

liquefaction are accomplished simultaneously, in the same chemical reaction. It has been postulated by Erasmus¹⁰ that coal is a polymer consisting mainly of relatively small aromatic and hydroaromatic units of about ten carbon atoms each, some of which are linked through linear, and some through cyclic-ether-oxygen, bonds. Such a structure would explain the close relationship between reduction of molecular weight and oxygen elimination, as well as the existence of two types of oxygen groups in the coal structure, as was postulated by Fisher and Eisner⁶ before Erasmus' book¹⁰ was published.

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Summary

An analysis is made of data on the effect of a stannous sulfide catalyst on the rate of change of

(10) P. Erasmus, "Über die Bildung und den chemischen Bau der Kohlen," Ferdinand Enke, Stuttgart, 1938, 90 pp.

readily measurable quantities in the hydrogenation of a bituminous coal in a small autoclave. The results show that the rate-determining step for the hydrogen absorption varies with temperature. Below 300° it is apparently a chemical reaction between a hydrogen carrier and unsaturated groups in the coal; between 300 and 370° diffusion of hydrogen through a liquid film on the surface of the coal and catalyst is the slowest step; above 370° the rate-determining step is a chemical reaction between a hydroaromatic and the oxygen and unsaturated groups in the products of the primary decomposition of the coal. The chief function of the catalyst is to increase the rate of regeneration of a hydrogen carrier, which is a hydroaromatic compound such as hexahydronaphthalene. The reactions of the hydrogen carrier with oxygen and unsaturated groups are largely non-catalytic. The effects of the catalyst on the rate of oxygen elimination and on that of liquefaction are very similar, and it is probable that both processes are intimately associated in one reaction or group of reactions.

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The Mutarotation of Glucose in Water-Methanol Mixtures¹

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The rate of the mutarotation of glucose has been studied extensively in water solution, both when catalyzed by the solvent, and when catalyzed by strong or weak acids and bases at various temperatures.² In solvents other than water, measurements have usually been made at one temperature only, and only a few catalysts have been used.³ It should be of interest, therefore, to measure the rate in various water-methanol mixtures, and to determine the temperature coefficients both for the solvent-catalyzed and for the acid-catalyzed reaction.

(1) This paper is in part taken from a thesis submitted by H. E. Dyas to the Graduate School of Arts and Sciences of Duke University, Durham, North Carolina, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

(2) Hudson, *THIS JOURNAL*, **32**, 889 (1910); Osaka, *Z. physik. Chem.*, **35**, 661 (1900); Lowry and Smith, *J. Chem. Soc.*, 2539 (1927); Kuhn and Jacob, *Z. physik. Chem.*, **113**, 389 (1924); Brønsted and Guggenheim, *THIS JOURNAL*, **49**, 2554 (1927); Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **A176**, 352 (1940); Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, **37**, 289 (1941); and many others.

(3) Worley and Andrews, *J. Phys. Chem.*, **31**, 742 (1927); Richards, Faulkner and Lowry, *J. Chem. Soc.*, 1753 (1927).

Particular interest attaches to this reaction in view of the statement of Nelson and Beegle⁴ that the equilibrium in this reversible isomerization is not changed by temperature. This statement has been accepted recently by Kendrew and Moelwyn-Hughes² in a paper appearing while the work was in process, although their data would seem to us to point strongly against its truth. If it were true, the entire free energy change of the reaction would necessarily be an entropy change, and the determination of the free energies and entropies of activation should be particularly interesting. Our work, however, seems to show definitely that the equilibrium constant does change with temperature, albeit in a rather unusual manner. The temperature coefficients of both the rates and the equilibrium constants will be shown to exhibit parallel anomalies which will need to be considered in any mechanism proposed for this reaction.

(4) Nelson and Beegle, *THIS JOURNAL*, **41**, 559 (1916).

