

Base-Catalyzed Hydrogen Exchange of Carbon Acids. I. Specific Salt Effects in Carbonate Buffer Solutions

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The inadequacy of the ionic strength principle was demonstrated by measuring the rates of detritiation of dibromochloromethane-*t* in aqueous hydrogen carbonate/carbonate buffer solutions. Results differing from each other were obtained when salts with monovalent or divalent anions were used to maintain the constant ionic strength. It is suggested that, besides the ionic strength, it is necessary to maintain the cation concentration constant when making a series of diluted carbonate buffer solutions.

General base catalysis of hydrogen exchange of carbon acids which show normal acid behavior,¹ is weak and difficult to detect.² Specific salt effects associated with buffer experiments in mixed solvents have been shown to lead to erroneous conclusions regarding the involvement of general acid catalysis in the hydrolysis of acetals and ortho esters.^{3,4} That this is possible also in wholly aqueous solutions, is reported here with experimental results on base-catalyzed hydrogen isotope exchange reactions in carbonate/hydrogen carbonate buffer solutions.

In order to detect possible general base catalysis, one traditionally makes a series of rate measurements in buffer solutions of constant buffer ratio ($BR = [\text{acid}]/[\text{base}]$) and constant ionic strength. The ionic strength constancy in the diluted buffer solutions is maintained with some added electrolyte. In an ideal case, the hydroxide ion concentration remains constant through the whole series of diluted buffer solutions.

In this work, the rates of detritiation of dibromochloromethane-*t* were measured in sodium hydrogen carbonate/sodium carbonate buffer solutions when the ionic strength was maintained constant by addition of salts with either monovalent or divalent anions.

Experimental

Materials. Tritium labelling of dibromochloromethane (Ega Chemie) was performed as described earlier.⁵ The carbonate buffer solutions were prepared by dissolving weighed amounts of both salts in water. Sodium hydrogen carbonate (E. Merck, *pro analysi*) was used without further treatment. Sodium carbonate was prepared by heating sodium hydrogen carbonate to 260–270 °C for 60–90 min.⁶

Kinetics. Accurate 5 cm³ aliquots of reaction mixture tritiated substrate, dissolved in temperature-equilibrated buffer solution, were withdrawn at suitable time intervals. These were run into stoppered 50 cm³ cylinders containing exactly 10 cm³ of cyclohexane and enough dilute hydrochloric acid to neutralize the base. The cylinders and their contents were shaken, and the layers were allowed to separate overnight. Accurate 5 cm³ samples of cyclohexane layers were taken and combined with 10 cm³ of toluene-based scintillation counting solution (5 g of 2,5-diphenyloxazole and 1 g of *p*-bis(*o*-methylstyryl)benzene per 1 dm³), and subjected to liquid scintillation counting (LKB-Wallac 81000).

Rate constants were calculated as slopes of plots of $\ln(C_t - C_\infty)$ as a function of time (C = counts per minute). Weighted least-squares

Table 1. The rate constants for detritiation of CTBr₂Cl in NaHCO₃/Na₂CO₃ buffer solutions at 25 °C. Ionic strength maintained at 0.100 mol dm⁻³ by addition of electrolyte E

$c(\text{CO}_3^{2-})/10^{-2} \text{ mol dm}^{-3}$	E	$k(\text{obs})/10^{-3} \text{ s}^{-1}$	$\frac{k(\text{obs})/c(\text{HO}^-)}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
$c(\text{HCO}_3^-)/c(\text{CO}_3^{2-}) = 0.125$			
3.2	—	2.569(13)	3.048
2.4	Na ₂ SO ₄	2.407(22)	3.009
2.4	NaCl	2.331(6)	2.914
2.4	NaClO ₄	2.301(17)	2.877
1.6	Na ₂ SO ₄	2.172(15)	2.967
1.6	NaCl	2.037(16)	2.782
1.6	NaClO ₄	2.051(30)	2.802
0.8	Na ₂ SO ₄	1.794(17)	2.971
0.8	NaCl	1.654(12)	2.738
0.8	NaClO ₄	1.616(10)	2.675
$c(\text{HCO}_3^-)/c(\text{CO}_3^{2-}) = 0.200$			
3.125	—	1.817(9)	3.093
2.344	Na ₂ SO ₄	1.755(20)	3.080
2.344	NaCl	1.667(19)	2.926
1.563	Na ₂ SO ₄	1.639(18)	3.038
1.563	NaCl	1.544(8)	2.862
0.7813	Na ₂ SO ₄	1.424(6)	3.014
0.7813	NaCl	1.268(8)	2.684

analysis with weighting factor ($C_i - C_\infty$) was used in the calculations.

Results and discussion

The observed first order rate constants for the loss of tritium from dibromochloromethane-*t* in NaHCO₃/Na₂CO₃ buffer solutions are presented in Table 1. The catalytic coefficients can be evaluated using the rate law (1) governing the base catalyzed detritiation.

$$k(\text{obs}) = k(\text{HO}^-)c(\text{HO}^-) + k(\text{CO}_3^{2-})c(\text{CO}_3^{2-}). \quad (1)$$

The variation of the observed rate constants with the buffer concentration was greater than expected. The general base catalysis for a related reaction, hydrogen exchange of chloroform, was found to be quite weak.² The carbonate ion is a fairly strong base so that significant hydrolysis of the base to hydroxide ion and hydrogen carbonate ion occurs. Variation of the extent of hydrolysis with the buffer concentration produces a series of solutions where the hydroxide ion concen-

tration decreases along with the buffer concentration. Such buffer failure is usually compensated for by adjusting observed rate constants within a given series of buffer solutions to a common hydroxide ion concentration. This correction is based on the hydroxide ion catalytic coefficient and calculated hydroxide ion concentrations.² When the hydroxide ion catalytic coefficient is unknown, and the measurements aim at obtaining that value, another procedure is suggested wherein modification of the rate law of equation (1) gives equation (2)

$$\frac{k(\text{obs})}{c(\text{HO}^-)} = k(\text{HO}^-) + k(\text{CO}_3^{2-}) \frac{c(\text{CO}_3^{2-})}{c(\text{HO}^-)}, \quad (2)$$

according to which, the catalytic coefficients are obtained by plotting $k(\text{obs})/c(\text{HO}^-)$ against $c(\text{CO}_3^{2-})/c(\text{HO}^-)$. With this treatment, results from buffers with different buffer ratios should fall in the same straight line.

