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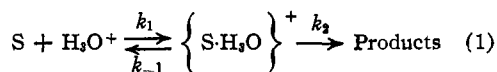
The Inversion of Sucrose

BY PAUL M. LEININGER¹ AND MARTIN KILPATRICK

In a paper on electrolyte effects in reactions between a non-electrolyte and the hydrogen ion² two typical examples were given, representative of electrolyte effects in (1) reactions showing specific catalysis by the hydrogen ion, and (2) reactions showing acid catalysis in the general sense. This classification has been clarified by experiments in solutions of heavy water,³ and by Pedersen's analysis of prototropic reactions.⁴

From an examination of the electrolyte effects it appeared that the inversion of sucrose and the hydrolysis of the acetals should be considered purely as catalysis by the hydrogen ion. Evidence of catalytic effects of acid molecules has been advanced by Hammett and Paul,⁵ and by Gross, Steiner and Suess.⁶ Experiments on the inversion of sucrose in acetate-acetic acid buffer solutions have shown, however, there is no detectable catalytic effect of the molecules of such a weak acid as acetic.⁷

If we are dealing with a case of specific hydrogen-ion catalysis, we can for aqueous solutions postulate the equilibrium



where $k_2 \ll k_{-1}$ and the equilibrium concentration is maintained at all times. The velocity constant is given by

$$k = \frac{k_1}{k_{-1}} k_2 = K k_2 \quad (2)$$

Now K will vary with the electrolyte concentration, and the resulting change in the concentration of the collision complex will cause a change in the measured velocity constant k . These changes have been observed for the hydrolysis of the acetals and for the inversion of sucrose, but even in dilute solution they seem larger than one would expect, by analogy, from an examination of the change, with electrolyte concentration, of the dis-

sociation constant of anilinium or *o*-chloroanilinium ion.^{8,9}

Pedersen determined these two equilibrium constants over a convenient range of temperature, and found no great change in the heat of dissociation (ΔH) with temperature, in contrast to the marked variation of the heat of dissociation with temperature for uncharged acids. By analogy it might be expected that for reactions between a non-electrolyte and an ion, as represented by equation (1), there would be little change with temperature in E_A , the heat of activation computed from the integrated form of the Arrhenius equation

$$E_A = \frac{2.303 RT_1 T_2}{T_1 - T_2} \log \frac{k_{T_1}}{k_{T_2}} \quad (3)$$

where k_{T_1} and k_{T_2} are the velocity constants at temperatures T_1 and T_2 , respectively. This seems to be the case for the hydrolysis of diethyl acetal.²

An examination of the extensive literature on sucrose inversion (on which some excellent experimental work has been done) yields a number of surprises. For example, in a recent number of THIS JOURNAL we have "The activation energy of 25.7 \pm 0.05 kcal. found in the present work on sucrose is in good agreement with 25.83 and 25.8 kcal. obtained by others."¹⁰ The statement \pm 0.05 kcal. seems hardly justified, since calculation of E_A by equation (3) over the three temperature intervals shows a variation of approximately \pm 1000 cal. In the same number a communication on the present study¹¹ calls attention to the fact that the energy of activation varies both with temperature and with concentration of hydrochloric acid. The effect of temperature was reported by Moelwyn-Hughes,¹² who showed that some of the earlier work also revealed a decrease in the activation energy with rise in temperature. The effect of electrolyte concentration on E_A calculated by a method similar to equation (3) has been independently reported by Duboux,¹³

(1) E. I. du Pont de Nemours and Company Fellow, 1938.
 (2) Riesch and Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935).
 (3) For references and discussion see Bonhoeffer, *Trans. Faraday Soc.*, **34**, 252 (1938).
 (4) Pedersen, *ibid.*, **34**, 237 (1938).
 (5) Hammett and Paul, *THIS JOURNAL*, **56**, 830 (1934).
 (6) Gross, Steiner and Suess, *Trans. Faraday Soc.*, **32**, 883 (1936).
 (7) These experiments were carried out in this Laboratory in 1929 by M. L. Kilpatrick.

(8) Pedersen, *Kgl. Danske Videnskab, selskab, Math.-fys. Medd.*, **14**, No. 9 (1937).
 (9) Pedersen, *ibid.*, **15**, No. 3 (1937).
 (10) Heidt and Purves, *THIS JOURNAL*, **60**, 1206 (1938).
 (11) Leininger and Kilpatrick, *ibid.*, **60**, 1268 (1938).
 (12) Moelwyn-Hughes, *Z. physik. Chem.*, **B26**, 281 (1934).
 (13) Duboux, *Helv. Chim. Acta*, **21**, 236 (1938).

but Duboux seems unaware of the decrease in energy of activation with increasing temperature reported by Moelwyn-Hughes. Quite recently Pearce and Thomas¹⁴ determined the velocity constants for the inversion of sucrose in 1 molar hydrochloric acid solution in the presence of various salts, and concluded that the heat of activation was practically constant and independent of the nature of the salt. Finally, an examination of the data in the literature indicates that the velocity constant and the energy of activation are also dependent on the initial sucrose concentration.

The present paper includes a report of the work with 0.0584 molar sucrose solutions over the temperature range 0–40°, and with concentrations of hydrochloric acid up to four molar. The results obtained indicate that the literature on the sucrose inversion presents a more understandable picture when one considers the variables, electrolyte and sugar concentration, as well as temperature and concentration of catalyst.

Experimental Part

Sucrose.—Merck best reagent sucrose was used. Several duplicate runs were made with Pfanstiehl special sucrose, but no difference in velocity was observed.

Hydrochloric Acid.—Baker c. p. analyzed hydrochloric acid was used. Here again the same results were obtained with solutions prepared from constant-boiling hydrochloric acid.

Sodium Chloride.—Kahlbaum "zur Analyse mit Gartieschein" grade of sodium chloride was used.

