UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 110: THE ACTION OF A SOLUTION OF POTASSIUM HYDROXIDE IN ALCOHOL ON OXALIC ESTERS, BY N. C. QUA and D. McLAREN

(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL, SOCIETY VOL. XXXVIII)·

THE UNIVERSITY LIBRARY: PUBLISHED BY
THE LIBRARIAN, 1916

University of Toronto Studies

9

[Reprinted from the Journal of the American Chemical Society,
Vol XXXVIII. No. 9. September, 1916.]

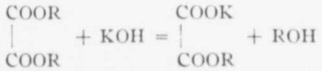
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TORONTO.]

THE ACTION OF A SOLUTION OF POTASSIUM HYDROXIDE IN ALCOHOL ON OXALIC ESTERS.

BY N. C. QUA AND D. McLAREN.

Received June 15, 1916.

One method of preparing the monoalkyl esters of dibasic acids is by the treatment of the dialkyl esters with the calculated amount of the alcoholic solution of potassium or sodium hydroxide, the reaction being represented thus:



$$\begin{array}{c}COOR\\ |\\ COOR\end{array} + KOH = \begin{array}{c}COOK\\ |\\ COOR\end{array} + ROH$$

But it is clear that we might expect the results in some cases to be represented thus:

$$2\begin{array}{c}COOR\\ |\\ COOR\end{array} + 2KOH = \begin{array}{c}COOK\\ |\\ COOK\end{array} + \begin{array}{c}COOR\\ |\\ COOR\end{array} + 2ROH$$

and, in other cases, the product might contain both dipotassium salt and the potassium alkyl salt.

Experiments were made with the esters of a number of dibasic acids. The ester was dissolved in the corresponding alcohol and the solution of potassium hydroxide in the same alcohol added in the proportion of a little less than one formula weight of potassium hydroxide to one formula weight of the ester. The precipitate, which usually began to appear after a few cubic centimeters of the alkali solution had been added, was filtered off, washed with the alcohol used and dried at 100°. This precipitate was analyzed by boiling with an excess of standard potassium hydroxide solution for about one and one-half hours, using a reflux condenser, and titrated back with standard acid, using phenolphthalein as indicator.

Oxalic esters gave practically pure potassium alkyl oxalate.

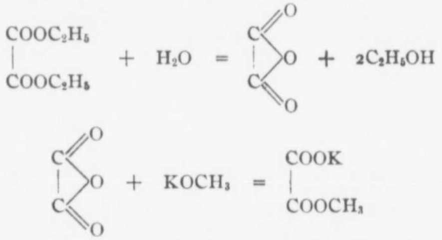
Tartaric esters gave potassium alkyl tartrate and a little dipotassium tartrate.

Succinic esters gave potassium alkyl succinate and considerable dipotassium succinate.

Phthalic esters gave dipotassium phthalate only.

Experiments with sodium hydroxide gave, in some cases, precipitates which would not crystallize and the reaction of oxalic esters with potassium hydroxide was selected for further study. It was found that for obtaining pure potassium alkyl oxalate from a dialkyl oxalate it is better not to use a very dilute solution of the ester, not to raise the temperature of the solution, and to use noticeably less than the calculated amount of potassium hydroxide.

Saloman[1] noticed that if ethyl oxalate be treated with a solution of potassium methylate in methyl alcohol the product was potassium methyl oxalate and he suggested representing this reaction in two stages:



Saloman's experiment was repeated, using an alcoholic solution of potassium hydroxide. Ten grams of diethyl oxalate were dissolved in 50 cc. methyl alcohol and 89 cc. of 0.767 *N* potassium hydroxide solution (in methyl alcohol) added, drop by drop, with constant shaking, the temperature being kept about 0°. This was the only case where it was found necessary to work below room temperature. The precipitate was washed with 50 cc. methyl alcohol, dried, and titrated as shown above. The re-

---

[1] *Ber.*, 8, 1509 (1875).

sult of the titration showed the precipitate to be potassium methyl oxalate. Solutions of potassium hydroxide in other alcohols were used with diethyl oxalate and also with other oxalic esters and the results are given in Table I.

TABLE I.—EFFECT OF KOH ON OXALIC ESTERS.

