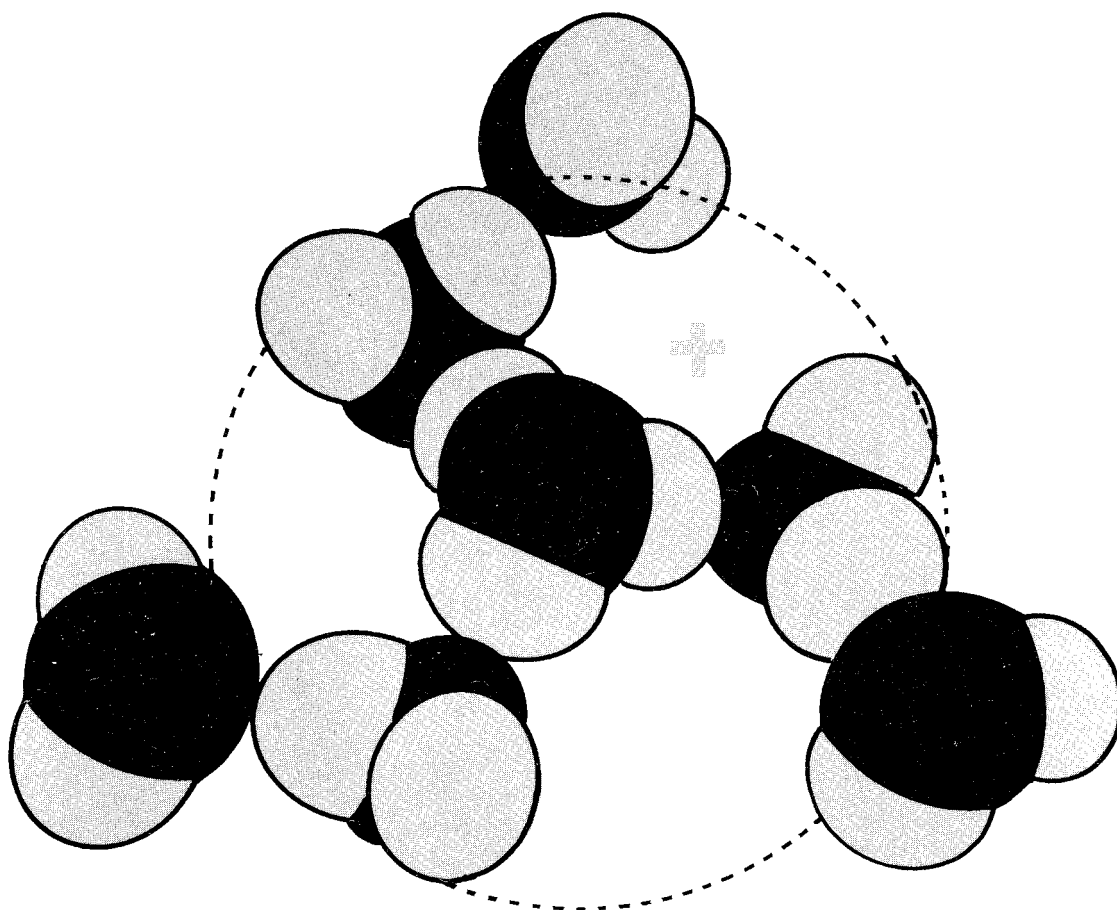


**RATE OF D-XYLOSE
DECOMPOSITION IN
SULFURIC ACID-SODIUM
2, 4 DIMETHYLBENZENESULFONATE-
WATER SOLUTIONS**



U. S. DEPARTMENT OF AGRICULTURE FOREST SERVICE

FOREST PRODUCTS LABORATORY MADISON, WISCONSIN.

SUMMARY

Xylose decomposition rate was measured in solutions containing 10 grams xylose per 100 milliliter, 0.05–0.2 molar sulfuric acid, and 0–1.563 molar 2,4 dimethylbenzenesulfonate over the temperature range 120° – 150° C. The observed specific rate was found to be exponentially related to the ionic strength and of the magnitude expected for a reaction involving an ion and an uncharged molecule. However, the primary salt effect exhibits a marked variation with catalyst concentration which is not satisfactorily explained. It is, perhaps, due to incomplete dissociation of xylenesulfonic acid or to the presence of concomitant reactions. The latter explanation is supported in part by the presence of base-catalyzed reactions in the salt-free solutions.