Dilatometer.—At 0° the dilatometer used was that described by Kilpatrick,¹⁵ except for runs lasting over two days, where sealed dilatometers were used. At all other temperatures the dilatometers used were similar to those described by Brönsted, Kilpatrick and Kilpatrick.¹⁶

Thermostats.—Water-baths regulated to $\pm 0.005^\circ$ were electrically heated and controlled by relay circuits of radio tube type similar to the one described by Beaver and Beaver.¹⁷ For the experiments at 0°, ice-packed Dewar flasks, kept in a refrigerator room, served as thermostats.

Determination of Temperature.—Temperatures were determined by means of a platinum resistance thermometer, calibrated by the Bureau of Standards, and used in conjunction with a Mueller bridge. Temperature regulation was better than $\pm 0.005^\circ$ at all temperatures with the possible exception of -0.01° for the long time runs. Although the individual temperatures are given only to one hundredth of a degree, the temperature interval was measured to one thousandth of a degree. The maximum possible error in the temperature interval was 0.01° .

Determination of Concentrations.—The sucrose concentration was known to 0.05%. The hydrochloric acid con-

centration was obtained by titration of the reacted mixture. The molarity of the hydrochloric acid was thus determined directly for each solution at the temperature at which the experiment had been carried out. The concentration of hydrochloric acid was known to 0.1%. The validity of the method was established by making a duplicate run with a hydrochloric acid solution made up by weight from constant-boiling acid.

Determination of Rate.—Solutions of sucrose and hydrochloric acid were brought to the temperature of the thermostat. A volume of the sucrose solution sufficient to make the resulting mixture 0.0584 molar with respect to sucrose was then added to the hydrochloric acid which had already been placed in the mixing vessel of the dilatometer. After thoroughly mixing, the solution was sealed off and the rate of contraction noted. At the higher temperatures it was necessary to evacuate the solutions before mixing in order to prevent formation of air bubbles during the course of the run. The reader is referred to an earlier paper¹⁸ for the technique employed at 0°. In the case of the acid-salt mixtures, the sucrose was added to a hydrochloric acid solution in which a definite amount of sodium chloride had been dissolved. The velocity constants were evaluated by Guggenheim's method.¹⁸

Results

The reaction was of the first order over the entire range of temperature and concentration investigated. Scatchard,¹⁹ and Reed and Theriault,²⁰ analyzing the data of Pennyquick,²¹ arrived at similar conclusions.

In Table I are given the values of the observed velocity constant k (the number of moles of sucrose reacting per mole of sucrose per minute) obtained at -0.01° . In this table are also given the values of $k_{\text{H}_2\text{O}^+} = k/C_{\text{H}_2\text{O}^+}$ experimentally determined (column 3), and computed as will be described later (column 4).

TABLE I
ELECTROLYTE EFFECT AT -0.01°

HCl (moles/liter)	10% min. ⁻¹	10% $k_{\text{H}_2\text{O}^+}$ obsd.	10% $k_{\text{H}_2\text{O}^+}$ calcd.
0.5900	0.1024	1.736	1.766
1.049	.2450	2.335	2.275
2.207	.9745	4.416	4.306
2.687	1.504	5.595	5.611
3.172	2.295	7.235	7.331
3.714	3.624	9.758	9.885
4.228	5.307	12.55	13.12
4.695	8.110	17.27	16.98
5.239	11.90	22.71	22.91
5.773	18.30	31.71	30.76

In Table II are listed the values of $k_{\text{H}_2\text{O}^+}$ obtained at temperatures other than zero. The effect of sodium chloride upon $k_{\text{H}_2\text{O}^+}$ is shown by

(14) Pearce and Thomas, *J. Phys. Chem.*, **42**, 455 (1938).

(15) Kilpatrick, *THIS JOURNAL*, **50**, 2891 (1928).

(16) Brönsted, Kilpatrick and Kilpatrick, *ibid.*, **51**, 428 (1929).

(17) Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

(18) Guggenheim, *Phil. Mag.*, **2**, 538-543 (1926).

(19) Scatchard, *THIS JOURNAL*, **48**, 2259 (1926).

(20) Reed and Theriault, *J. Phys. Chem.*, **34**, 950 (1931).

(21) Pennyquick, *THIS JOURNAL*, **48**, 6 (1926).

the experiments marked with an "a" in the table; in all cases the addition of the salt caused an increase in $k_{H_2O^+}$, but in no case was the increase as large as that corresponding to the addition of an equal amount of acid.

TABLE II
SUMMARY OF $k_{H_2O^+}$ VALUES

Temp., °C.	No. of expts.	HCl (moles/liter)	$10^4 k_{H_2O^+}$
10.00	1	1.124	1.305
10.00	2	2.141	2.178
10.00	2	2.997	3.365
10.00	2	3.905	5.350
10.00	2	4.592	7.767
10.00	1	1.122	2.019 ^a
15.00	1	1.124	2.864
15.00	1	1.493	3.445
15.00	2	2.142	4.698
15.00	1	1.120	4.297 ^a
20.00	2	0.9528	5.651
20.00	1	1.123	6.143
20.00	2	1.493	7.271
20.00	2	2.140	9.811
20.00	2	2.999	14.78
20.00	1	1.120	9.127 ^a
25.00	1	0.4767	9.420
25.00	4	.9599	11.77
25.00	1	1.123	12.62
25.00	1	1.493	15.05
25.00	3	2.121	20.00
25.00	2	1.116	18.77 ^a
30.00	1	0.2506	17.41
30.00	1	.4746	19.30
30.00	3	.6517	20.91
30.00	3	.9457	23.85
30.00	1	1.120	25.65
30.00	1	1.488	30.05
35.00	1	0.4767	37.90
35.00	4	.9519	46.68
35.00	1	.9500	44.00 ^b
40.00	2	.2508	67.69
40.00	2	.4741	74.35
40.00	4	.6530	80.16

^a Solution 1.003 molar with respect to added sodium chloride.

