

THE REACTION OF ALKOXIDE IONS WITH CARBON DIOXIDE

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A study of the rate of the reaction $\text{OCH}_2^- + \text{CO}_2 \longrightarrow \text{CH}_3\text{OCO}_2^-$ has been made by Faurholt (1927). His indirect method causes hydroxide and methoxide ions to compete for a relatively small amount of carbon dioxide in aqueous methanol. Under these conditions the end products, carbonate and methylcarbonate ions, are formed in a ratio dependent only upon their relative rates of formation. This ratio is ascertained by adding barium chloride, which precipitates the carbonate ion immediately but the methylcarbonate ion only slowly; the two precipitates of barium carbonate are then weighed or titrated. The secondary precipitation depends on the gradual decomposition of methylcarbonate ion to carbonate ion and methanol.

The present work repeats Faurholt's measurements and extends them to greater concentrations of methanol. His theoretical treatment of the data is not plausible because it neglects important variables, but neither have we been able to devise a sound method of calculating the rate constant for the reaction; too many factors remain unknown. We are therefore reporting only empirical results, with a minimum of interpretation.

EXPERIMENTAL

All alcoholic alkali solutions were adjusted to 0.2 N with respect to sodium hydroxide and to various concentrations of methanol. After each solution had been aged overnight, 100 ml portions of it were cooled to 0° and treated with 100 ml of gaseous carbon dioxide during 6 to 10 minutes. Ten ml of 20 percent barium chloride solution was added to each portion and the precipitated barium carbonate was immediately thrown down by centrifuging and washed free from alkali. This separation must be performed in 10 minutes or less to minimize error due to alkylcarbonate decomposition in the mother liquor.

The washed barium carbonate was boiled with excess standard acid solution and the excess acid back-titrated after cooling. On the following day, the precipitate resulting from the gradual decomposition of methylcarbonate ion was washed and titrated in the same way.

This procedure was tested in various ways to insure its reliability. The recovery of barium carbonate precipitated from aqueous methanol by known amounts of sodium carbonate was found to be 99.5%. No alkylcarbonate was indicated when aqueous alkalies were carbonated, and no immediate precipitate of barium carbonate appeared when a solution containing only sodium methoxide was tested. The ratio of methylcarbonate to carbonate was the same whether sodium hydroxide or sodium methoxide was the original alkali added.² Reversal of the hydrolysis of methylcarbonate ion could not be detected, contrary to Faurholt's claim.

The corresponding results for ethanol were 66% of CO_2 converted to $\text{C}_2\text{H}_5\text{CO}_2^-$ at 14.0 ml/100 ml of solution, 69% at 20.0 ml/100 ml, and 79% at 50 ml/100 ml. For this system Faurholt reported 44% at 14.1 ml/100 ml, and 63% at 23.4 ml/100 ml (concentrations recalculated). It is evident that the agreement with his results is not good.

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² White (1928) found that the conductance of alcoholic alkali is the same whether sodium hydroxide or sodium alkoxide is dissolved in aqueous alcohol.

TABLE I
Variation in methylcarbonate-carbonate ratio with concentration of methanol in 0.2 N alkali.

Alcohol concn. ml/100 ml soln.	% CO ₂ changed to CH ₃ CO ₃ ⁻ (±3)	Alcohol concn. ml/100 ml soln.	% CO ₂ changed to CH ₃ CO ₃ ⁻ (±3)
0.0	0	30.0	80
0.5	19	40.0	81.5
1.0	35	50.0	83
2.0	45	60.0	85
4.0	65	80.0	90
8.0	75	90.0	95
16.0	77	100.0	100
20.0	78		

Faurholt obtained the values 54-58% at 4.1 ml/100 ml, 69% at 6.5 ml/100 ml, and 88% at 16.2 ml/100 ml (concentrations recalculated to permit comparison).

An additional point investigated concerns the rate of the equilibration reaction: $\text{CH}_3\text{OH} + \text{OH}^- \longrightarrow \text{OCH}_3^- + \text{H}_2\text{O}$

Faurholt assumed that "the process, . . . like other neutralizations, proceeds instantaneously." On the other hand Jones and Hughes (1934) concluded from the drift of conductivities after addition of water to solutions of sodium alkoxides in alcohol that such reactions are slow, though faster for methanol than for ethanol. In the present work one carbonation was carried out not more than 20 seconds after the preparation of the alcoholic alkali (0.2 N NaOH, 4N CH₃OH) from sodium hydroxide solution and methanol. Thirty-nine percent of the carbon dioxide appeared as methylcarbonate; this is nearly 40% below the equilibrium value (77%). When the carbonation was performed after 6.5 minutes from the time of mixing, 60% of the reaction product was methylcarbonate. Evidently the reaction of methanol with hydroxide ion is fairly fast but by no means instantaneous.

It may also be mentioned that both acetone and phenol were tested in alkaline solution for ability to produce delayed precipitation as 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 form a small amount (perhaps 10%) of secondary precipitate, indicating the presence of phenylcarbonate ion, C₆H₅OCO₃⁻. This renders somewhat doubtful the statement in practically all organic textbooks that carbon dioxide completely displaces phenols from alkaline solution.

LITERATURE CITED

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