The manifestation of base reactions at acid concentrations as high as 0.1 molar has not previously been reported. Their occurrence invalidates the use of the xylose decomposition rate as a measure of acidity in dilute acid solutions (0.15 molar). Probably a glucoside or a disaccharide such as cellobiose would serve satisfactorily in this range. For the acid concentration range 0.15 to 1.0 molar, xylose is a suitable measure. For less than 1 percent of the xylose would decompose through the base-catalyzed reaction sequence.

RATE OF D-XYLOSE DECOMPOSITION IN SULFURIC ACID--SODIUM 2, 4 DIMETHYLBENZENESULFONATE-- WATER SOLUTIONS

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INTRODUCTION

This Research Paper describes the results of a study that forms part of a larger program of research directed toward the conversion of wood residues to chemical products. During the course of studying the kinetics of the removal of hemicelluloses and lignin from wood, it became desirable to have a measure of the acidity of the reagent. Such a measure would be useful in interpreting the relative importance of the various physical and chemical phenomena occurring in these complex heterogeneous systems. The frequently used H_0 acidity scale of Hammett and Deyrup (9,17)² seemed unsuited for the purpose, primarily because the temperatures under study were considerably higher than those for which H_0 has been measured. The task of extending the experimental measurement of H_0 to a high

temperature range appeared difficult, and a better approach was thought to be the use of a kinetic measurement in a manner quite similar to that suggested by Brönsted and Grove (4). Here, the experimentally determined first-order rate constant of an acid-catalyzed unimolecular reaction (an A-1 reaction in Ingold's (12) terminology) is taken as a direct measure of the ability of the reaction medium to transfer a proton.

This study was undertaken to evaluate the suitability of using the decomposition rate of xylose as a measure for characterizing the reactivity of H_2SO_4 -sodium xylenesulfonate- H_2O solutions with regard to reactions involving a proton and a neutral molecule. Xylose was used because previous work (19) indicated that, despite the complexity of the degradation mechanism,

¹Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

²Underlined numbers in parentheses refer to Literature Cited at the end of this paper.

its disappearance is controlled by a reaction that is purely acid catalyzed. The experimental techniques of previous studies³ (19) were readily adapted to this work. The solution H₂SO₄-sodium xylenesulfonate-H₂O has attracted interest as a

delignifying reagent and has been extensively studied at this Laboratory.⁴ A measure of the variation of acidity with reaction condition is necessary for interpretation of these results.

EXPEIRIMENTAL

The general technique used to gather the rate data involved the use of 1-millimeter pyrex glass tubing for batch reactors, holding these ampoules at isothermal conditions for the desired time, and analyzing the mixture for residual xylose. Loading of the reactors was accomplished with a modified hypodermic syringe that allowed rapid metering of about a 0.03-milliliter charge of reactant solution with a precision of at least 0.5 percent. A detailed description of the loading technique, heat transfer, and safety and strength characteristics of the glass reactors is available elsewhere.³ The heating-bath medium was a hydrogenated cottonseed oil which was vigorously agitated by an air-driven motor stirrer. Temperature control was effected by means of the on-off control of a small part of the total heat input. The temperature was held to within $\pm 0.1^\circ$ C. of the desired level. Exact time of the duration of reaction was measured by using an electric timer, that automatically started when the samples were immersed in the heating bath and stopped upon their removal. Samples were quenched immediately upon their withdrawal from the heating medium. Measurements of the reaction time interval are accurate to ± 0.2 second.