^b Sucrose concentration reduced to 0.0146 molar.

Where more than one experiment was carried out at a given temperature and acid concentration, the average deviation of $k_{H_2O^+}$ from the mean was computed; the average of the average deviations for these experiments is 0.3%.

In Fig. 1, $\log k_{H_2O^+}$ for a given concentration of hydrochloric acid is plotted against the reciprocal of the absolute temperature; the curves reading from top to bottom represent acid concentration of 4.592, 2.999, 2.140, 0.9528 and 0.4767 molar. In addition to our own results, we have plotted

results obtained by other workers, as stated in the legend below the figure.

Hitchcock and Dougan²² also used the dilatometric method to study the rate of inversion of sucrose; for solutions containing two grams of sucrose in 100 cc. of solution, their value of $k_{H_2O^+}$ at 25° differs by only 0.4% from ours at an acid concentration of one molar, but at half molar the difference is 1.9%.

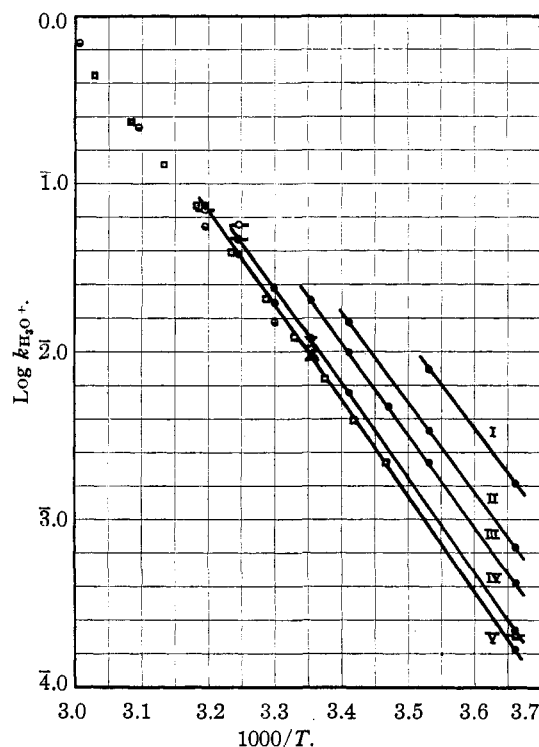


Fig. 1.—Variation of $\log k_{H_2O^+}$ with $1000/T$. Our data sucrose 2 g. per 100 cc. and: I, HCl 4.592 molar; II, HCl 2.999 molar; III, HCl 2.140 molar; IV, HCl 0.9528 molar; V, HCl 0.4767 molar. \square , Moelwyn-Hughes,¹⁸ 5% sucrose, HCl 0.19 molar. \bullet , Heidt and Purves,¹⁰ 0.01 molar sucrose, HCl 0.00965 molar. \square -, Duboux,¹³ sucrose 11.42 g. per 100 cc., HCl 0.4767 molar. ∇ , Sturtevant,²³ sucrose 0.1082 molar, HCl 0.5310 molar; sucrose 0.1152 molar, HCl 0.9059 molar. Δ , Hitchcock and Dougan,²² sucrose 2 g. per 100 cc., HCl 0.486 molar; sucrose 10 g. per 100 cc., HCl 0.486 molar. \circ -, Pennycuik,²¹ sucrose 0.5 molar, HCl 0.507 molar and sucrose 0.5 molar, HCl 0.905 molar (at 35°); sucrose 0.5 molar, HCl 0.02 molar (at 40°).

Tables I and II and Fig. 1 show that at any temperature $k_{H_2O^+}$ is a function of the concentration of hydrochloric acid, increasing with increase in the concentration of acid. At a given temperature, over the range of concentration investi-

gated, the effect may be expressed by the equation

$$\log k_{\text{H}_3\text{O}^+} = \log k^{\circ}_{\text{H}_3\text{O}^+} + \beta C \quad (4)$$

where $k_{\text{H}_3\text{O}^+}$ represents the velocity constant for molar hydrogen ion in a solution C molar in hydrochloric acid. Figure 2 shows the applicability of equation (4) to our data at -0.01° .

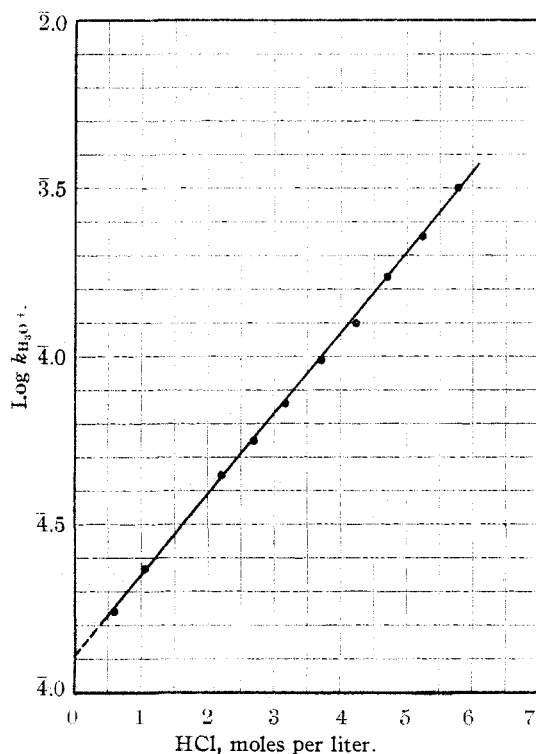


Fig. 2.—Electrolyte effect at -0.01° .