The change of α - into β -glucose is a reversible isomerization which comes to an equilibrium with considerable quantities of each form present. It is presumed to involve an opening and reforming of the pyranose ring. Lowry and Faulkner⁵ have shown that both an acid and a basic catalyst are necessary, and that the reaction shows general acid and basic catalysis. By choosing the proper conditions, the effects of the different catalysts may be isolated. The rate constant found experimentally may be expressed by

$$k = k_0 + k_A C_A + k_B C_B + k_X C_X$$

where k_0 is the constant for the solvent catalyzed reaction, A and B are acid and base, respectively, and X may represent any other catalysts present. Our rates were measured in solutions containing from 0.01 to 0.05 *N* hydrochloric acid, so that no bases (other than the solvent) are important, and only the first two terms need be considered.

Experimental

Glucose (c. p.) was separated into α and β forms by the methods given by Hudson and Dale.⁶ The rate studies were made on α -glucose, since that was the more readily purified, and since Hudson showed that the same constant is obtained whether α or β is the starting material. For the equilibrium studies, the two isomers were recrystallized until their rotation did not change on further recrystallization.

Commercial absolute methanol was treated with magnesium and distilled.

For the kinetic studies, solutions containing a desired weight per cent. of methanol and a known concentration of hydrochloric acid were prepared by mixing calculated quantities of water, methanol and standard 0.1 *N* hydrochloric acid. The density of the latter was assumed to be the same as that of water, which introduces only a negligible error. The solution was allowed to come to the temperature of the thermostat, a quantity of α -glucose added, and the mixture transferred to a polarimeter tube as soon as solution was complete. Water from the thermostat was circulated through the jacket of the polarimeter tube, and the temperature actually maintained in the experiment read by a thermometer immersed in the glucose solution. This was kept constant to 0.05°. The polarimeter was a Schmidt and Haensch instrument reading to 0.01°, and using 20-cm. tubes. A sodium vapor lamp furnished the light for observation. Time was read on two stop watches and recorded to the nearest second. Concurrent readings of rotation and time were taken over at least one hour, and a final reading the next day for the equilibrium rotation.

First order reaction rate constants were calculated in accord with the equation of Lowry⁷

$$k_1 + k_2 = k = \frac{2.303}{t} \log \frac{a_0 - a_\infty}{a - a_\infty}$$

(5) Lowry and Faulkner, *J. Chem. Soc.*, **127**, 2883 (1925).

(6) Hudson and Dale, *THIS JOURNAL*, **39**, 320 (1917).

(7) Lowry, *J. Chem. Soc.*, **75**, 211 (1899).

in which k_1 is the constant for the transformation of α - into β -glucose and k_2 that for the reverse process, a_0 the initial rotation, a_∞ the final rotation (at equilibrium), and a that at time t .

Actually, time (in minutes) was plotted against $\log(a - a_\infty)$ and k determined from the slope of the resulting straight line. In this method a_0 , which is the least accurate of the readings, does not add its error to all the results.

The values of k obtained were plotted against the hydrochloric acid concentration and good straight lines obtained. The slope of such a line should be k_{H^+} and the intercept k_0 in accord with the equation

$$k = k_0 + k_{H^+} C_{H^+}$$

where k_0 is the constant for the solvent catalyzed reaction, and k_{H^+} that for the acid catalyzed. In the present work, this catalyst was assumed to be hydronium ion. Although graphical methods may be open to suspicion, we believe the excellent straight lines obtained in each plot indicate an error not greater than 4% in the constants.

In the equilibrium studies, solutions of methanol and water of the proper concentration were allowed to come to the temperature of the thermostat, and a weighed quantity of one of the pure forms of glucose added, the time of addition being noted. The mixture was stirred in the thermostat until solution was complete, and then more solvent added until the total volume was 25 ml. This solution was transferred to the jacketed polarimeter tube and a series of readings of the rotation taken over half an hour. By plotting the log of the rotation against time and extrapolating to zero time, an initial reading could be obtained which was free of the error caused by mutarotation during the time required for solution. Such extrapolations for duplicate runs agreed within 0.5°. In most cases two drops of ammonia were added as a catalyst to the polarimeter tube after the initial period, and a reading of the final rotation taken after equilibrium was attained.