Diethyl oxalate.		Dimethyl oxalate.		Diisoamyl oxalate.	
Solvent alcohol.	Result.	Solvent alcohol.	Result.	Solvent alcohol.	Result.
Methyl	K methyl oxalate	Ethyl	K ethyl oxalate	Methyl	K methyl oxalate
Propyl	K propyl oxalate	Propyl	K propyl oxalate	Ethyl	K ethyl oxalate
Isoamyl	K isoamyl oxalate	Isobutyl	K isobutyl oxalate	Propyl	K propyl oxalate
		Isoamyl	K isoamyl oxalate	Isobutyl	K isobutyl oxalate

In every case the oxalic ester when treated with slightly less than the calculated amount of potassium hydroxide in alcoholic solution gave a practically pure potassium alkyl salt in which the alkyl corresponded to the alcohol used as solvent. Further experiments showed that if mixed alcohols were used as solvent the product consisted of the two potassium alkyl salts corresponding to the alcohols used.

(*a*) Dimethyl oxalate with potassium hydroxide in a solvent consisting of ethyl alcohol and acetone in equal proportions gave potassium ethyl oxalate.

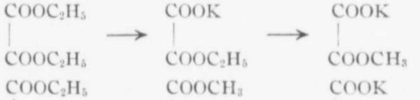
(*b*) Dimethyl oxalate was dissolved in ethyl alcohol and, after two hours, the alcohol was evaporated and the remaining ester was pure, unchanged dimethyl oxalate.

Some solubility determinations were made at room temperature with the following results:

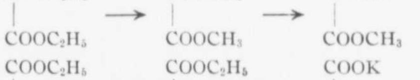
100 cc. methyl alcohol dissolved:	100 cc. ethyl alcohol dissolved:
3.0 g. potassium methyl oxalate	0.15 g. potassium methyl oxalate
5.6 g. potassium ethyl oxalate	0.30 g. potassium ethyl oxalate
0.016 g. dipotassium oxalate	0.004 g. dipotassium oxalate

The precipitation of potassium alkyl oxalate rather than dipotassium oxalate is not due to greater insolubility of the former and, also, the precipitation of potassium ethyl oxalate rather than potassium methyl oxalate from ethyl alcohol solution is not due to greater insolubility of the potassium ethyl oxalate.

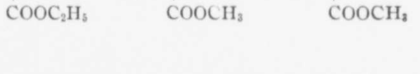
It would be possible to represent the reaction we are considering in three ways:

(1)


$$\begin{array}{c}COOC_2H_5\\ |\\ COOC_2H_5\end{array} \longrightarrow \begin{array}{c}COOK\\ |\\ COOC_2H_5\end{array} \longrightarrow \begin{array}{c}COOK\\ |\\ COOCH_3\end{array}$$

(2)


$$\begin{array}{c}COOC_2H_5\\ |\\ COOC_2H_5\end{array} \longrightarrow \begin{array}{c}COOCH_3\\ |\\ COOCH_3\end{array} \longrightarrow \begin{array}{c}COOK\\ |\\ COOCH_3\end{array}$$

(3)


$$\begin{array}{c}COOC_2H_5\\ |\\ COOC_2H_5\end{array} \longrightarrow \begin{array}{c}COOC_2H_5\\ |\\ COOCH_3\end{array} \longrightarrow \begin{array}{c}COOK\\ |\\ COOCH_3\end{array}$$

If either (2) or (3) is the better representation we might expect to find dimethyl oxalate or methyl ethyl oxalate in the residual dialkyl ester when considerably less than the calculated amount of potassium hydroxide solution is used.

Four cc. diethyl oxalate were dissolved in 10 cc. methyl alcohol and to this was added 2 cc. of 0.769 *N* potassium hydroxide solution in methyl alcohol but no precipitate was obtained although it was left for several hours. The alcohol was allowed to evaporate at room temperature and the dialkyl ester extracted with chloroform. The oily residue obtained by evaporation of the chloroform at room temperature might be diethyl oxalate, diethyl oxalate and dimethyl oxalate or diethyl oxalate and methyl ethyl oxalate but could not be dimethyl oxalate since the melting point of the latter is 54°. This residue was titrated and the results indicate either 7.5% dimethyl oxalate and 92.5% diethyl oxalate or 16.8% methyl ethyl oxalate and 83.2% diethyl oxalate.