By the method of least squares we obtained the equation

$$\log k_{\text{H}_3\text{O}^+} = 4.1057 + 0.2394 C \quad (\text{at } -0.01^\circ) \quad (4a)$$

valid at -0.01° . The values of $k_{\text{H}_3\text{O}^+}$ (calcd.) given in the fourth column of Table I were computed by equation (4a); the average deviation from the observed value is 2.0%.

Using the polarimetric method, Duboux¹³ recently has measured the rate of inversion of sucrose at 0° over a wide range of concentration of hydrochloric acid. His solutions contained 11.42 g. of sucrose in 100 cc. of solution, as compared to our 2.00 g. Upon recomputing his values on the basis of molarity, and applying to the recomputed values the method of least squares, we obtained

$$\log k_{\text{H}_3\text{O}^+} = 4.1898 + 0.2392 C \quad (\text{Duboux, } 0^\circ) \quad (4a')$$

The agreement between the two values of β is excellent. The difference in the value of the in-

tercept can be attributed to the difference in the sucrose concentration. That increase in concentration of sucrose causes an increase in $k_{\text{H}_3\text{O}^+}$ may also be seen in Table II. For a solution 0.95 M in hydrochloric acid, and containing 2 g. of sucrose per 100 cc., $k_{\text{H}_3\text{O}^+}$ (observed) is 46.68×10^{-3} at 35° , while for a solution containing 0.5 g. per 100 cc., $k_{\text{H}_3\text{O}^+}$ (observed) is 44.00×10^{-3} .

The following equations, analogous to (4a), express the effect of acid concentration upon $k_{\text{H}_3\text{O}^+}$ at the other temperatures investigated.

$$\log k_{\text{H}_3\text{O}^+} = 4.8660 + 0.2230 C \quad (\text{at } 10.00^\circ) \quad (4b)$$

$$\log k_{\text{H}_3\text{O}^+} = 3.2198 + .2116 C \quad (\text{at } 15.00^\circ) \quad (4c)$$

$$\log k_{\text{H}_3\text{O}^+} = 3.5587 + .2045 C \quad (\text{at } 20.00^\circ) \quad (4d)$$

$$\log k_{\text{H}_3\text{O}^+} = 3.8793 + .1992 C \quad (\text{at } 25.00^\circ) \quad (4e)$$

$$\log k_{\text{H}_3\text{O}^+} = 2.1932 + .1922 C \quad (\text{at } 30.00^\circ) \quad (4f)$$

$$\log k_{\text{H}_3\text{O}^+} = 2.4902 + .1846 C \quad (\text{at } 35.00^\circ) \quad (4g)$$

$$\log k_{\text{H}_3\text{O}^+} = 2.7857 + .1806 C \quad (\text{at } 40.00^\circ) \quad (4h)$$

These equations were derived from the data given in Table II; they represent the lines obtained by plotting $\log k_{\text{H}_3\text{O}^+}$ against the acid concentration, at the temperature in question.

It was hoped that a quantitative expression for the effect of sucrose concentration upon $k_{\text{H}_3\text{O}^+}$ might also be formulated from the existing data. While this has not proved possible, there is considerable experimental evidence of the existence of the effect. In addition to the evidence already cited, we mention the following. Hitchcock and Dougan,²² using the dilatometric method at 25° , noted that at constant acid concentration an increase in the concentration of sucrose caused an increase in $k_{\text{H}_3\text{O}^+}$. The same thing is shown by a comparison of $k_{\text{H}_3\text{O}^+}$ obtained by Sturtevant²³ at 25° , using the calorimetric method, with $k_{\text{H}_3\text{O}^+}$ computed from our equation (4e); by a comparison of the values of $k_{\text{H}_3\text{O}^+}$ obtained by Heidt and Purves¹⁰ at 30 and 40° , using the copper reduction method, with values computed from our equations (4f) and (4h); by a comparison of the values of $k_{\text{H}_3\text{O}^+}$ of Pennycuick²¹ at 35 and 40° , obtained by the polarimetric method, with values computed from our equations (4g) and (4h); and by a comparison of the values of $k_{\text{H}_3\text{O}^+}$ of Moelwyn-Hughes¹² obtained polarimetrically at 15.45 and 19.40° , with our values, after making a correction for the difference in temperature. From all the work examined, with the sole exception of that of Pearce and Thomas,¹⁴ the same conclusion was drawn.

In Table III is given the Arrhenius energy of activation, E_A , computed by means of equation

(23) Sturtevant, *THIS JOURNAL*, **59**, 1528 (1937).

TABLE III
ELECTROLYTE EFFECT ON ENERGY OF ACTIVATION

Temp. range, °C.	HCl (moles/liter)	k_{T_2}/k_{T_1}	E_A , cal.
-0.01 to 10.00	1.124	5.506	26,180
- .01 to 10.00	2.141	5.246	25,440
- .01 to 10.00	2.997	5.055	24,870
- .01 to 10.00	3.905	4.872	24,310
- .01 to 10.00	4.592	4.842	24,210 ^b
- .01 to 20.00	0.9528	26.20	25,960
- .01 to 20.00	1.123	25.93	25,880
- .01 to 20.00	1.493	25.03	25,600
- .01 to 20.00	2.140	23.64	25,150
- .01 to 20.00	2.999	22.18	24,640
10.00 to 20.00	1.124	4.707	25,550
10.00 to 20.00	2.141	4.505	24,820
10.00 to 20.00	2.998	4.392	24,400
10.00 to 20.00	1.121	4.521	24,880 ^a
15.00 to 25.00	1.124	4.406	25,310
15.00 to 25.00	1.493	4.369	25,170
15.00 to 25.00	2.132	4.257	24,730
15.00 to 25.00	1.118	4.368	25,160 ^a
20.00 to 30.00	0.9493	4.220	25,420
20.00 to 30.00	1.122	4.175	25,230
20.00 to 30.00	1.491	4.133	25,060
25.00 to 35.00	0.4767	4.023	25,410
25.00 to 35.00	.9559	3.966	25,150
30.00 to 40.00	.2507	3.888	25,610
30.00 to 40.00	.4744	3.852	25,440
30.00 to 40.00	.6524	3.834	25,350

^a Solution 1.003 molar with respect to sodium chloride.

