carbon group is attached to *four* sulfur atoms. Thus

$S_2C_2H_4S_2$ (Thiokol)
$S_2C_6H_2S_2$ (Sulfur dye from benzene)

Summary

1. By contacting vapors of organic compounds with molten sulfur *below* 300°, two new classes of sulfur organic compounds have been prepared, with hydrogen sulfide as a by-product.

2. Products prepared at 240–260° are resinous sulfur dyes, while products prepared at 260–300° are non-resinous and are not sulfur dyes.

3. High sulfur content is necessary in the sulfur dyes for the production of intense colors.

4. Additional ideas as to the structure of sulfur dyes prepared by vapor methods have been presented.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 455, AND FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, NO. 217, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Inversion of Sucrose

BY LAWRENCE J. HEIDT AND CLIFFORD B. PURVES

Recently we published data on the rates of hydrolysis of several fructosides including sucrose at 30 to 60° and calculated energies of activation, E, assuming that E did not vary with temperature. At the same time Leininger and Kilpatrick[1] found that in more concentrated solutions of sucrose E was smaller at 30 than at 0°, but that dE/dT approached zero as T increased. In addition, their data gave smaller values of E at 5.8 than at 0.5 N hydrochloric acid. Nevertheless, the rate constants obtained by extrapolating their data to our acid concentration of 0.01 N gave, within the limits of error, the same values of E and dE/dT between 25 and 35° as our previously published[2] values of $E = 25.75$ kcal. and $dE/dT = 0$ between 30 and 60°. They followed the inversion by noting the accompanying contraction of a fixed weight of solution. We used the copper reduction technique to measure the rate of formation of reducing sugars. The divergence of dE/dT from 0 obtained by the dilatometric method at temperatures lower than 25° led us to see whether this divergence could also be observed by the copper reduction technique when working in the same range of temperature and at the same concentrations of reactants used in reference 1. We were especially interested in this problem because conclusions like those we drew by comparing activation energies for the hydrolysis of fructosides[2] would be vitiated, of course, if the values of E were determined where dE/dT was not zero.

The reagents,[2] experimental procedure[2] and apparatus[3] have been described. Reactions at 10.00° took place in a thermostat kindly lent by Professor Scatchard. Especial care was taken to transfer each sample quickly from the reaction cell to just enough caustic soda solution at 0° so that the resulting solution was neutral to phenolphthalein. These neutral solutions were kept at 0° until analyzed.[2]

Corrections for the sucrose, sodium chloride, and concentrations of the reducing sugars present in the analyses were usually negligible. For example, 5 cc. of a 5% solution of sucrose formed cuprous oxide equivalent to 8 cc. of the 0.002 M sodium thiosulfate[4] and 1 cc. of a 23% solution of sodium chloride increased by 3.5% the cuprous oxide formed by the invert sugar. To reduce titration errors, the estimations of the reducing sugar in each sample withdrawn from the reaction cell were made at several concentrations scattered over the range covered in the calibrations.

Concentrations were referred to a liter of solution at the temperature the sucrose was inverted. Acid concentrations were obtained in each case by titrating with standard base weighed aliquots whose volumes at the temperature of the hydrolysis were carefully measured. Phenolphthalein was used as the indicator. The titrations agreed in every case with calculations based on the dilution of the standardized acid used to make up the sucrose solutions, so no measurable amount of acid was produced or consumed during the inversion.[5]

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(1) Leininger and Kilpatrick, THIS JOURNAL, **60**, 2891 (1938).

(2) Heidt and Purves, *ibid.*, **60**, 1206 (1938).

(3) Heidt, *ibid.*, **61**, 3455 (1939).

(4) In the earlier work[3] this hypo was denoted as 0.002 N.

(5) These titrations, however, would not reveal slight decreases in the pH like those noted in the photosensitized reaction: Heidt, THIS JOURNAL, **61**, 3223 (1939).

The fraction of sucrose inverted was the same within 1%, whether calculated by the methods described by Mathews and Jackson[6] or by Guggenheim,[7] or from the concentration of invert sugar when inversion was complete.

The invert sugar found when inversion was complete agreed within 1% with the value obtained for the equivalent quantity, (360/342) × wt. of sucrose, of equal weights of glucose and fructose. The invert sugar, therefore, was not affected measurably by the hydrochloric acid present in our experiments. This is in accord with previous work.[6]

The logarithm of the concentration of sucrose remaining in an experiment was a linear function of time within the limits of error. The fraction of sucrose inverted per minute, given as the velocity constant k in Table I, was obtained, therefore, from the slope of the straight line through these points. Each line was obtained by the method of least squares with each point given a weight about equal to the average volume of the neutralized solutions used in the analysis. Reaction rates were followed until at least 60% of the sucrose had been inverted. In the earlier work,[2] k was obtained graphically.