The contents of the ampoules were analyzed for xylose by the Somogyi method (20), using Nelson's chromogenic reagent (16). The analytical procedure is described in detail by Root.³ As a check on the possible interference of salt with the xylose analysis, two sets of experiments were performed. In the first set, known sugar samples were prepared, one containing no salt, and the other 35 grams of sodiuffixylenesulfonate per 100 milliliters of solution. The average xylose concentration of the two groups by six

analyses was 9.30 ± 0.13 milligrams per cubic centimeter and 9.32 ± 0.12 milligrams per cubic centimeter. In the second set of experiments, samples containing zero and 35 grams of sodium xylenesulfonate per 100 milliliters of solution were reacted until approximately 80 percent of the xylose disappeared. Before analyzing for xylose, each of the two groups of reacted samples was divided, and a known amount of xylose (about 20 percent of that originally present) was added. The results showed all xylose accounted for within experimental error in each of the two groups, indicating that the presence of salt and reaction products was probably not influencing the analysis.

Materials used for preparing the reactant solutions consisted of chemically pure xylose (Pfanstiehl Laboratories), reagent-grade sulfuric acid, and sodium 2,4 dimethylbenzenesulfonate. The salt was the purest form obtainable from Distillation Products Industries, Rochester, N.Y.; it was used as received, correction being made for the moisture present. In making up the solutions, 10 grams of xylose, along with the desired amount of salt, were weighed into a 100-milliliter volumetric flask. The appropriate quantity of a standard sulfuric-acid solution was pipetted into the flask and the contents diluted to the mark with distilled water. The concentrations and densities of the various solutions used are listed in table 1.

Within the experimental accuracy, the disappearance of xylose was linear on a semi-logarithmic plot of residual xylose versus time. Typical results are shown in figure 1. The associated first-order disappearance rate constant for each group of data was obtained by minimizing the sum.

³—Root, D. F. 1957. Kinetics of the acid-catalyzed conversion of xylose to furfural. Ph. D. Thesis, Chem. Eng. Dept., Univ. of Wisconsin, Madison, Wis. Dissertation Abs. 17:584.

⁴—Springer, E. L. 1961. Rate studies of the hydrotropic delignification of aspen wood. Ph. D. Thesis, Chem. Eng. Dept., Univ. of Wisconsin, Madison, Wis. Dissertation Abs. 22: 1930.

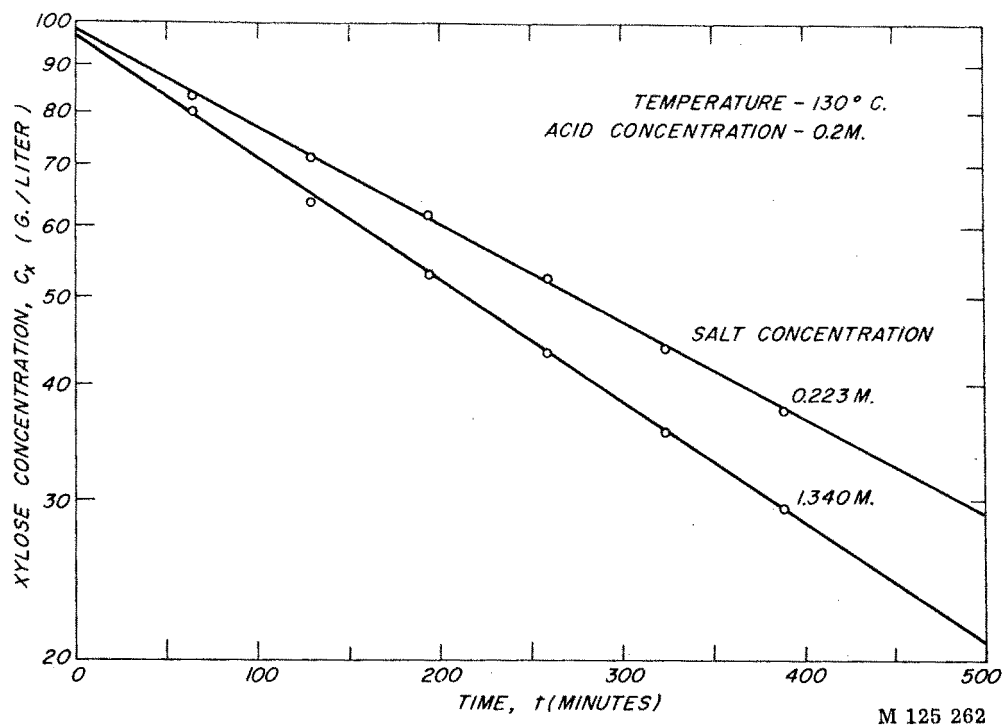


Figure 1.--The decomposition of xylose as a function of time.