^b In ref. 11, 4.842 given for hydrochloric acid molarity should be 4.592.

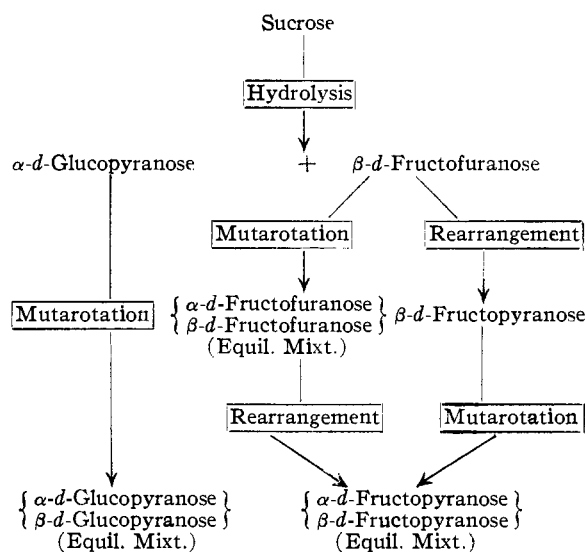
(3) from the values of $k_{H_3O^+}$ listed in Table II, and from values calculated by equation (4a). At this point it is desirable to discuss the probable accuracy of the determination of E_A . For the temperature interval 20 to 30°, errors of 0.3% in the values of $k_{H_3O^+}$, in opposite directions, would result in an error of 104 cal. in E_A at 25°. Errors of 0.1% in the values of the acid concentration, taken in opposite directions, would affect E_A to the extent of 33 cal. Since the effects of possible errors in temperature, time and concentration of sucrose are negligible, the maximum error in E_A determined from velocity constants at temperatures other than -0.01° may be taken as ± 150 cal. In similar fashion, a possible error of 2.0% in $k_{H_3O^+}$ at -0.01° yields ± 400 cal. for E_A at 5°, and ± 250 cal. at 10°.

The two values marked with an "a" in the last column of Table III show a diminution of E_A in the presence of sodium chloride; the effect is, however, less than that of an equal amount of acid. Duboux¹³ has made similar observations. On the other hand, Pearce and Thomas¹⁴ report no appreciable effect of salt upon E_A . An exami-

nation of the results of these authors, however, reveals a distinct trend in the values of E_A in the solutions of barium chloride, which leads us to the conclusion that E_A does decrease with increasing electrolyte concentration.

In view of the change in E_A with electrolyte concentration and temperature reported in Table III, it seems advisable to consider the possibility of reactions other than hydrolysis affecting the measured rate and to reconsider the validity of the dilatometric method.

The following scheme represents the probable reactions involved.



The mutarotation of α -D-glucopyranose is approximately fifty times faster than the observed rate under our experimental conditions.²⁴⁻²⁶ The mutarotation of β -D-fructopyranose is faster than that of α -D-glucopyranose.^{25,27,28} No rate data are available for hydrochloric acid solutions on the other processes indicated. For enzymes, however, the rate of change of β -D-fructofuranose to equilibrium fructose has been shown to be three times faster than the mutarotation of β -D-fructopyranose.²⁹ The possibility of acid decomposition of the equilibrium mixtures of glucose and fructose is ruled out. For the conditions investigated the acid decomposition of the fructose equilibrium mixture is four powers of ten slower

(24) Hudson, THIS JOURNAL, 29, 1571 (1907).

(25) Nelson and Beegle, *ibid.*, 41, 559 (1919).

(26) Brønsted and Guggenheim, *ibid.*, 49, 2554 (1927).

(27) Riiber and Esp. *Ber.*, 58, 737 (1925).

(28) Hudson, THIS JOURNAL, 30, 1564 (1908); *ibid.*, 31, 66 and 655 (1909).

(29) Bailey and Hopkins, *Biochem. J.*, 27, 1957 (1933).

than the observed rate.³⁰ The glucose portion of invert sugar is less readily attacked by acids than the fructose.³¹ Although complete rate data are not available for all processes, the fact that the reaction was of the first order in all experiments indicates that the measured reaction is simple and free from complications.

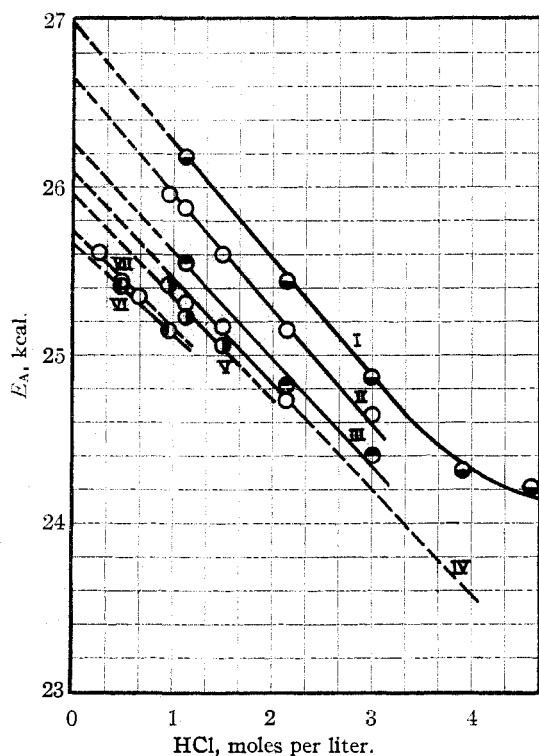


Fig. 3.—Electrolyte effect on energy of activation: I, -0.01 to 10.00° ; II, -0.01 to 20.00° ; III, 10.00 to 20.00° ; IV, 15.00 to 25.00° ; V, 20.00 to 30.00° ; VI, 25.00 to 35.00° ; VII, 30.00 to 40.00° .