Hydroxide ion concentrations of the buffer solutions were calculated from the stoichiometric

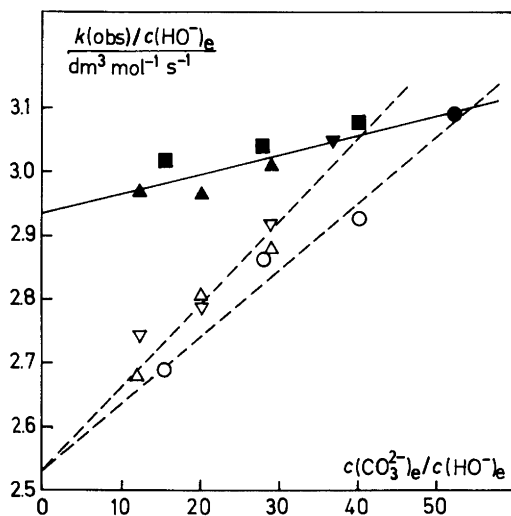


Fig. 1. Presentation of the rate constants for detritiation of CTBr_2Cl in $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ buffer solutions at 25°C . All concentrations are calculated equilibrium concentrations. Ionic strength was maintained at $0.100 \text{ mol dm}^{-3}$ by addition of different electrolytes (buffer ratio 0.200: ● no added electrolyte, ■ Na_2SO_4 , ○ NaCl and buffer ratio 0.125: ▼ no added electrolyte, ▲ Na_2SO_4 , ▽ NaCl , △ NaClO_4).

concentrations of buffer components and the concentration basicity constant of carbonate ion. Thermodynamic dissociation constant of hydrogen carbonate ion, $\text{p}K_a(\text{HCO}_3^-) = 10.329$,⁷ of water, $\text{p}K_w = 13.9965$ and ionic activity coefficients recommended by Bates⁸ were used for this purpose.

The modified rate law (2) was applied to the rate constants for detritiation of CTBr_2Cl and the results are presented in Fig. 1. When constant ionic strength was maintained by addition of sodium chloride, the electrolyte generally used for this purpose, separate plots for buffers with different buffer ratio were obtained. The plots had the same intercept $2.53(5) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, but the slopes showed an increase when the buffer ratio was decreased. With sodium perchlorate as the added electrolyte, similar rates were observed as with sodium chloride.

The behavior expected in buffers with different buffer ratios was achieved when sodium sulfate was used to maintain the desired ionic strength. All the points fell in the same straight line and

gave considerably smaller values for the carbonate ion and higher for the hydroxide ion catalytic coefficient, $k(\text{HO}^-) = 2.94(2) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, than with electrolytes with monovalent anions.

The observed discrepancy is suggested as being produced by the change in the sodium cation concentration when the buffer components are replaced by other salts. The buffer solutions used in these experiments were rather basic, sodium carbonate being the major buffer component. When this was replaced with sodium salts of monovalent anions, the sodium cation concentration changed from $0.0680 \text{ mol dm}^{-3}$ ($\text{BR} = 0.125$) or $0.0688 \text{ mol dm}^{-3}$ ($\text{BR} = 0.200$) in the most concentrated buffer solution, to $0.100 \text{ mol dm}^{-3}$ at the intercept. When a divalent salt, sodium sulfate, was used as the compensating electrolyte, the sodium ion concentration at the intercept was $0.0667 \text{ mol dm}^{-3}$. In the latter case, both ionic strength and sodium ion concentration remained practically constant through the whole series of diluted buffer solutions.

The possible salt effect on the isotope exchange reaction itself was examined by measuring the rate of detritiation of CTBr_2Cl in dilute sodium hydroxide solutions. The second order rate constant showed a slight dependence on the sodium ion concentration, changing from $3.039(14) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in $c(\text{Na}^+) = 0.002 \text{ mol dm}^{-3}$ to $2.831(10) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in $c(\text{Na}^+) = 0.100 \text{ mol dm}^{-3}$, where the increase in the Na^+ concentration was due to addition of sodium chloride. This effect was smaller than that observed in carbonate buffer solutions. Additional salt effects must have operated in the present case.

Specific interactions between ions of opposite sign, sodium cation and anions in the acid-base equilibrium in carbonate buffers, can be assumed to change along with the concentrations of sodium ion.⁹ This changes the concentration basicity constant of carbonate ion used in the calculations of hydroxide ion concentrations. A recalculation of basicity constant, which is assumed to change by some 10% when going from a buffer with no added electrolyte to wholly sodium chloride solution, at the intercept gives hydroxide ion concentrations which make the results match those with divalent salts.

In the present case, the value for the hydroxide ion catalytic coefficient obtained as the intercept, when sodium sulfate was used to maintain the ionic strength, was in accord with that measured

in sodium hydroxide solutions. However, it is suggested that in experiments in hydrogen carbonate/carbonate buffer solutions, the ionic strength be kept constant with an appropriate combination of monovalent and divalent salts.

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