[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF COLORADO]

The Ionization Constant and Rate of Hydrolysis of Succinimide

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The ionization constant of succinimide has been determined potentiometrically between 0 and 35°. At 25°, $K = 2.38 \times 10^{-10}$, $\Delta H^0 = 6510$, $\Delta C_p = -160$. Our value of K is about ten times that reported previously. The rate of hydrolysis has been measured over a narrow range of conditions.

Recently we had occasion to titrate solutions containing succinimide, $(CH_2CO)_2NH$, using a glass electrode pH meter, and obtained curves which were inconsistent with the value of 3×10^{-11} reported by Wood[2] for the ionization constant of this acid. For example, the pH of half neutralization of succinimide by sodium hydroxide was 9.45 in a solution of ionic strength 0.01, and 9.50 in one of ionic strength 0.2. Wood determined the ionization constant by a catalytic method. Since exact data over a range of temperatures for acids of this order of weakness are few, it seemed appropriate to study the ionization of succinimide by an electromotive force method, using a cell without liquid junction.

Preliminary tests showed that the hydrogen electrode could not be used in succinimide solutions, for hydrogen reduces succinimide in presence of platinum black. The silver–silver chloride and mercury–mercurous chloride electrodes were also useless, for succinimide solutions dissolve silver chloride and calomel appreciably, presumably forming complexes. A cell which was found to be satisfactory, and was used for all the measurements, was

Ag, AgBr | KBr (M_1), HS (M_2), NaS (M_3) | glass electrode

where "HS" stands for succinimide and NaS for its sodium salt. The molal concentrations M_1, M_2 and M_3 were in the ratio 10:2:1 for most of the tests.

The e.m.f. of this cell is given by the equation

$$E = E^0 + \frac{RT}{F} \ln a_{H^+} + a_{Br^-} = E^0 + \frac{RT}{F} \ln \frac{a_{HS}a_{Br^-}}{a_{S^-}} + \frac{RT}{F} \ln K \quad (1)$$

where K is the ionization constant of the acid and the a's are activities. ln K is found by plotting $E' = \left(E - E^0 - \frac{RT}{F} \ln \frac{M_{HS}M_{Br^-}}{M_{S^-}}\right)$ against the ionic strength and extrapolating to zero ionic strength.

Experimental

The measuring circuit used a Leeds and Northrup student potentiometer and thermionic amplifier. The potentiometer was calibrated and found to be linear within 0.1 millivolt over the entire range used. Potentials were measured to ±0.1-0.2 millivolt; greater accuracy was unnecessary, owing to fluctuations and the uncertainties caused by the hydrolysis of succinimide (see below). Temperatures were controlled thermostatically to ±0.01° or better.

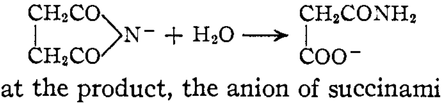
A Beckman Type E glass electrode was used, since this has a quite negligible sodium ion error under the conditions used. The standard potential, E^0, was determined before and after each run by introducing 0.00780 molar hydrobromic acid and measuring the e.m.f.; the activity coefficient at the different temperatures used was taken from the data of Harned.[3] Now the makers do not recommend the Type E glass for use in acid solutions, because of the deterioration which occurs on prolonged contact. It was therefore desirable to test the validity of the hydrobromic acid calibration. This was done at 0, 25 and 35° by measuring E with solutions containing boric acid, sodium borate and potassium bromide, plotting E' against ionic strength, and comparing the extrapolated value of E' with that calculated from the very accurate ionization constants of boric acid determined by Owen.[4] Agreement was within experimental error: E' (extrapolated) − E' (calculated) was 0.3 mv. at 35°, 0.0 mv. at 25°, −0.2 mv. at 0°.