The data are summarized in Table I.

In Fig. 1, lines A and C show the change in log k^* with $1/T$, and the B lines the change in log k^* with the concentration of HCl. The equations for these lines were calculated by the method of least squares and the quadratic mean errors in the constants of the equations were obtained in a way outlined elsewhere.[8] The probable error equals the quadratic mean error multiplied by 0.6745. The dots in Fig. 1 represent the common logarithm (log) of our average values of k^*.

The ordinates for the B lines are on the left side of the figure. The lower of these lines represents the data obtained at −0.01° by Leininger and Kilpatrick,[1] who found (1), log $k^* = \bar{4}{\cdot}1057 + 0.2394\,[\mathrm{HCl}]$. The upper of the B lines represents our data at 0.00° which gave (2), log $k^* = \bar{4}{\cdot}1189 + 0.2495\,[\mathrm{HCl}]$. The difference between the slopes of these lines is greater than the reproducibility of the velocity constants in either method.

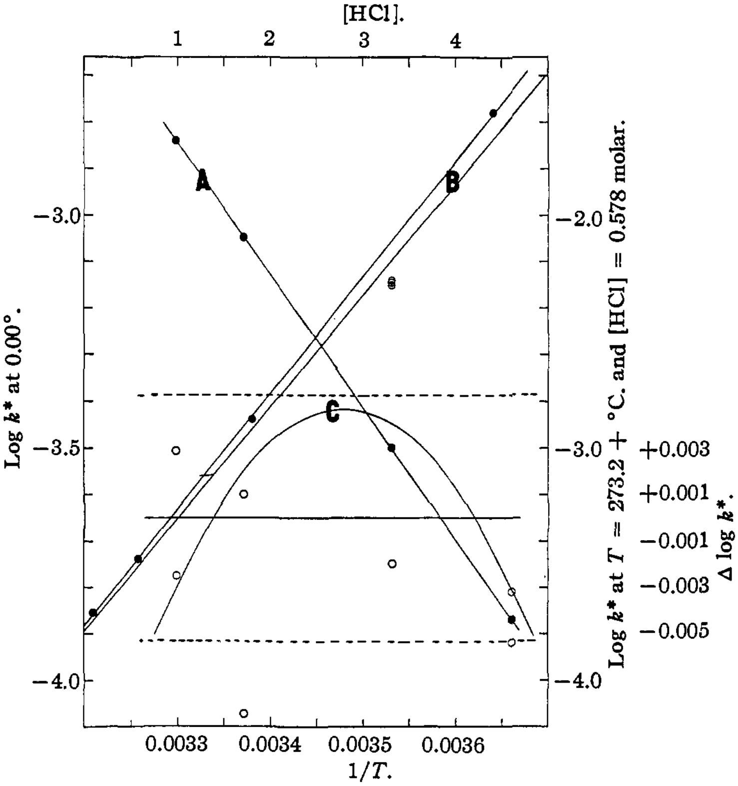

Fig. 1.

TABLE I

There was present initially about 2 g. of sucrose, weighed to 0.1 mg. per 100 cc. of solution. The fraction inverted per minute = k and $k^* = k/[\mathrm{HCl}]$.

Moles of HCl in a liter	10^4k	10^4k^*	°C.
4.41	74.1	16.8	0.00
4.41	73.1	16.6	.00
1.81	6.55	3.62	.00
1.81	6.63	3.67	.00
0.575	1.05	1.82	.00
.580	1.06	1.83	.00
.0965	0.136	1.40	.00
.0965	0.135	1.40	.00
.578	5.74	9.93	10.00
.578	5.92	10.3	10.00
.576	5.88	10.2	10.00
.576	5.89	10.2	10.00
.578	46.6	80.6	23.40
.578	45.6	78.9	23.40
.577	122	211	30.05
.577	120	208	30.05

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

(7) Guggenheim, *Phil. Mag.*, **1**, 538 (1926).

(8) Whittaker and Robinson, "The Calculus of Observations," Chap. IX, D. Van Nostrand Co., New York, N. Y., 1924.

A manipulation tending to make our values of k^* high was the short time, about thirty seconds, that the solution undergoing hydrolysis was warmed slightly by the pipet, initially at 25°, while being transferred to the caustic soda solution. This produced a negligible effect upon k^* when $k < 0.0005$ at 0° so that it affected less than 1% any of the rate constants obtained at 0.58 N hydrochloric acid; however, it would account for part of the increasing divergence of the B lines as the concentration of hydrochloric acid was increased.