$$S = \sum_i [\ln(C_x)_i - \ln(C_o) \exp(-k t_i)]^2 \quad (1)$$

where C_o (calculated initial xylose concentration) and k (first-order rate constant) are the calculated constants, and $(C_x)_i$ is the experimental xylose concentration at time, t_i . It should be noted that this is slightly different than minimizing the sum,

$$S^1 = \sum_i [\ln(C_x)_i - \ln(C_o) + kt_i]^2 \quad (2)$$

A least-squares treatment was also used to determine all the constants describing the salt and acid effect and the activation energy. Considering that approximately 800 data points were collected in this study, such a method of calculation would be prohibitive without use of data-processing equipment. Consequently, all experimental data were transferred directly to punched cards. A program was written that took all the data points (N) for one set of conditions (one k) and calculated a k and C_o by the above method.

Using these values, the square of the deviation for each experimental point was determined and the largest value discarded. With the remaining data points, a new k and C_o were calculated along with the probable error in any point. Using the new k and C_o , a deviation of the discarded point was found. If this was within five times the probable error, the calculation was complete and the first value of k and C_o was accepted. If the deviation exceeded five times the probable error, this point was rejected, and the entire

Table 1.--Density of sodium xylenesulfonate-sulfuric acid-xylose solutions at 24° C. (10 grams xylose per 100 milliliters in all solutions)

Acid concn- tration: C _a	Salt concn- tration: C _s	Density p	Acid concn- tration: C _a	Salt concn- tration: C _s	Density p
Molarity: centimeter	Molarity: centimeter	Grams per cubic centimeter	Molarity: centimeter	Molarity: centimeter	Grams per cubic centimeter
0.05	0	1.038	0.20	0	1.048
	.223	1.054		.223	1.063
	.446	1.070		.446	1.080
	.892	1.103		.892	1.113
	1.340	1.136		1.340	1.145
	1.563	1.152		1.563	1.161
.10	0	1.041	2.00	0	1.094
	.223	1.057		.223	1.111
	.446	1.073		.446	1.127
	.892	1.106		.892	1.159
	1.340	1.139		1.340	1.189
	1.563	1.155		1.563	1.205

calculation made again by finding the largest square of the deviation from the new constants with the remaining points (N-1). This arbitrary selection procedure allowed the rejection of any data that were grossly inconsistent with the rest of the set. Less than 10 percent of the data points were discarded by this procedure. Results taken from the data-processing equipment were: the values of \underline{k} and C_o , the probable error in \underline{k} , the number of data points used to calculate the constants, the maximum deviation of the points used, and the necessary identification. Periodic plots of the data were made as a check, or when there was some suspicion about the calculated rate (too few data points used, high probable error, inconsistent with other rates, etc.). When as few as four points were used by the computer, the entire experiment was repeated at that set of conditions. The computed values of the probable error in \underline{k} were about 3 percent, which is approximately the same as the precision with which a given rate can be experimentally reproduced. Values of C_o and \underline{k} calculated in this manner are listed in table 2.

It is apparent, both from table 2 and figure 1, that the intercept value, C_o , is in general, significantly less than the initial xylose concentration of 10 grams per 100 milliliters; however, the difference is small, never exceeding 6 percent of the experimental value. The precision of the results precludes the possibility of establishing quantitative trends of this difference, but it is apparent that both temperature and salt concentration affect it, indicating possible shifts in equilibria involving the xylose. A similar effect was observed with glucose by Fetzer and co-workers (7), in an extensive study of glucose