Table II contains the data of a series of experiments in which varying amounts of 0.769 *N* solution of potassium hydroxide in methyl alcohol were used with 4 cc. ethyl oxalate dissolved in 10 cc. methyl alcohol. The 4 cc. ethyl oxalate used would require 38.5 cc. of the potassium hydroxide solution to completely convert it to potassium alkyl oxalate and the amount of this solution used is expressed in the first row of the table as the precentage of the total amount necessary to convert the diethyl oxalate to potassium alkyl salt. As the last three experiments in the series gave residual esters containing crystals of dimethyl oxalate the analyses of these residual esters were interpreted as indicating the proportions of dimethyl oxalate and diethyl oxalate and these appear in the last row. The analyses were done in duplicate and the average taken.

TABLE II.

Diethyl Oxalate (4 cc.) Dissolved in 10 cc. of Methyl Alcohol.

KOH sol. Me alc., %	5.2	10.4	15.6	20.8	26.0
Dimethyl oxalate, %	7.5	33.0	59.5	84.6	98.7

The results of this series of experiments show that a methyl alcohol solution of potassium hydroxide converts diethyl oxalate into dimethyl oxalate and that the amount of dimethyl oxalate formed depends on the amount of potassium hydroxide used. This reaction is accompanied by another reaction which produces potassium methyl oxalate. If, in the last experiment, a further amount of 28.5 cc. of the potassium hydroxide solution had been added there would have been complete conversion to potassium methyl oxalate and it would have been the conversion of dimethyl oxalate and not of diethyl oxalate to potassium methyl oxalate.

The two stages of the reaction are, therefore, represented as first, the change of diethyl oxalate to dimethyl oxalate and, second, the change of dimethyl oxalate to potassium methyl oxalate, see (2) above.

Since experiment (*b*) on page 1805 showed that an oxalic ester is not converted to a different ester by treatment with another alcohol, the change must take place under the influence of the alcoholic solution of potassium hydroxide or, possibly, the potassium alkyl salt first formed acts as a catalyzer for the reaction.

Potassium ethyl oxalate was added to ethyl oxalate dissolved in methyl alcohol and, after a few hours, the dialkyl ester was found to be unchanged diethyl oxalate.

In a solution of potassium hydroxide in methyl alcohol it may be considered that potassium hydroxide and potassium methylate are in equilibrium. Addition of water to this solution would disturb this equilibrium forming more potassium hydroxide. Hence, the addition of water to the potassium hydroxide solution would hasten or retard the formation of dimethyl oxalate depending on whether the potassium hydroxide or the potassium methylate is the determining influence in the reaction.

Table III contains the results of experiments in which the solutions of potassium hydroxide in methyl alcohol contain varying amounts of water. These solutions were made up by adding the necessary weight of water to the methyl alcohol solution of the potassium hydroxide and the methyl alcohol used for dissolving the diethyl oxalate was also diluted with water.

TABLE III.

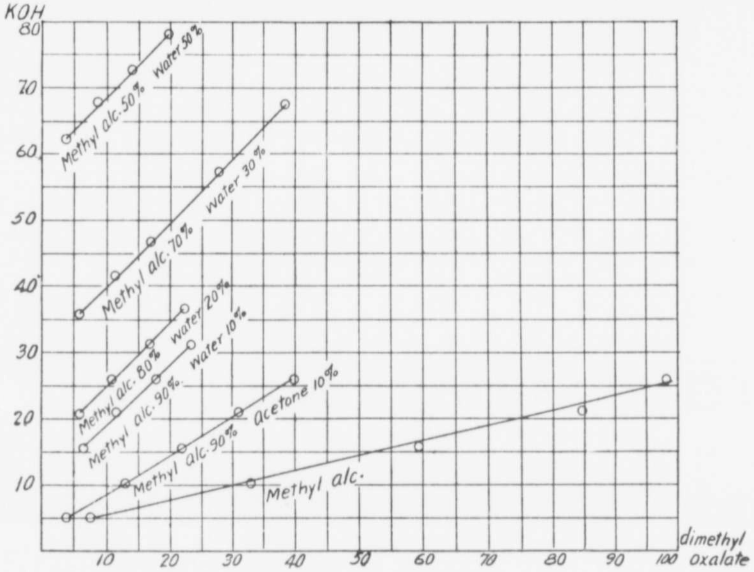
Diethyl Oxalate 4 cc. and Methyl Alcohol of Varying Strength.