At 18° and above, succinimide hydrolyzes at an appreciable rate to form succinamic and succinic acids. Before measuring electromotive force, therefore, solutions containing potassium bromide and sodium hydroxide, but no succinimide, were prepared and allowed to come to temperature equilibrium with the thermostat. A weighed amount of solid succinimide was then introduced and the time noted. The solution was transferred to the cell and the electromotive force measured at intervals for 20–30 minutes after mixing; the data were extrapolated to zero time, and this extrapolated e.m.f. was used in calculating E'.

The succinimide was a very pure product kindly supplied by Thomas D. Waugh of Arapahoe Chemicals, Inc., and was used without further purification. It was non-hygroscopic and melted sharply at 124°. The pH of an 0.10 molal solution was 5.50 at 20°; potentiometric titration revealed no trace of an acid stronger than succinimide. The sodium hydroxide solution used for the partial neutralization of the succinimide was prepared "carbonate-free" in the usual way; by titration, its carbonate content was less than 0.5% of the hydroxide content. Freshly boiled distilled water was used to prepare all the solutions. In calculating M_{HS} and M_{S^-} from the quantities of succinimide and sodium hydroxide taken, allowance was made for the hydrolysis of S^- to give HS + OH^-.

Results

(a) Rate of Irreversible Hydrolysis.—Measurements of the hydrolysis rate were made, but they were only incidental to the main work of determining ionization constants and were not very accurate. Let us assume that the irreversible hydrolytic reaction is



$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>N^- + H_2O \longrightarrow \begin{matrix} CH_2CONH_2 \\ | \\ COO^- \end{matrix}$$

and that the product, the anion of succinamic acid, is a much weaker base than the anion of succinimide. It can then be shown that

$$d\,pH/dt = -(k/2.303) \quad (2)$$

where k is the velocity constant for this reaction.

Our observations are summarized in Table I. They lead to the conclusion that the reaction is in part base-catalyzed and has an activation energy of 20.5 ± 0.5 kcal./mole.

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[1] Based on a thesis submitted by A. A. Schilt in partial fulfillment of the requirements for the degree of Master of Science at the University of Colorado.

[2] J. K. Wood, *J. Chem. Soc.*, **89**, 1831 (1906).

[3] H. S. Harned, A. S. Keston and J. G. Donelson, THIS JOURNAL, **58**, 989 (1936).

[4] B. B. Owen, *ibid.*, **56**, 1695, 2785 (1934).

TABLE I

RATE OF IRREVERSIBLE HYDROLYSIS OF SUCCINIMIDE

Temp., °C.	$[HS]/[S^-]$	dE/dt, mv./min.	$d\,pH/dt$	k, min.$^{-1}$ $\times 10^3$
35	2	−0.15	−0.00245	5.7
30	2	− .08	− .00133	3.1
25	2	− .045	− .00077	1.8
	0.5	− .060	− .00103	2.4
18	2	− .025	− .00043	0.8
	0.5	− .020	− .00034	1.0

(b) Ionization Constants.—Figure 1 shows the values of E' (corrected for hydrolysis) plotted against ionic strength for the six temperatures used. It will be noted that in certain cases, $HS:S^-$ ratios other than the standard ratio of 2:1 were used. In Fig. 2, the logarithm of the ionization constant is plotted against the temperature.

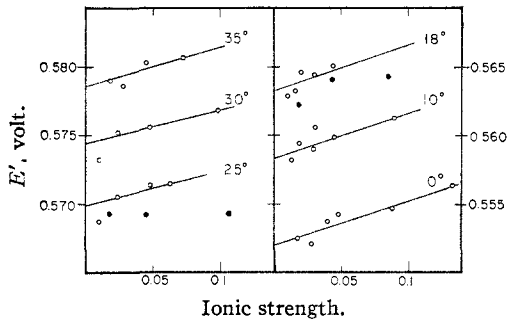

Fig. 1.—Open circles, $HS:S^-$ = 2:1; filled circles, $HS:S^-$ = 1:2.

