

EQUILIBRIA AND RATES IN THE
CARBONATION OF ALCOHOLIC ALKALI

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CARBONATION OF ALCOHOLIC ALKALI

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INTRODUCTION

Alcoholic alkalies have been used for perhaps a century without a great deal of question as to the amount or form of their constituents. The solution of a base in an alcohol is a common laboratory reagent. Metal salts of the alcohols are used commercially. Calcium, barium, and strontium salts are employed in refining sugar. Gasoline can be sweetened by using alcoholic alkalies. They are also used as catalysts in a wide variety of organic syntheses.

HISTORICAL

The first record of a reaction between a base and an alcohol was reported by Engel in 1886 (6). He studied the reaction of potassium hydroxide in absolute alcohol and recorded it as follows: $\text{KOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{KOC}_2\text{H}_5 + \text{H}_2\text{O}$. He proposed the name alcoholate (unfortunately, as it turned out) for this group of salts. Later Lescoeur (14) reported the same reaction. Neither man was interested in the yield of the "alcoholates", but they did isolate the alkoxides and studied them.

Various means of converting sodium hydroxide to sodium ethoxide, all similar in principle, have been patented by Walker (24), Wacker (21), Bulgach (1), Kyrides (13), and Cunningham (4).

Walker, by the use of the difference of boiling points of benzene-alcohol-water mixtures and the water-alcohol constant-boiling mixture, made solutions enriched in sodium ethoxide. By the addition of more sodium hydroxide and further distillation he prepared a more concentrated solution of the alkoxide. To find out how much alkoxide there was, he first titrated for total alkalinity. Then, to another sample, he added ethyl acetate and boiled the reacting mixture for an hour. This he titrated with benzoic acid in anhydrous alcohol. The difference in alkalinity represented the percent alkoxide since only sodium hydroxide will saponify ethyl acetate. He reported over fifty percent of the sodium to be converted to the alkoxide. This

method is not very accurate and is not applicable except to alcohol solutions containing little water.

Upon saponifying phthalide with sodium hydroxide in various alcohol-water mixtures, Caudri (2) found a peculiar relation between the rate constant and the amount of water present. Similar observations on the saponification of other esters were made earlier by Kremann (12), and upon the Williamson synthesis of ethers by Lobry de Bruyn and Steger (15). The latter authors attributed the effect to the conversion of most of the hydroxyl ion to ethoxyl ions even in the presence of much water, but Caudri showed that this interpretation is untenable and considered that sodium ethoxide in absolute ethanol is considerably hydrolyzed by even a little water. The relative degree of hydrolysis of sodium methoxide is much less than that of sodium ethoxide.

Wegscheider (25) in his theoretical article also differed with the conclusions of Lobry de Bruyn and Steger that the sodium was present mostly as the alkoxide.

Nearly every elementary organic text book has a sentence or two concerning the decomposition of the alkoxides in water. A few of these are quoted below.

Ray, "The alcoholates are readily decomposed by water and carbonic acid." (16)

Williams, "Sodium methylate, CH_3ONa , is in other words almost completely hydrolyzed into sodium hydroxide and methyl alcohol in the presence of water." (30)

Conant, "The compound $\text{C}_2\text{H}_5\text{ONa}$ is completely hydrolyzed in water forming alcohol and sodium hydroxide." (3)

Wertheim, "In the presence of water such salts are hydrolyzed, since water is more highly ionized than are these alcohols." (27)

Quantitative experiments have been attempted by several investigators. It might seem that the amount of alkoxide hydrolyzed could be calculated from the ionic product of water and the strength of the acid using the equation $K_h = \frac{K_w}{K_a}$. However, we do not know the dissociation constant of alcohol in water, if the relation is true at all for acids weaker than water. Moreover, any appreciable increase in the concentration of alcohol and corresponding decrease in the concentration of water will cause a shift of the equilibrium because of the mass law effect.