In regard to the dilatometric method the volume change for the mutarotation of α -*D*-glucopyranose is approximately 3% of the measured change and in the opposite direction.^{26,32} For β -*D*-fructopyranose the volume change is also an expansion amounting to 23% of the measured volume change.²⁷ Since these processes are rapid the volume change may still be proportional to the percentage of sucrose reacted. The validity of the dilatometric method rests upon the comparison of this method with the polarimetric method²² and the fact that the dilatometric, polarimetric, calorimetric²³ and copper reduction methods¹⁰ all yield first order constants which

(30) Mathews and Jackson, *Bur. Standards J. Research*, **11**, 619 (1933).

(31) Rischbieth, *Ber.*, **20**, 1773 (1887).

(32) Riiber, *ibid.*, **87**, 1599 (1924).

are in good agreement when electrolyte and sucrose effects are taken into consideration. Finally, a comparison of the electrolyte effect of hydrochloric acid at 0° (see Table I and equation 4a) obtained by the dilatometric method is in excellent agreement with results obtained by the polarimetric method (see equation 4a').¹³

In Fig. 3 the value of E_A at the mid-point of the temperature interval is plotted against the concentration of hydrochloric acid. Reading from the top down, the curves represent the effect of acid concentration upon E_A at temperatures of 5, 10, 15, 20, 25, 35 and 30° , respectively. It is evident that E_A decreases with rise in temperature up to 30° , and that E_A decreases with increase in acid concentration. For concentrations not greater than four molar, E_A appears to be a linear function of the acid concentration; at the higher temperatures, however, E_A could not be determined over a wide range of concentration.

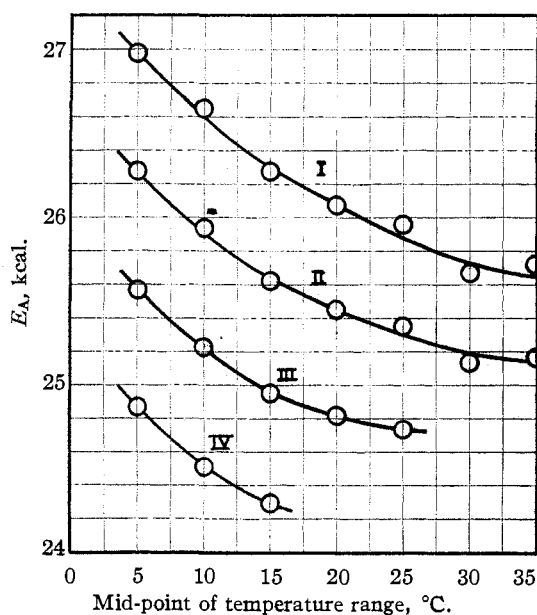


Fig. 4.—Effect of temperature on energy of activation: I, 0 molar HCl; II, 1 molar HCl; III, 2 molar HCl; IV, 3 molar HCl.

Figure 4 and Table IV illustrate the variation of E_A with temperature. The four curves represent E_A at acid concentrations of 0, 1, 2 and 3 molar, respectively, as read off from the lines in Fig. 3.

The graphically determined values of E_A at zero acid concentration were confirmed by computation, by means of equation 3, from the intercepts of equations (4a), (4b), etc. The figure

TABLE IV
TEMPERATURE EFFECT ON THE ENERGY OF ACTIVATION

Temp. range, °C.	E_A , cal.			
	0 molar HCl	1 molar HCl	2 molar HCl	3 molar HCl
-0.01 to 10.00	26,980	26,280	25,570	24,870
-.01 to 20.00	26,650	25,940	25,230	24,510
10.00 to 20.00	26,280	25,620	24,950	24,290
15.00 to 25.00	26,080	25,450	24,820	...
20.00 to 30.00	25,960	25,350	24,740	...
25.00 to 35.00	25,670	25,130
30.00 to 40.00	25,720	25,160

shows E_A to decrease with increase in temperature, the rate of change, $\Delta E_A/\Delta T$, being approximately -70 cal. per degree at 10° and smaller at higher temperatures.

It already has been mentioned that a decrease in E_A with increase in temperature was observed previously by Moelwyn-Hughes.¹² His values of E_A are consistently lower than ours for the same temperature and concentration of hydrochloric acid, as may be seen in Fig. 1. Using 5% sucrose solutions, Moelwyn-Hughes found $\Delta E_A/\Delta T$ to be -94 cal. per degree at 33.6° , which is much larger than the rate of change observed by us at this temperature. The early work of Urech,³³ cited by Moelwyn-Hughes in support of his statement of change of E_A with temperature, does not appear to be sufficiently accurate for the purpose in hand. In his analysis of Urech's data, Moelwyn-Hughes averaged values of E_A obtained at different acid concentrations, which is unjustifiable in view of the effect of acid concentration upon E_A . The data of Spohr,³⁴ also cited by Moelwyn-Hughes, are not convincing proof of the effect of temperature on E_A . Spohr's value of E_A at 32.5° for 0.250 *N* hydrobromic acid is in good agreement with our value for hydrochloric acid. Computation of E_A from the data of Heidt and Purves¹⁰ for the temperature intervals 30-40, 40-50, and 50-59.7° fails to show a consistent effect of temperature.

In addition to the effects upon E_A of temperature, and of concentration of electrolyte, there is probably a slight effect of the sucrose concentration. At a given acid concentration our value of E_A at the mid-point of the 0-25° interval is consistently higher than that of Duboux.¹⁸ The difference between the two values varies from 200 to 900 cal. Duboux's solutions contained 11.42 g. of sucrose per 100 cc., ours, 2 g.

