061 (1914); Strohecker, *Z. Natur.-Genussm.*, **31**, 121 (1916); Wilke, *Z. anorg. Chem.*, **119**, 365 (1921); Thiele, *ibid.*, **121**, 211 (1922).