Williams and Truesdail (32) used calcium carbide to estimate the amount of water formed when sodium hydroxide and absolute alcohol react. They calculated alcohol was about 8% as highly ionized as water, which is in rough agreement with the results of Danner and Hildebrand (5). Later infra-red spectra were used by Williams and Bost (31) to determine the amount of water present in a solution of sodium hydroxide in absolute alcohol after boiling the mixture an hour. This method was only approximate but they reported that 75 to 100% of the sodium present was converted to the ethoxide.

It might also be possible to determine the activities of alcohol and water in alcoholic alkali solutions by means of partial pressures. If such partial pressures were measured for known mixtures in the presence of a neutral salt (instead

of alkali) and then for the alkali, interpretation might be possible. All methods involving study of alcohol or water activities or concentrations, however, are really concerned with the wrong variable; measurement of hydroxyl or alkoxy is much more logical, at least for dilute solutions.

The equilibrium constant of the system $\text{CH}_3\text{O}^- + \text{HOH} \rightarrow \text{CH}_3\text{OH} + \text{OH}^-$ was studied by Unmack (18) by several different methods. From conductance measurements, the value of the constant appeared to be 0.21. Freezing point determinations gave a slightly larger constant, ranging from 0.24 to 0.41. Data on reactions led her to believe it was less than one. She concluded from these data that the most probable value was 0.35. Later she set up half cells

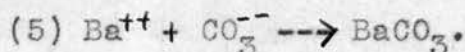
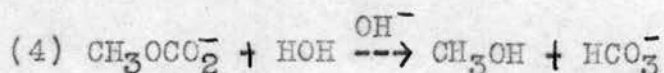
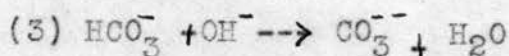
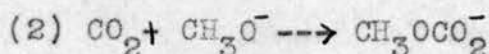
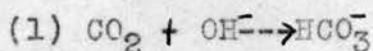


and from the data secured from e.m.f. measurements, calculated the constant to be 0.47 (19). The concentrations of methyl alcohol in these were from 0 to 24.9 M (absolute methanol). Further calculations (20) using the ionization constants of methanol and water with the same data gave the constant values between 0.98 and 2.00.

A procedure using carbon dioxide to "freeze" the system was reported by Faurholt (7). He was seeking to measure the rate of reaction between carbon dioxide and the methoxide ion. His method consisted of passing carbon dioxide into an alcoholic alkali solution, then adding barium chloride. This precipitated the carbonate ion immediately

as barium carbonate, which was thrown down by centrifuging. The supernatant liquid was then poured off and allowed to stand, whereupon a second precipitation of barium carbonate took place.

The mechanism of these reactions is as follows:



Barium carbonate is precipitated at two different times because reaction (3) is instantaneous whereas reaction (4) is the hydrolysis of an ester and therefore slow.

The two precipitates were washed and titrated separately. This gave a measure of extent of formation of carbonate and methylcarbonate ions. The calculation of his results is explained below.

(1) $\frac{dC_{\text{CO}_2}}{dt} = k_{\text{CH}_3\text{CO}_3^-} \cdot C_{\text{OH}^-} \cdot C_{\text{CO}_2}$ Assuming the reaction $\text{CH}_3\text{OH} + \text{OH}^- \rightarrow \text{CH}_3\text{O}^- + \text{HOH}$ to be at equilibrium and neglecting the water, the equilibrium constant can be expressed as,

$$(2) K_{\text{CH}_3\text{O}^-} = \frac{C_{\text{CH}_3\text{OH}} \cdot C_{\text{OH}^-}}{C_{\text{CH}_3\text{O}^-}} \quad \text{Solving for } C_{\text{CH}_3\text{O}^-},$$

$$(3) C_{\text{CH}_3\text{O}^-} = \frac{C_{\text{CH}_3\text{OH}} \cdot C_{\text{OH}^-}}{K_{\text{CH}_3\text{O}^-}} \quad \text{Substituting in (1)}$$