10.9 cc. CH_3OH (90%).		11.7 cc. CH_3OH (80%).		12.9 cc. CH_3OH (70%).		17.5 cc. CH_3OH (50%).		11.1 cc. 90% CH_3OH; 10% CH_3COCH_3.	
KOH sol. Me. alc. (90%). %.	Dimethyl oxalate. %.	KOH sol. Me. alc. (80%). %.	Dimethyl oxalate. %.	KOH sol. Me. alc. (70%). %.	Dimethyl oxalate. %.	KOH sol. Me. alc. (50%). %.	Dimethyl oxalate. %.	KOH sol. Me. alc (90%). Acetone (10%). %.	Dimethyl oxalate. %.
5.2	0.0	10.4	0.0	26.0	0.0	57.2	0.0	5.2	4.0
10.4	0.0	15.6	0.0	31.2	0.0	62.4	3.9	10.4	12.9
15.6	6.5	20.8	6.0	36.4	6.0	67.8	8.75	15.6	22.0
20.8	11.5	26.0	10.9	41.6	11.5	72.8	14.0	20.8	31.1
26.0	17.9	31.2	16.9	46.8	17.0	78.0	20.0	26.0	39.9
31.2	23.5	36.4	22.6	57.2	28.0	..	..	..	..
..	..	..	..	67.6	38.5	..	..	..	..

Table III shows that under the influence of a given amount of potassium hydroxide dissolved in methyl alcohol much less dimethyl oxalate is formed when water is present and that the more water is present the less dimethyl oxalate is formed. It must be considered that the potassium methylate rather than the potassium hydroxide is the influence causing the reaction.

The last two columns which record experiments in which the alcohol was diluted with acetone instead of water shows a smaller production of dimethyl oxalate than when pure methyl alcohol was used but a much greater production than when the alcohol was diluted with the corresponding amount of water.

The results of these experiments have been represented graphically, using as one axis the amount of potassium hydroxide solution used (expressed as the percentage of the amount necessary to completely convert the diethyl oxalate to potassium methyl oxalate) and, as the other axis the percentage of dimethyl oxalate found in the residual dialkyl ester.



Saloman's representation of this reaction need not be seriously considered. It would be better to assume the formation of an addition compound of the ester with the potassium alcoholate, but, with the information at present available, it is not thought that this would help in the study of the reaction.

Summary.

1. Dialkyl oxalates, when treated with slightly less than the calculated amount of potassium hydroxide in alcoholic solution, give a practically pure potassium alkyl oxalate in which the alkyl corresponds to the alcohol used as solvent.

2. A few solubility determinations were made which indicate that the results obtained in these experiments do not depend on the relative insolubility of the possible potassium alkyl salts.

3. If much less than the calculated amount of the methyl alcohol solution of potassium hydroxide is used with diethyl oxalate the residual dialkyl ester contains an amount of dimethyl oxalate which depends on the amount of potassium hydroxide solution used.

4. The change from diethyl oxalate to potassium methyl oxalate is represented as, first, the change of diethyl oxalate to dimethyl oxalate and, second, the change of dimethyl oxalate to potassium methyl oxalate.

5. The presence of potassium ethyl oxalate in the solution of diethyl oxalate in methyl alcohol does not cause the formation of any dimethyl oxalate.

6. If the solution of potassium hydroxide in methyl alcohol be said to contain potassium hydroxide and potassium methylate, the potassium methylate is a stronger factor than the potassium hydroxide in causing the change from diethyl oxalate to dimethyl oxalate.

These experiments were done under the direction of Professor F. B. Allan and it is proposed to continue them using solutions of other alkalies.

TORONTO, CANADA.