The possible errors in their refined dilatometric method have been discussed ably by Leininger and Kilpatrick.[1] Their data extended from 0.6 to 5.8 N hydrochloric acid where the logarithm of the activity of the acid also varies almost linearly with its concentration although deviating sharply from linearity in more dilute solutions. Nevertheless, they were careful to dot in the extension of their lines beyond their experimental values and thus correctly assumed that their linear plots could be extrapolated to give k^* down to $[\mathrm{HCl}] = 0$. They thereby implied that k^* was not directly proportional to the activity of the hydrochloric acid, and their hypothesis is supported by our data at 0.1 N hydrochloric acid which, within the limits of error, falls on our linear plot instead of paralleling the activity of the hydrochloric acid.

Line A, whose ordinates are given on the right side of the figure, gives the linear dependence upon $1/T$ of our values of (3), $\log k^* = (17.0172 \pm 0.0678) - (5669 \pm 19.5)(1/T)$. The circles in the figure represent the deviations from line A of the individual values of $\log k^*$ included in the average values represented by the dots. The ordinates of these deviations, $\Delta \log k^*$, are on a scale obtained by magnifying one hundred times the scale of ordinates used for line A. An observation which did not deviate from line A would fall on the solid horizontal line in the figure, and one representing the probable deviation, 0.0053, would fall on either of the dotted horizontal lines. The second degree parabola representing the observed deviations is given by line C. The equation for this line plus that for line A is (4), $\log k^* = (14.1882 \pm 2.0960) - (4040 \pm 1208)(1/T) - (234057 \pm 173840)(1/T)^2$.

The quadratic mean error in the coefficient of $(1/T)^2$ in equation (4) is so large, according to the t test,[9] that the straight line given by equation (3) adequately represents our data.[10] The probable deviation in any experimental value of $\log k^*$ is 0.0053 from (3) and 0.0046 from (4) or 1.2% in k^*.

The energy of activation, in kcal., by equation (3) is 25.94. If equation (4) differed significantly from (3), E would be 26.35 at 0° and 25.55 at 30°. At the same concentrations of reactants, the average value of E from the measurements with a dilatometer[1] was 26.0 kcal. decreasing[11] from 26.6 at 0° to 25.4 at 30°.

When our concentrations are expressed as mole fractions, k^* is replaced by $k' = k^*(55.5062\,d - 1.0240\,N - 1.0517)$. The normality, N, of the acid is given in Table I, and d, the weight in grams of one ml. of solution at the temperature of inversion, was roughly 1.017 at 0.0°, 1.0122 at 10.0°, 1.0116 at 23.4° and 1.0085 at 30.0°. Our data now fit the equations (5), $\log k' = (18.7083 \pm 0.0626) - (5655 \pm 18)(1/T)$ and (6), $\log k' = (14.5375 \pm 2.0499) - (3251 \pm 1180)(1/T) - (346044 \pm 169935)(1/T)^2$. The probable deviation in any experimental value of $\log k'$ is 0.0049 from (5) and 0.0045 from (6). Also, from (6) E equals 26.5 kcal. at 0° and 25.35 at 30°, but again the quadratic mean error in the coefficient of $(1/T)^2$ is so large that the straight line adequately represents the data. Moreover, expressing concentrations as mole fractions instead of moles per liter of solution does not improve significantly the fit of our data to either a straight line or second degree parabola.

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(9) R. D. Fisher, "Statistical Methods for Research Workers," Chapter V, Oliver and Boyd, London, 1936. The "Table of t" given near the end of this book lists a probability equal to 0.3 of getting by accident 234057 as the coefficient of $(1/T)^2$. This probability is much greater than the value of 0.05 given arbitrarily by this author as an upper limit for a significant result.

(10) Any systematic errors in the measurements *not* having the same percentage effect upon each value of k^* could vitiate this conclusion.

(11) The data of Leininger and Kilpatrick[1] (L. and K.) at 10, 15, 20, 25 and 30° and 1.120 to 1.124 N hydrochloric acid, and $\log k^*$ at 1.122 N acid and $-0.01°$ calculated from their equation 4a give (7), $\log k^* = (16.9111 \pm 0.0856) - (5608 \pm 25)(1/T)$ and (8), $\log k^* = (11.7937 \pm 0.8956) - (2663 \pm 515)(1/T) - (423057 \pm 74000)(1/T).^2$ The probable deviation of $\log k^*$ is 0.0049 from (7) and 0.0017 from (8), and the probability is less than one in a hundred of obtaining accidentally the coefficient of $(1/T)^2$ given in (8) from which E equals 26.2 kcal. at 0° and 25.0 at 30°. These calculations, therefore, support the conclusion of L. and K. that their data give values of E changing with T. Moreover, when their concentrations are converted to mole fractions, values of $\log k'$ are obtained giving values of E also changing significantly with T. In addition, a comparison of the nearly equal probable deviations of the data from equations (3), (4) and (7) with that of $\log k^*$ from (8) reveals that unless $\log k^*$ can be determined to 0.4% or less over an interval of 30° changes in E with T as small as found by L. and K. are not significant. Moreover, corrections for the effect of the mutarotation of glucose upon the rates observed by L. and K. would straighten their plots of $\log k^*$ *vs.* $1/T$. It is quite possible that these and other corrections would change $\log k^*$ as much as 0.5% more at 0° than at 30° which would remove from their data any significant change in E with T for the inversion of sucrose.