$$(4) \frac{dC_{CO_2}}{dt} = -k_{CH_3CO_3^-} \cdot \frac{C_{CH_3OH} \cdot C_{OH^-} \cdot C_{CO_2}}{K_{CH_3O^-}}$$

$$(5) \text{ Again, } \frac{dC_{CO_2}}{dt} = k_{HCO_3^-} \cdot C_{OH^-} \cdot C_{CO_2}$$

$$(6) \text{ And the ratio } \frac{\frac{dC_{CO_2}}{dt}}{\frac{dC_{CO_2}}{dt}} =$$

$$\frac{\% \text{ Monomethylcarbonate}}{\% \text{ Carbonate}}$$

$$(7) \text{ Dividing, } \frac{\frac{dC_{CO_2}}{dt}}{\frac{dC_{CO_2}}{dt}} = \frac{\% \text{ Monomethylcarbonate}}{\% \text{ Carbonate}} =$$

$$\frac{k_{CH_3CO_3^-} \cdot C_{CH_3OH} \cdot C_{OH^-} \cdot C_{CO_2}}{k_{HCO_3^-} \cdot K_{CH_3O^-} \cdot C_{OH^-} \cdot C_{CO_2}}$$

If the C_{OH^-} and C_{CO_2} be canceled out, the only variable on the right hand side of the equality is the concentration of methanol, the two velocity constants and the equilibrium constant being constant. The expression then becomes

$$\frac{\% \text{ Monomethylcarbonate}}{\% \text{ Carbonate}} = K \cdot C_{CH_3OH}$$

confirmed the constancy of this expression, at $K = 1.3$. By assuming on various grounds that $K_{CH_3O^-}$ is 16, and using the literature value (17) for $k_{HCO_3^-}$, the rate of formation of bicarbonate ion, he calculated $k_{CH_3CO_3^-}$ to be 5×10^5 from the equation

$$\frac{k_{CH_3CO_3^-}}{k_{HCO_3^-} \cdot K_{CH_3O^-}} = 1.3.$$

Much less attention has been paid to the rate of reaction of alkalies with alcohol. Faurholt assumed that this reaction, like other neutralizations, proceeds instantaneously. On the other hand Jones and Hughes (11) say, "When these water additions are made to solutions of sodium alkoxides in absolute alcohol, the conductivity values change with time, taking in some cases several hours to come to equilibrium. This suggests that reactions of the type $\text{OEt}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{EtOH}$ are slow. Such drifts with time are also observed in methyl alcohol, but they are more rapid and the changes are much smaller."

EXPERIMENTAL

The method used in this work was much the same as that of Faurholt. His work was repeated and the procedure extended to include higher concentrations of alcohol. A more detailed account of the procedure is given here than in the original publication.

Several attempts were made to prepare silver ethoxide or methoxide, with a view toward devising a half cell which could be used for direct potentiometric measurement of alkoxy ion concentration. However, double decomposition reactions between sodium alkoxides and alcoholic silver nitrate solutions always give a precipitate too rich in silver to be the pure silver alkoxide; apparently if such compounds exist at all they are quite unstable. This accords with the report that silver oxide slowly oxidizes the lower alcohols in aqueous solution (4a).

Reagents:

None of the reagents was expensive or rare so there was no difficulty in procuring them chemically pure. They were methyl alcohol, sodium hydroxide, carbon dioxide, hydrochloric acid, and barium chloride. The apparatus consisted of a centrifuge and pyrex tubes, burettes, and balance.

The acid and base were standardized by the method recommended by Hall (10). The acid was 0.5167 N. and the base 0.5529 N.

