The Carbonic Acid Dehydration and its Activation Energy

POUL ERIK SØRENSEN* and ARNE JENSEN

The Royal Danish School of Pharmacy, Chemical Laboratories A and D, DK-2100 Copenhagen Ø, Denmark

Extensive experimental work has been carried out on the kinetics of the CO$_2$–H$_2$O-system since the work of Faurskov 1 1924. However, several problems concerning, for example, temperature dependence of the reaction rates and catalysis of the reactions still exist.

By mixing equal volumes of 0.02 M NaHCO$_3$ and 0.01 M HCl in a Durum-Gibson stopped-flow spectrophotometer ** we have examined the dehydration of H$_2$CO$_3$ in a wide temperature range (2–45°C) and the activation energy is calculated. Bromophenol blue was used as an indicator. The theory of Brinkman et al. 1 is used to interpret the plots of pH versus time obtained. Using the initial concentrations of the reactants mentioned above, the integrated rate expression *** approximates:

$$k_{dch} = 2.303 \times 1.06 \times \frac{pH_2 - pH_1}{t_2 - t_1}$$

Fig. 1 shows a trace of percent transmittance versus time, directly photographed from the storage oscilloscope screen.

Fig. 2 shows the curve in Fig. 1 transformed to a plot of pH versus time. Approximately, this is seen to be a straight line in accordance to first order kinetics. $k_{dch}$ is calculated from the slope of the line to 62 sec$^{-1}$ (34.8°C). The slight curvature may be due to hydrogen ion catalysis; cf. three last paragraphs.

Fig. 3 shows the Arrhenius plot calculated from Table 1 and compared with the results of other authors. $E_A$ is cal-

---

* Present address: Chemistry Department A, The Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark.
** Durum Instrument Corporation, 3950 Fabian Way, Palo Alto, California 94303, U.S.A.
*** $k_{dch}$ in Table 1 is calculated from the expression shown which, however, has been multiplied by 1.13 due to the spectrophotometric properties of the indicator used.

---


Received May 4, 1970.

Acta Chem. Scand. 24 (1970) No. 4
Fig. 1. Transmittance-time plot directly photographed from the oscilloscope screen. Temperature: 34.8°C. 1 unit on the time axis = 0.02 sec.

Fig. 2. The curve shown on Fig. 1 transformed to a pH-time plot.

Fig. 3. Arrhenius plot from the results of the present investigation and from those of other authors. ● Present investigation. △ Roughton⁵ (E_A calculated to 16.5 kcal/mol). ○ Scheurer et al.⁴ (Only a few values from this work are included here) (E_A calculated to 16.1 kcal/mol). ▲ Magid and Turbeck⁴ (E_A calculated to 14.6 kcal/mol). ■ Sirs⁶ (E_A calculated to 16.5 kcal/mol). ○ Dalziel⁷ (Only a few values from this work are included here) (E_A calculated to 16.9 kcal/mol). (1) Ho and Sturtevant.② (2) Eigen et al.⁴ (3) Gibbons and Edsall.① (4) Saal.① (5) Meier and Schwarzenbach.② (6) Gibson and Roughton.③ (7) Brinkman et al.⁴ (8) Faurholt.①

*Acta Chem. Scand. 24 (1970) No. 4*
culated from our experiments to be 15.1 kcal/mol by a least squares method, but a slight temperature dependence is observed. $E_A$ changes from 13.1 kcal/mol at the low temperatures, to 16.5 kcal/mol at the high temperatures. This behaviour has not been reported before and could be accounted for by a possible temperature drift at temperatures differing from room temperature. However, since such a drift would cause S-formed Arrhenius plots and since the reproducibility of the measurements of $k_{diss}$ is within ±4% in the whole temperature range, this source of error can be disregarded. A corresponding change in $E_A$ of the reverse reaction studied here is found by Pinesset et al.\(^{14}\) ($E_A=19.0$ kcal/mol (0°C), $E_A=10.8$ kcal/mol (38°C)) and Maren\(^{12}\) ($E_A=14$ kcal/mol (1–8°C), $E_A=7$ kcal/mol (25–37°C)). The results of the works of these authors and of the present paper do not agree with those of Magid and Turbeck,\(^{5}\) who find both $E_A$ values independent of temperature. It is very likely that at least one of the $E_A$-values in question changes with temperature because of the considerable temperature dependence of $\Delta H$ of the process. Roughton\(^{3}\) found that $\Delta H$ changes from 2.9 kcal/mol at 0°C to 0.5 kcal/mol at 37°C.

Another problem concerning the dehydration process is the disagreement between different authors' determinations of $k_{diss}$ cf. Fig. 3. The fact that the lowest values normally originate from experiments at pH 7–8 and the highest values from experiments at pH 3–5 suggests that $k_{diss}$ depends on pH. This as well as the deviation from linearity in Fig. 2 could be due to a slight hydrogen ion catalysis, although this phenomenon, according to our knowledge, has been reported only once before. Koefoed and Engel\(^{14}\) give data for the catalytic constant and simultaneously treat the possibility of catalysis of the process by means of the assumption of polymeric forms of $H_2CO_3$ as earlier pointed out by Meier and Schwarzenbach.\(^{14}\) The mechanisms connected with this postulated phenomenon have not yet been satisfactorily elucidated. Furthermore, the possibility of the existence of consecutive reactions of the type $H_2CO_3\rightarrow H_2CO_3+H_2O\rightarrow CO_2+2H_2O$ has not been taken into account. The orthocarbonic acid, $H_2CO_4$, may be formed to a certain degree under the present experimental conditions, i.e. $HCO_3^-+H_2O\rightarrow CO_3^{2-}+H_2O$. Such reactions have not been dealt with before and the experimental data of the present work do not allow definite conclusions to be drawn about this possibility.

Apparently, the dehydration of carbonic acid is not as simple as usually assumed, and the deviation from linearity in the Arrhenius plot could be due to this.

Acknowledgement. The authors are indebted to Professor Carl Faurholt for valuable discussions.


Received March 25, 1970.