In order to facilitate comparison with data in

(33) Urech, *Ber.*, **16**, 762 (1883); **17**, 2165 (1884).

(34) Spohr, *Z. physik. Chem.*, **2**, 194 (1888).

the literature, we have in Table V given B as computed from the equation

$$\log_{10} k_{H_3O^+} = B - \frac{E_A}{RT} \quad (5)$$

where $k_{H_3O^+}$ is expressed in sec.^{-1} , the values of $k_{H_3O^+}$ employed were obtained from equations (4a), (4b), etc., and E_A was taken from Figure 4.

TABLE V
VARIATION OF B WITH TEMPERATURE AND ACID CONCENTRATION

Midpoint of temp. range, °C.	B			
	0 molar HCl	1 molar HCl	2 molar HCl	3 molar HCl
10.00	36.00	35.25	34.56	33.80
15.00	35.45	34.79	34.08	33.40
20.00	35.07	34.44	33.85	...
25.00	34.72	34.20	33.69	...
30.00	34.47	34.02
35.00	34.33	33.91

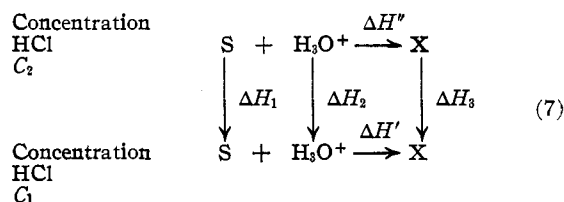
From Table V it appears that B decreases both with increase in temperature and with increase in acid concentration. The effect of temperature decreases markedly at the higher temperatures, as does the effect of temperature upon E_A .

Discussion

Inspection of Tables IV and V indicates that the activation energy is the quantity of first importance in the problem, and that the change in activation energy with concentration is the more important effect. From the point of view of the transition state theory,³⁵⁻³⁷ the activation energy can be set equal to the increase in heat content, ΔH , for the reaction



The change in ΔH with change in concentration can then be found by considering the heats of transfer in the following cycle



where $\Delta H'' - \Delta H' = \Delta H_1 + \Delta H_2 - \Delta H_3$

The heat of transfer (ΔH_1) of a mole of sucrose from a solution of concentration \bar{C} in sucrose and \bar{C}_2 in hydrochloric acid, to a solution \bar{C} in sucrose and \bar{C}_1 in hydrochloric acid may be considered small in comparison to ΔH_2 and is neglected in

(35) Eyring, *Trans. Faraday Soc.*, **34**, 41 (1938).

(36) Wigner, *ibid.*, **34**, 29 (1938).

(37) Evans and Polanyi, *ibid.*, **34**, 11₂ (1938).

this calculation. The heat of dilution of H_3O^+ from C_2 to C_1 can be computed from the heat of dilution of hydrochloric acid and potassium chloride on the assumption that the heat of dilution of the chloride ion in hydrochloric acid solutions may be taken as one-half the heat of dilution of potassium chloride for the same change in concentration.

Table VI gives the approximate changes in ΔH_2 per mole at 18° , calculated from the data given by Bichowsky and Rossini.³⁸

TABLE VI
COMPARISON OF ΔH_2 AND ΔE_A

C_2 Moles per liter	C_1 Moles per liter	ΔH_2	Calories per mole	
			$\Delta E_A, 20^\circ$	$\Delta E_A, 5^\circ$
4	3	300	610 ^a	550 ^a
3	2	300	620 ^a	700
2	1	300	630	710
1	0	500	630	700

^a Read from Fig. 4.

The value for the heat of transfer (ΔH_3) of a mole of the activated complex between solutions of different hydrochloric acid concentration is dependent on the structure assigned to the activated complex. If we assume that the hydrogen ion makes contact at the oxygen atom joining the two lactone rings of the sucrose molecule,¹⁴ we would have an ion which might be expected to have a heat of dilution intermediate between those of sucrose and hydrogen ion. This would mean that the maximum value of $\Delta H'' - \Delta H'$ would be equal to ΔH_2 . The change in E_A for the various intervals compared in Table VI should not exceed the values given for ΔH_2 . E_A shows the expected decrease with increasing concentration, but the observed values of ΔE_A are consistently larger than ΔH_2 . The heat of dilution of the hydrogen ion is greater at lower temperatures and the values of ΔE_A at 5° show an increase over ΔE_A at 20° except at four molar.

In regard to the effect of sucrose concentration on E_A , calculation of ΔH_1 for solutions of sucrose^{33,40} up to 0.5 molar indicates that E_A should decrease by approximately 100 cal. in going from 0.05 to 0.5 molar. Here again the observed effect seems larger than the calculated, though in the right direction.

From these calculations it seems that the change in the energy of activation with electrolyte con-

(38) Bichowsky and Rossini "The Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

(39) "International Critical Tables," Vol. V, p. 161.

(40) Pratt, *J. Franklin Institute*, **185**, 663 (1918).

centration is understandable on the basis of the transition state theory. The fact that the magnitude of the effect as calculated from the theory is not in agreement with the experimentally determined values may be due to our neglect of the heat of transfer of sucrose (ΔH_1) from one concentration of hydrochloric acid to another. In addition our values for ΔH_2 are based on heats of dilution for aqueous solutions which did not contain sucrose.

A similar picture will result if we do not consider the critical complex at the top of the energy barrier, but consider a pre-equilibrium between a collision complex and the reactants, the assumption being made that equilibrium is maintained between the collision complex and the reactants at all times. From equation 2 we have

$$\ln k = \ln K + \ln k_2 \quad (8)$$

$$\frac{\frac{\Delta S}{R}}{\frac{\Delta H}{RT}} \cdot b \cong \frac{\Delta S^*}{R} - \frac{\epsilon_A}{RT}$$

where K is the equilibrium constant, ΔH the difference in heat content between the collision complex and reactants, ΔS is the entropy difference, b is a constant, and ϵ_A the activation energy for the unimolecular decomposition of the collision complex. The constant b will include the entropy of activation of the transition state theory.