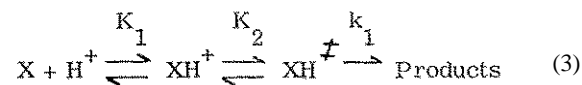
polymerization. They found that solutions of glucose, under the influence of heat and dilute acid, reach an equilibrium at which part of the glucose is polymerized to the disaccharide and polysaccharides of higher molecular weight. At a pH of 1.5 and a temperature of 145° C., this equilibrium was attained in about 25 minutes. The rate increased with increasing acid concentration and with increasing temperature. The degree of reversion increased with increasing sugar concentrations; glucose solutions, which were initially 10, 20, and 40 percent glucose, were, respectively, 9.37, 17.52, and 29.7 percent free glucose after equilibration at 145° C. Since the mechanism of polysaccharide hydrolysis is the same for both hexosans and pentosans, it would be expected that the reversion of xylose to polysaccharide would also occur to some degree. This is the logical explanation for the lower intercepts, although epimerization and anhydride formation may contribute slightly (18, 21). The formation of anhydrides and reversion products will result in a direct loss of xylose accounted for, since the analysis is based upon the reducing power of the aldehydic group.

The presence of these side reactions complicates the separation of the actual decomposition rate from the rates of reversion. A quantitative elucidation of even the primary side reactions would require a sizeable investigation with special attention to analytical techniques, and was considered outside of the scope of this study. If, however, equilibrium of these reactions is rapidly attained, then as the xylose decomposition proceeds, the equilibrium shifts, eventually making all of the xylose available. Since the effect is small, no correction has been made to the rate constant, \underline{k} , calculated as previously described.

RESULTS AND DISCUSSION

From this and other experimental work we have done, it appears that the presence of salt constitutes only an environmental change that produces a change in reaction rate, but does not alter the route of xylose decomposition. An explanation of such an inert salt effect has been offered by Brönsted (3) and has received wide experimental support; namely, that the accompanying change in reaction rate could be accounted for by the change

in the ratio of activity coefficients of the reactants and transition complex (primary salt effect). The xylose reaction can be represented schematically as,



If the concentrations of XH^+ and XH^{\ddagger} are small

Table 2.--Experimental and calculated rates of xylose decomposition in sodium xylenesulfonate-sulfuric acid-water solutions --Con.

Acid concentration: C_a	Salt concentration: C_s	Density: ρ	Ionic strength: μ	Hydrogen ion: C_H	Intercept: C_o	Rate constant		
						Experimental: $k \times 10^3$	Calculated: $k_c \times 10^3$	Deviation: δ
Molarity ³	Molarity	Grams per cubic centimeter	Molarity	Molarity	Grams per 100 milliliter	Minutes ⁻¹	Minutes ⁻¹	Percent
TEMPERATURE -- 120° C.								
0.05	0	0.9818	0.049	0.0483	9.57	0.221	0.218	1.2
	.2115	.9970	.263	.0496	9.87	.241	.244	-1.1
	.4230	1.0121	.476	.0507	9.90	.277	.272	1.6
	.8460	1.0433	.904	.0529	9.77	.326	.338	-3.6
	1.2689	1.0745	1.331	.0549	9.76	.438	.418	4.5
	1.4804	1.0897	1.545	.0559	9.58	.459	.464	-1.1
.10	0	.9847	.097	.0960	9.71	.412	.409	.8
	.2115	.9998	.311	.0973	9.80	.440	.444	-.8
	.4230	1.0149	.526	.0986	9.94	.484	.482	.5
	.8460	1.0462	.954	.1011	9.97	.566	.567	-.2
	1.2689	1.0774	1.382	.1037	9.80	.679	.668	1.5
	1.4804	1.0925	1.596	.1050	9.50	.725	.725	-.1
.20	0	.9913	.193	.1913	9.78	.815	.813	.3
	.2115	1.0055	.408	.1927	9.87	.857	.860	-.4
	.4230	1.0216	.622	.1941	10.07	.910	.910	.0
	.8460	1.0528	1.050	.1969	9.80	1.02	1.02	-.1
	1.2689	1.0830	1.479	.1999	9.78	1.19	1.14	4.0
	1.4804	1.0982	1.694	.2015	9.50	1.18	1.21	-2.5
TEMPERATURE -- 130° C.								
.05	0	.9733	.048	.0476	9.87	.617	.607	1.6
	.2097	.9883	.260	.0485	9.84	.672	.677	-.7
	.4194	1.0033	.471	.0494	9.72	.728	.751	-3.2
	.8388	1.0342	.894	.0509	9.80	.958	.926	3.3
	1.2582	1.0652	1.316	.0526	9.77	1.17	1.14	2.3
	1.4679	1.0802	1.528	.0533	9.74	1.24	1.26	-1.8
.10	0	.9761	.096	.0948	9.86	1.12	1.15	-3.0
	.2097	.9911	.307	.0957	9.88	1.31	1.25	5.2
	.4194	1.0061	.519	.0966	9.56	1.33	1.34	-1.2
	.8388	1.0371	.942	.0984	9.68	1.56	1.57	-.2
	1.2582	1.0680	1.364	.1003	9.80	1.81	1.83	-1.0
	1.4679	1.0830	1.576	.1013	9.64	2.00	1.98	1.5
.20	0	.9827	.190	.1891	9.91	2.21	2.22	-.6
	.2097	.9967	.402	.1900	9.77	2.42	2.35	2.8
	.4194	1.0127	.614	.1910	9.73	2.43	2.49	-2.3
	.8388	1.0436	1.037	.1930	9.69	2.80	2.78	.5
	1.2582	1.0736	1.461	.1951	9.81	3.12	3.11	.4
	1.4679	1.0886	1.673	.1963	9.74	3.31	3.29	.4