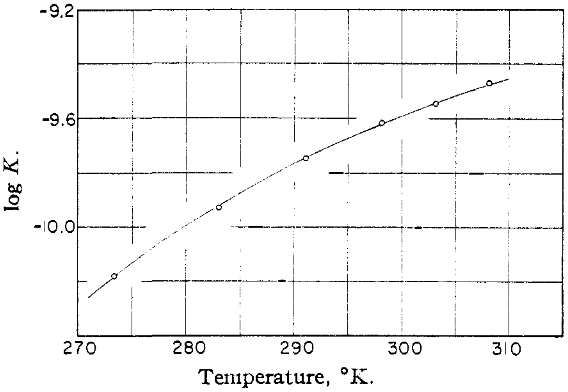

Fig. 2.

Here the experimental points are shown as circles, and the line is a plot of the equation

$$\log K = -36.92 + 0.167\,T - 2.53 \times 10^{-4}\,T^2 \quad (3)$$

This equation represents the data to within the experimental error, which is about ±0.01 in log K; the error is somewhat greater at 35° than at the lower temperatures. The following thermodynamic constants follow from this equation at T = 298.1° K.

$K = 2.38 \times 10^{-10}$

$\Delta F^0 = 13130 \pm 15$ cal. mole^{-1}, $\Delta S^0 = -22.0 \pm 0.5$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^0 = 6510 \pm 100$ cal. mole^{-1}, $\Delta C_p = -160 \pm 50$ cal. deg.$^{-1}$ mole^{-1}

In the empirical equation of Harned and Embree,[5] $\log K - \log K_{max} = -p(T - \theta)^2$, θ = 330.0° K., $K_{max} = 4.4 \times 10^{-9}$. The constant p is 2.53×10^{-4}, or five times Harned's constant of 5×10^{-5}.

Discussion

We have used a simple quadratic to express log K in terms of T, in spite of its theoretical inadequacy, because it fits the data well and the accuracy of the data is not sufficient to warrant more elaborate treatment. Comparing our results with the compilations of Everett and Wynne-Jones[6] and of Harned,[7] the most striking feature is the large value of $-\Delta C_p$, which is two or three times the largest value there reported.

This quantity, however, results from a second differentiation and is very susceptible to experimental error. We have attempted to estimate a minimum value of $-\Delta C_p$ by assuming a very unfavorable and unlikely combination of errors in E'. The probable error in E' is 0.5 mv. at 0°, rising to 1.0 mv. at 35° on account of irreversible hydrolysis. An error of 0.5 mv. causes an error of 0.01 in log K. If we displace our interpolated log K-temperature curve (Fig. 2) upwards by 0.01 at 0° and by 0.02 at 35°, and downwards by 0.025 at 18°, we calculate $\Delta C_p = -50$ cal. deg.$^{-1}$ mole^{-1}. It is most unlikely that ΔC_p is any less negative than this.

A value of $\Delta C_p = -110$ cal. deg.$^{-1}$ mole^{-1} has just been reported for sulfamic acid.[8] Values around −40 cal. deg.$^{-1}$ mole^{-1} are found for acids containing polar substituents, such as salicylic, lactic and glycollic.[6] A high negative ΔC_p may be connected with the close proximity of polar groups to the ionizing hydrogen. Succinimide is the first acid of its type to be studied in this way, and a study of other uncharged acids in which the proton is attached to a nitrogen atom may help to elucidate the effect of constitution upon acidic properties.

It is a pleasure to acknowledge the help of Arapahoe Chemicals, Inc., Boulder, Colorado, both in supplying the material and in suggesting the problem originally.

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[5] H. S. Harned and N. D. Embree, THIS JOURNAL, **56**, 1050 (1934).

[6] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

[7] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Chapter 15, 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950.

[8] E. J. King and G. W. King, THIS JOURNAL, **74**, 1212 (1952).