Specific rotations for each form and for the equilibrium mixture were calculated, and equilibrium constants determined from the equation

$$K = \frac{k_1}{k_2} = \frac{[\beta]}{[\alpha]} = \frac{\alpha_\infty - \alpha_0^\alpha}{\alpha_0^\beta - \alpha_\infty}$$

where α is the specific rotation of the substance indicated.

The method of Hudson and Yanovsky⁸ in which equilibrium constants are obtained from the rotation of saturated solutions was found unsatisfactory in all but pure water solutions. The time required for preparing a saturated solution in mixtures high in alcohol allowed much mutarotation to occur, and still more occurred during the slow filtration of the viscous solutions obtained at the higher temperatures. It was necessary to adopt the more laborious method of measuring initial and final rotations on pure α - and β -glucose.

Kinetics

The values of the rate constants are given in Table I (time in minutes).

It will be observed that addition of alcohol decreases the rate of the solvent-catalyzed reac-

(8) Hudson and Yanovsky, *THIS JOURNAL*, **39**, 1013 (1917).

TABLE I

% MeOH	T, °C.	k_0	k_{H^+}
0 ^a	20	0.0147	0.406
40	20	.0054	.503
60	20	.0026	.59
75	20	.0018	.753
0 ^a	29.2	.0346	1.04
40	29.2	.0139	1.35
60	29.2	.0092	1.51
75	29.2	.0045	2.09

^a Calculated from the data of Moelwyn-Hughes and co-workers,² using their values of the activation energy to obtain the rate constants at our temperatures.

tion. This is confirmed by the work of Worley and Andrews³ at 25°. It would seem that water is a much better catalyst than methanol, and that probably the water in the solvent is the effective catalyst in these experiments. However, addition of alcohol increases the rate of the acid catalyzed mutarotation. Both effects are in the right direction if the catalysts are water and hydronium ion, respectively, and if the principal effect of changing the solvent is to change the dielectric constant. In a reaction⁹ between an ion and a neutral molecule, the logarithm of the rate constant should increase in proportion to the reciprocal of the dielectric constant. Likewise, the rate of a reaction between two polar molecules should decrease with a decrease in the dielectric constant, and should give a straight line if $\log k$ is plotted against $(D - 1)/(2D + 1)$. Figure 1 gives such a plot for the acid catalyzed

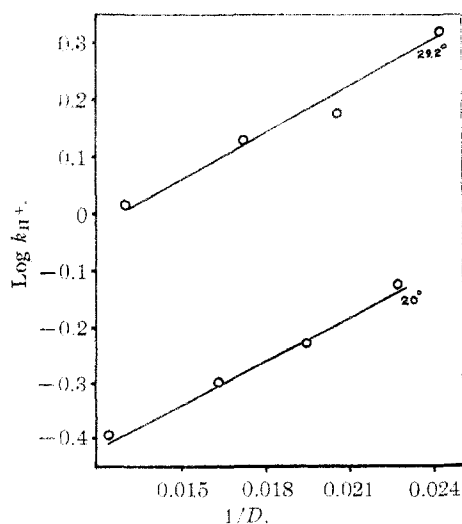


Fig. 1.

(9) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," Chapter VIII, McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

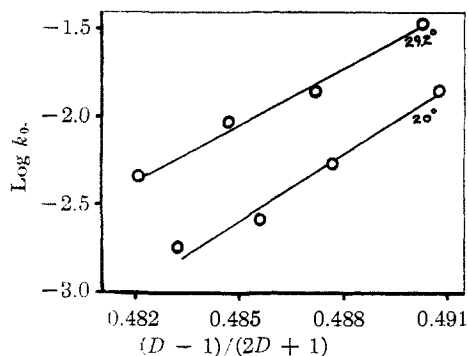


Fig. 2.

reaction, and Fig. 2 for that catalyzed by the solvent. Although the points fall approximately on a straight line, indicating that the reaction rate is affected by dielectric constant as predicted by theory, the linearity is not what might be expected. This leads us to suggest that the dielectric constant of the medium is not the only factor influencing the rate.