Summary

Rates of inversion of sucrose measured by the reducing sugars produced were found to be slightly higher than the rates previously obtained by the dilatometric method at the same temperatures and concentrations of hydrochloric acid and sucrose.

The activation energy obtained is 25.9 kcal. and does not vary significantly with the temperature between 0 and 30°.

The logarithms of the velocity constants at 0° are a linear function of the concentration of hydrochloric acid between 0.1 and 4.4 *N*.

CAMBRIDGE, MASS. RECEIVED JANUARY 23, 1940

CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XII. The Heats of Combustion of Urea and Guanidine Carbonate and their Standard Free Energies of Formation

BY HUGH M. HUFFMAN

In continuation of our program,[1] involving the study of the thermal properties of organic compounds of physiological interest, we have determined the heats of combustion of urea and of guanidine carbonate. These data have been used in conjunction with other data to calculate the standard free energies of formation of these compounds.

Experimental

Calorimetric Method.—The calorimetric method has been described in previous publications.[2] Since no important changes have been made, only the essential details will be given. All of the combustions were made in a Parr bomb having a volume of 0.380 liter and with an initial oxygen pressure of 30 atmospheres and with 1 ml. of water in the bomb.

The energy equivalent of the calorimetric system was controlled throughout the investigation by frequent calibration with Bureau of Standards benzoic acid standard sample 39e, having for its isothermal heat of combustion under standard conditions[3] and at 25° the value of $-\Delta U_B/m = 26{,}419$[4] N.B.S. international joules. The conditions in our bomb are not quite standard, necessitating a correction of this value to 26,418 N.B.S. international joules.

A minor change was made in the calorimeter after the combustions on guanidine carbonate and hence a recalibration was required. The energy equivalent of the calorimetric system in the guanidine carbonate series was 3157.4 cal., mean of fifteen calibration experiments, with a standard deviation of 0.0016% and in the urea series 3157.0 cal., mean of seventeen calibration experiments, with a standard deviation[5] of 0.0021%. The results of all of our combustion experiments are expressed in terms of the defined conventional calorie which is derived from the N.B.S. international joule by dividing by 4.1833. The units and corrections are the same as those given in previous papers.[6] The molecular weights are based on the 1939 table of atomic weights. All of the thermal data are given for the isothermal process at 25° and for true mass.

Purification and Heats of Combustion

Urea.—Three combustion samples a, b and c were prepared from J. T. Baker C. P. urea by one and three crystallizations from redistilled water and by two crystallizations from purified methyl alcohol, respectively.

Guanidine Carbonate.—Material from Eastman Kodak Co. was dissolved in hot water and allowed to cool, it was then precipitated by the addition of about 2.5 volumes of purified ethyl alcohol. This process was repeated to give sample (a). Material from Hoffman–LaRoche was precipitated once as above to give sample (b).

Nitrogen determinations on the urea gave the theoretical results and the ash content was negligible. Titrations of the guanidine carbonate with dilute hydrochloric acid gave 99.7 and 99.8% of the theoretical. The ash content was about 0.03%.

The results of the combustions of these compounds are given in Table I. In the case of guanidine carbonate we have arbitrarily corrected the mass by subtracting from the observed mass the mass of ash found after each combustion. The uncertainties given in the table are the mean deviations from the mean.

In addition to the experimental values we have also calculated the quantities $-\Delta U_B$, $-\Delta U_R$, $-\Delta H_R$ and $-\Delta H_f^\circ$ which we have defined previously.[2b] To obtain the values of $-\Delta H^\circ_{f298}$ we have used for the heats of formation of water and carbon dioxide at 25° the value 68,318.1[7] and 94,030[8] calories, respectively.

Discussion

Urea has been burned by several workers (Berthelot 1890, Stohmann 1893, Krummacher 1904, Emery and Benedict 1911). It is not possible to make a careful comparison of our results

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(1) Huffman and Borsook, THIS JOURNAL, **54**, 4297 (1932).

(2) (a) Huffman and Ellis, *ibid.*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935).

(3) Washburn, *Bur. Standards J. Research*, **10**, 552 (1933).

(4) Jessup and Green, *ibid.*, **13**, 496 (1934).

(5) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(6) Huffman, THIS JOURNAL, **60**, 1171 (1938).

(7) Rossini, *Bur. Standards J. Research*, **22**, 407 (1939).

(8) Rossini and Jessup, *ibid.*, **21**, 491 (1938).