From the above we have

$$\ln k = \ln C + \frac{\Delta S + \Delta S^*}{R} - \frac{\Delta H + \epsilon_A}{RT} \quad (9)$$

C being a constant.

At a concentration of acid C_1 we have

$$k_1 = C e^{(\Delta S_1 + \Delta S_1^*)/R} e^{-(\Delta H_1 + \epsilon_A)/RT} \quad (10)$$

and at C_2

$$k_2 = C e^{(\Delta S_2 + \Delta S_2^*)/R} e^{-(\Delta H_2 + \epsilon_A)/RT} \quad (11)$$

The change in the measured energy of activation with change in acid concentration will be

$$(\Delta H'' + \epsilon_A'') - (\Delta H' + \epsilon_A')$$

and our approximate calculations are valid if we assume $\epsilon_A'' = \epsilon_A'$. ϵ_A need not be considered as the true energy of activation, but can be related to it by the equation $\epsilon_1 = \epsilon_A + SRT$ where S is the number of degrees of freedom.

Any attempt at an explanation of the change in B which is associated with the changes in $\Delta S + \Delta S^*$ seems unprofitable until we are able to know something of the order of magnitude of the equilibrium constant K .

Experimental studies on various acetals⁴¹ indicate that E_A does not show any great change with temperature or with concentration of electrolytes, but the reactions are too sensitive to hydrogen ion to allow investigation over any wide range of concentration of acid. We plan to extend this study to a reaction of a less complicated substrate than sucrose, which can be studied over a similar range of hydrochloric acid concentration and temperature.

Summary

1. The velocity constant $k_{H_2O^+}$ for the inversion of sucrose has been measured from 0 to 40° over a wide range of hydrochloric acid concentration.

2. Equations for the effect of the electrolyte, hydrochloric acid, on $k_{H_2O^+}$ are given at 5° inter-

(41) Unpublished results, Riesch and Kilpatrick.

vals between 10 and 40° and at -0.01°. The effect of electrolyte decreases with increasing temperature.

3. It has been shown that $k_{H_2O^+}$ increases with increasing sucrose concentration.

4. The energy of activation calculated from the Arrhenius equation shows that E_A and B decrease with increasing concentration of hydrochloric acid. This appears to be a general electrolyte effect.

5. The energy of activation also decreases with increasing sucrose concentration.

6. The decrease in E_A and B with increasing temperature has been confirmed.

7. An explanation of these results has been attempted on the basis of the transition state theory and the consideration of a pre-equilibrium between reactants and the collision complex.

PHILADELPHIA, PENNA.

RECEIVED AUGUST 11, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Action of *t*-Butylmagnesium Chloride with Acetyl Chloride

BY FRANK C. WHITMORE AND W. R. WHEELER

Researches in this Laboratory have shown that ketones of the type $RCOCH_3$ may be obtained by the action of tertiary alkylmagnesium halides and an acid halide.¹ In the present study *t*-butylmagnesium chloride was added to an excess of acetyl chloride in ether solution to determine the by-products.

Pinacolone, the normal product, was obtained in but 17% yield. $(CH_3)_3CMgCl + CH_3COCl \rightarrow (CH_3)_3CCOCH_3 + MgCl_2$. Other products were pinacolyl acetate, ethyl acetate, mesityl oxide, isobutylene, isobutane, carbon monoxide and hexamethylethane.

Pinacolyl alcohol, the product from the reducing action of the Grignard reagent on the ketone, appeared as its acetate in 8% yield.

Ethyl acetate, present to the extent of 9%, based on the acid chloride, was probably formed by interaction of acetyl chloride with the solvent ether rather than by direct reduction of the acid chloride to the primary alcohol.² This is confirmed by the formation of only 6.6% of isobutylene. Also, results from this Laboratory³ have

(1) Whitmore and Badertscher, *THIS JOURNAL*, **55**, 1559 (1933).

(2) Cf. Greenwood, Whitmore and Crooks, *ibid.*, **60**, 2028 (1938).

(3) Whitmore, Whitaker, Mattil and Popkin, *ibid.*, **60**, 2790 (1938).

shown that ethyl esters are formed in the reaction of *n*-propyl, *n*-butyl and *n*-amyl Grignard reagents with *t*-butylacetyl chloride, in which cases formation of ethyl alcohol by reduction is excluded. Since acid halides are known to cleave ethers in the presence of anhydrous zinc chloride,⁴ an experiment was undertaken which demonstrated that the anhydrous magnesium chloride, formed during the course of the reaction, may act in the same way as zinc chloride.

Several modes of formation are possible for the mesityl oxide, which occurred in 6.6% yield. Karasev⁵ observed that *t*-butylmagnesium chloride reacts with ethyl acetate to produce acetone and its condensation products, mesityl oxide and phorone. Kondakow⁶ prepared mesityl oxide from isobutylene and acetyl chloride in the presence of anhydrous zinc chloride. Recalling the similarity of zinc and magnesium chlorides in promoting the cleavage of ethers, the latter formation is also possible. In that case the small yield of isobutylene would be explained. Further studies on the mechanism of the forma-

(4) Norris and Rigby, *ibid.*, **54**, 2088 (1932); Gustus and Stevens, *ibid.*, **54**, 3461 (1932); **55**, 378 (1933).

(5) Karasev, *J. Gen. Chem.*, **7**, 179 (1937); *C. A.*, **31**, 4268 (1937).

(6) Kondakow, *J. Russ. Phys.-Chem. Soc.*, **26**, 12 (1894).