The activation energies, E , calculated from the Arrhenius equation are given in the second and third columns of Table II. The subscripts refer to the solvent catalyzed and to the acid catalyzed reaction, respectively, the units being kilocalories.

TABLE II

% MeOH	E_0	E_{H^+}	ΔF_0^*	$\Delta F_{H^+}^*$	ΔS_0^*	$\Delta S_{H^+}^*$
0	16.9	19.0	22.0	20.0	-17.4	-3.3
40	18.0	18.0	22.6	19.9	-15.7	-3.8
60	24.0	17.9	23.0	19.8	+3.3	-6.5
75	17.5	19.3	23.2	19.7	-19.5	-1.4

Columns four and five give the free energy of activation calculated according to the Eyring⁹ equation

$$k = \frac{kT}{h} e^{-\Delta F^*/RT}$$

The final columns give the entropy of activation in calories per degree, assuming that the Arrhenius activation energy is nearly equal to the heat of activation, so that $\Delta S^* = (E - \Delta F^*)/T$. The values in pure water are calculated from the data of Kendrew and Moelwyn-Hughes² and Johnson and Moelwyn-Hughes, using their value of the equilibrium constant to determine the total rate constant for the reaction.

All the constants and energies are calculated using the total rate constant k . Actually, k is the sum of the constants for the forward and the reverse reactions, and may be separated into these two constants by the use of the data below.

However, the equilibrium constant does not vary greatly from 1.5, and the separation reveals no new facts either in regard to the rates themselves or the energies. Therefore a table of these values has been omitted.

As pointed out by Kendrew and Moelwyn-Hughes, the Arrhenius energies are not in the order to be expected, since the rate is faster in the acid catalyzed than in the solvent catalyzed reaction. Their data extend over a wide temperature range, and they have shown that it is better fitted by an equation of the type

$$\ln k = \text{const.} + \frac{J}{R} \ln T - \frac{E_A}{RT}$$

They, therefore, call E_A the apparent activation energy, and calculate a true activation energy, E , from the equation

$$E_A = E + JT$$

However, if the Eyring equation is written in the logarithmic form, we obtain

$$\ln k = \text{const.} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

so that one would expect to get about the same value for ΔF^* as for the "true activation energy" of Kendrew and Moelwyn-Hughes. They obtain 23.0 for this energy, which is in fairly good agreement with our value for ΔF_0^* in the water catalyzed reaction. The method used by Kendrew and Moelwyn-Hughes and that of Eyring thus agree both theoretically and experimentally. This is to be expected from the pioneer work of LaMer.¹⁰ Which will prove a more satisfactory method remains for the future to decide. In the present experiments, the Eyring method alone is applicable, since we have data at only two temperatures. Where more complete data are available, the experimental approach may be more attractive.

Our results show definitely that the solvent has a profound influence on the energies of the reaction as well as on the rates. Since the Arrhenius energies show either a maximum or minimum in 60% alcohol, which is not found in the free energies of activation we suggest that solvation must be very important in the mechanism of the reaction. It would appear to differ with the concentration of water in the solvent, and would be expected to appear as it does in both the heats and entropies of activation.

(10) LaMer, *J. Chem. Phys.*, **1**, 289 (1933).

Equilibrium

In Table III the specific rotations of α - and β -glucose and of the equilibrium mixture are given for both temperatures and for all the concentrations measured.

TABLE III

% MeOH	α_0^α		α_0^β		α_0^∞	
	20°	30°	20°	30°	20°	30°
0	108.8 ^a	112.4 ^a	19.7	21.4	52.5 ^a	52.9 ^a
40	113.9	116.5	19.2	20.1	57.4	57.9
60	116.1	111.9	19.4	19.5	58.0	58.3
75	115.8	116.2	19.8	20.6	60.9	61.0

^a Taken from the work of Kendrew and Moelwyn-Hughes.²

It is evident that there are changes in the specific rotation of both of the forms of glucose with temperature, although they are small in the case of the β -form. However, the rotation of the equilibrium mixture changes only very slightly with the temperature. This has probably given support to the belief mentioned earlier that the equilibrium was temperature independent. That even the former is untrue was shown by the very careful measurement of Isbell and Pigman¹¹ on the rotation of equilibrium glucose.