PROCEDURE

Preparation of the alcoholic alkalies and other reagents:

The sodium hydroxide (1.6 g in every case) is weighed out and dropped in a 200 ml. volumetric flask. Then the required amount of alcohol is pipetted in and diluted to 200 ml with water; shake a time or two to speed up the solution of the solid and allow to stand over night. It is well to fill a bottle with carbon dioxide to serve as a gas-holder and prepare the barium chloride solution beforehand, as this speeds up subsequent operations. Barium chloride solution is made up by dissolving 20 grams of barium chloride in 100 ml of water.

Technique of a run:

On the following day, the alcoholic alkali solution is separated into two approximately equal parts (100 ml each) and poured into the centrifuge tubes. These samples are cooled to 0 °C. and 100 ml of carbon dioxide is bubbled in during 6 to 10 minutes. Then 10 ml of the barium chloride solution is added to each tube. They are balanced against each other and centrifuged at 2000 r.p.m. for five minutes. The solution above the precipitate is at once decanted into other tubes. This operation, from the addition of barium chloride solution to the decantation, should not require over 10 minutes. More time than this will result in reduced amounts of the second precipitate because of premature decomposition of the alkylcarbonate. The solution decanted should be clear.

The precipitated barium carbonate left in the tubes is washed three times with water to remove any traces of alcohol or alkali. This operation consists of adding the water, shaking, centrifuging, and siphoning off. About 50 ml of water and a drop of phenolphthalein solution is now added to each tube and the red color is dissipated with a drop or two of dilute hydrochloric acid. Then 10 or 15 ml of standard acid solution is added and all carbon dioxide is expelled from the solution by boiling it. After cooling, the excess acid is back titrated with standard sodium hydroxide solution. The amount of acid used is a direct measure of the carbonate originally present in the solution.

On the following day the precipitate resulting from the gradual decomposition of alkylcarbonate is washed and titrated in the same way.

There are several pitfalls to be avoided in this procedure. As has been mentioned, the time elapsed between the addition of barium chloride and decantation must be as short as possible. Also, an excess of carbon dioxide is to be avoided since it would convert all the alkali present to bicarbonate, which cannot be precipitated by barium. Centrifuge tubes must be balanced reasonably well. The decanted solution should not be exposed to the air for any great length of time, because of possible absorption of carbon dioxide. There must be an excess of barium chloride for complete precipitation.

Testing the analytical method:

This procedure was varied in several ways to prove the accuracy of the method. First a weighed amount of barium carbonate, about as much as an ordinary run would produce, was allowed to stand in the alcohol-water-sodium hydroxide mixture overnight. This "precipitate" was then washed and titrated in the regular way. The results were as follows:

gms. of BaCO_3 by weight	gms. of BaCO_3 by titration
.3958	.3941
.4066	.4074

Next a known weight of sodium carbonate was dissolved in a sample of the alcoholic alkali and the barium carbonate precipitated in the usual way. The results were as follows:

gms. Na_2CO_3 by weight	gms. Na_2CO_3 by titration
.2147	.2156
.2349	.2339

Nevertheless there is considerable experimental error. Results that check within 2% are to be considered good. In view of the data in the table, this statement may appear inconsistent. These values, however, are the average of the results of several runs; some are the composite of even as many as half a dozen.

As further test of the reliability of the method a number of experiments designed to check the mechanism of the reactions involved were performed. When a solution of sodium dissolved in methanol was made up to .2 M and then diluted with water to 4 M methanol, the results of the carbonation were the same as those using .2 M sodium hydroxide. This

agrees with White's (28) observations. She found the conductance of alcoholic alkali to be the same whether sodium hydroxide or sodium alkoxide is dissolved in aqueous alcohol.

It was also thought that the reactions (1) $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ and (2) $\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$ might reverse if allowed time enough and cause the formation of methylcarbonate. Sodium carbonate was allowed to stand in 4 M methanol in both alkaline (0.2M) and neutral solutions overnight. These were precipitated as usual and there was no second precipitation, indicating the absence of monomethylcarbonate ions.

The thought also occurred that a barium chloride-methanol complex might be responsible for the delayed precipitation of barium carbonate. With this in mind, the barium chloride was added to the solution in the absence of carbonate ions. Then on the addition of sodium carbonate there was no second precipitation.