The equilibrium constants and the heats and entropies of reaction calculated from these values are given in Table IV.

TABLE IV

% MeOH	$K_{(20)}$	$K_{(30)}$	ΔH , cal.	ΔS
0	1.7	1.9	+3200	+12
40	1.6	1.6	0	+1
60	1.5	1.4	-1300	-4
75	1.3	1.4	+1300	+5

It will be seen that the equilibrium constant is temperature dependent, and that it decreases with increasing methanol concentration. However, the temperature coefficient reverses as the concentration changes, so that the heat of reaction is at a minimum in 60% methanol. It is at this same concentration that the Arrhenius activation energies also reverse their trend. Since ΔF for the reaction is in no case far from 200 calories, the entropy change may be calculated, and of necessity a minimum at 60% methanol is found.

Discussion

Since the plot of $\log k$ against $1/D$ for the hydron catalyzed rate deviates from a straight line, it is necessary to assume that some other factor enters into the medium effect than merely the di-

(11) Isbell and Pigman, *Bur. Standards J. Research*, **10**, 337 (1933).

electric constant. In a paper published since this work was completed, Amis and Holmes¹² reported deviation from such a straight line plot for the acid catalyzed inversion of sucrose in ethanol-water mixtures, and a slope of sign opposite to that of ours. In a similar plot when dioxane-water mixtures were used as solvent, the slope was similar to ours. They suggest that the formation of $C_2H_5OH_2^+$ ion instead of H_3O^+ in solutions high in alcohol may cause the irregularity. A similar explanation may be offered for our deviations in methanol-water mixtures, although since mutarotation shows general acid catalysis, the slope of the curve should still be normal. Certainly no proof may be adduced for the hypothesis at present. Studies such as those of Amis and Holmes using other solvents than methanol will be needed to explain the deviations in mutarotation. It should be pointed out that glucose mutarotation is much more sensitive to acid catalysts than is the inversion of sucrose.

In agreement with the work of Amis and Holmes and with theory, the activation energy in mixtures of constant composition and of constant dielectric constant is nearly the same. This should be the case if only one of the reactants carries a charge.

We have not been able to find any properties of water-alcohol mixtures which change at about 60% methanol in the abrupt fashion indicated by the heats both of activation and of reaction. However, many of the properties of methyl alcohol-water mixtures deviate from the simple additivity laws. Such deviations in density, refractive index and viscosity, probably indicating strong interaction between the two substances, are at a maximum between 50 and 60% methanol,

where our energy maxima and minima appear. It seems possible that the same factors may be responsible in each case, and we suggest that changes in the solvation either of the reactants or of the activated complex may be responsible for the sudden change. It is hoped that further investigations now in progress using other catalysts and solvents may throw more light on the question.

At present we can only accept from our results the apparent truth that a methanol-water mixture as solvent in the mutarotation of glucose must have three distinct roles. The solvent provides a medium of definite dielectric constant in which the reaction may take place. It serves as a catalyst for the reaction. Finally, it in some fashion influences markedly the energies both of reaction and of activation in the same manner.

Summary

The rate of the mutarotation of glucose has been studied in several water-methanol mixtures at two temperatures. The rates change in the directions to be predicted from the dielectric constants of the mixtures, but do not strictly follow the theoretical laws for this effect.

The specific rotations of pure α - and β -glucose and of the equilibrium mixture have been measured in the same solvents at two temperatures, and equilibrium constants calculated for the reaction. Contrary to previous statements, the equilibrium constants are not independent of temperature.

The heats of reaction and heats of activation show large and parallel changes with methanol concentration, with maxima or minima in a 60% methanol solution.

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(12) Amis and Holmes, *THIS JOURNAL*, **63**, 2231 (1941).