These experiments show that the method actually gives reliable measurements.

DISCUSSION OF RESULTS

The experimental results shown in the table agree reasonably well with those obtained by Faurholt. He worked with dilute solutions, not reporting the use of concentrations higher than 4 M. His constant for the ratio $\frac{\% \text{Monomethylcarbonate}}{\% \text{Carbonate}} \cdot C_{\text{CH}_3\text{OH}}$ ranged between 1.2 and 1.8. This work, employing the same concentrations, resulted in finding a constant lying between 1.5 and 1.8.

In higher alcohol concentrations, this constant falls from 1.8 to 0.4 while the alcohol is raised from 7.9 to 40 mole percent. Then the value starts to rise and reached 0.9 in 80 mole percent methanol. The values for ethyl alcohol between 8.2 and 23.4 mole percent are 0.46 ± 0.1 .

Faurholt also stated that the reaction of monomethylcarbonate ion to form carbonate ion is reversible. If such reversal were as fast as the equilibration of alcoholic alkali, the method would be unsuitable for measuring rates of carbonation. In this work it is shown that no such reversal occurs.

Since Faurholt and Jones and Hughes disagree concerning the rate of equilibration, a run was made no more than 20 seconds after the preparation of alcoholic alkali (0.2N alkali, 4M methanol). The solution was poured into a centrifuge tube filled with carbon dioxide, shaken, treated with barium chloride, and centrifuged. The percentage of monomethylcarbonate indicated was 39%, which is nearly 40% below the equilibrium value. If carbon dioxide was bubbled into the freshly prepared alcoholic alkali solution in the ordinary

way, a drop of 17% from the equilibrium value was recorded. The time taken to bubble in the carbon dioxide was 6.5 minutes. This proves that the reaction is not instantaneous, but takes some time to reach equilibrium.

The application of the simple mass law equation met with difficulty in the higher concentrations of methanol. $K_{\text{CH}_3\text{O}^-}$, the equilibrium constant for the reaction of hydroxyl ions with methanol, increases from a value of 4.4 for 22.3 M methanol to 115 for 0.25 M methanol. Evidently other effects than that of concentration play a part.

Water concentration is entirely neglected by Faurholt's derivation. It is customary to do so when the concentration of water is large, but this procedure cannot be justified when it is low.

He also deduced, on rather doubtful grounds, $K_{\text{CH}_3\text{O}^-}$ for the hydroxyl-methoxyl ion equilibrium. To this constant he assigned a value of 16. By Unmack's latest calculations, the constant falls between 0.98 and 2.00. Moreover, a more recent determination (16a) of the rate of reaction of carbon dioxide with hydroxyl ion at 13.7°C has yielded the value $k_{\text{HCO}_3^-} = 3.7 \times 10^3$. Recalculation, using this new rate constant, Unmack's results and Faurholt's equation, yields a velocity constant for the formation of monomethylcarbonate lying between 4.8×10^3 and 9.6×10^3 . Faurholt reported a value of 5×10^5 .

An assumption made that has not been mentioned is that the velocity constant for the formation of bicarbonate ion is the same at 0° in alcohol-water solutions as it is at

13.7° in water, in which the literature values were obtained.

Future work should continue along two separate lines. The velocity constant, $k_{\text{CH}_3\text{CO}_3^-}$, should be determined independently, perhaps by the same method which yielded $k_{\text{HCO}_3^-}$. This would lead to another value for $K_{\text{CH}_3\text{O}^-}$.

The other line of work should be with the rate of equilibration of alcoholic alkalies. This should be done with other alcohols as well as methanol. The principal difficulty with methanol is that the equilibration is so fast that only the last stages can be studied and therefore would not lead to a reliable rate constant. There have been no values worked out as to the rate of reaction of alkalies with alcohols and this might prove to be a fruitful field.

It may be mentioned that both acetone and phenol were tested in alkaline solution for ability to produce delayed precipitation and evidence of the existence of alkyl or arylcarbonate ions. Acetone gave no secondary precipitate whatever, so that the enolate anion presumably yields no stable addition product with carbon dioxide. Phenol, on the other hand, did appear to form a small amount (perhaps 10%) of arylcarbonate, $\text{C}_6\text{H}_5\text{OCO}_2^-$. This is in direct contradiction to the statement found in Whitmore (29) and practically other organic textbooks, to the effect that carbon dioxide completely displaces phenols from alkaline solution according to the equation $\text{C}_6\text{H}_5\text{ONa} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{NaHCO}_3$. Evidently more work here would be of considerable interest.

VARIATION IN METHYLCARBONATE-CARBONATE RATIO
WITH ALCOHOL CONCENTRATION

Moles CH_3OH	ml CH_3OH per 100 ml soln.	Mole Per- cent CH_3OH	Moles H_2O	% CO_2 Chang- ed to CH_3CO_3^-	Mass Law K	Faur- holt's K
.0	.0	.0	55.6	.0		
.125	0.5	0.2	55.2	19.0	110.0	1.8
.25	1.0	0.4	55.0	35.0	115.0	1.7
.5	2.0	0.9	54.4	45.0	89.0	1.6
1.0	4.0	1.9	53.3	65.0	98.0	1.8
2.0	8.0	3.8	51.1	75.0	80.0	1.5
4.0	16.0	9.4	46.6	77.0	34.0	.83
4.8	20.0	11.8	44.4	78.0	32.0	.74
7.4	30.0	16.0	38.8	80.0	19.0	.54
9.6	40.0	22.4	33.3	81.5	12.0	.47
12.4	50.0	31.7	27.7	83.0	9.0	.40
14.8	60.0	40.0	22.2	85.0	8.0	.39
19.8	80.0	64.1	11.1	90.0	4.7	.46
22.3	90.0	80.3	5.5	95.0	4.4	.90
24.8	100.0	100.0	0.0	100.0	0.0	

Ethanol

Moles $\text{C}_2\text{H}_5\text{OH}$	ml $\text{C}_2\text{H}_5\text{OH}$ per 100 ml soln.	Mole Per- cent $\text{C}_2\text{H}_5\text{OH}$	Moles H_2O	% CO_2 Chang- ed to $\text{C}_2\text{H}_5\text{CO}_3^-$	Mass Law K	Faur- holt's K
4.0	14.0	8.2	47.7	66.0	30.0	.46
5.1	20.0	10.3	44.4	69.0	20.0	.45
8.5	50.0	23.4	27.7	79.0	13.0	.47

Strength of Alkali - 0.2M

SUMMARY

1. The nature of alcoholic alkalies has been investigated by employing the method of Faurholt.
2. It has been proved that the reaction of a base with an alcohol is not instantaneous.
3. The variation of partition of carbon dioxide between methylcarbonate and carbonate has been determined at various concentrations of alcohol.
4. The findings confirm and extend Faurholt's results.
5. Faurholt's interpretation of his data has been critically examined and a new value for the rate constant for formation of methylcarbonate ion calculated. This calculation is based on newer literature values for the other constants involved.
6. The need for further work has been pointed out and suggestions made as to the variables to be measured.

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BIOGRAPHY

John A. Woodside was born at Jonesboro, Arkansas, April 27, 1916. He received his grade school and high school education at the Thomasville Schools, Thomasville, Missouri. In September, 1932, he entered Arkansas State College, Jonesboro, Arkansas, and received his Bachelor of Science degree in May, 1936. After working in the Henry Ford Trade School during the summer of 1936, he entered Iowa State College, Ames, Iowa. Leaving there in June, 1937, he has been employed by Cities Service Oil Company. In September, 1940, he entered the graduate school of Oklahoma A. & M. College, Stillwater, Oklahoma.

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