compared to X and K_1 and K_2 are equilibrium constants, the rate can be expressed as,

$$\frac{dC_X}{dt} = -k_1 K_2 K_1 C_X C_H \frac{f_H^i}{f^{\ddagger}} \quad (4)$$

where f_x^i , f_h^i , f^{\ddagger} are the molar activity coefficients

$$\frac{1}{C_X} \frac{dC_X}{dt} = k = k_o C_H f_H^i / f^{\ddagger} \quad (5)$$

Table 2.--Experimental and calculated rates of xylose decomposition in sodium xylenesulfonate-sulfuric acid-water solutions--Con.

Acid concentration:	Salt concentration:	Density:	Ionic strength:	Hydrogen ion ¹ :	Intercept:	Rate constant		
C_a	C_s	ρ	μ	C_{H^+}	C_0	Experimental: $k \times 10^3$	Calculated: $k_c \times 10^3$	Deviation ² δ
<u>Molarity³</u>	<u>Molarity</u>	<u>Grams per cubic centimeter</u>	<u>Molarity</u>	<u>Molarity</u>	<u>Grams per 100 milliliter</u>	<u>Minutes⁻¹</u>	<u>Minutes⁻¹</u>	<u>Percent</u>
TEMPERATURE -- 140° C.								
0.05	0	0.9641	0.048	0.0469	10.04	1.58	1.59	-0.5
	.2077	.9790	.256	.0476	9.89	1.86	1.77	5.0
	.4154	.9939	.465	.0482	9.85	1.88	1.97	-4.5
	.8308	1.0245	.883	.0493	9.81	2.40	2.42	-.9
	1.2461	1.0552	1.301	.0505	9.70	3.06	2.99	2.1
	1.4538	1.0700	1.510	.0511	9.84	3.34	3.32	.4
.10	0	.9669	.094	.0936	9.93	2.99	2.97	.8
	.2077	.9818	.303	.0942	9.84	3.23	3.20	.9
	.4154	.9966	.512	.0949	9.76	3.38	3.45	-2.1
	.8308	1.0273	.930	.0961	9.77	4.08	4.02	1.4
	1.2461	1.0580	1.348	.0975	9.66	4.63	4.68	-1.1
	1.4538	1.0728	1.557	.0982	9.59	5.12	5.05	1.4
.20	0	.9734	.188	.1869	9.82	5.90	5.87	.5
	.2077	.9874	.397	.1876	9.76	6.33	6.20	2.1
	.4154	1.0032	.606	.1882	9.70	6.42	6.55	-1.9
	.8308	1.0338	1.024	.1896	9.71	7.20	7.30	-1.4
	1.2461	1.0635	1.442	.1910	9.50	8.23	8.15	1.0
	1.4538	1.0784	1.651	.1918	9.50	8.70	8.61	1.0
TEMPERATURE -- 150° C								
.05	0	.9547	.047	.0463	9.75	4.02	4.07	-1.1
	.2057	.9694	.253	.0468	9.78	4.57	4.51	1.2
	.4114	.9841	.460	.0472	9.69	5.07	5.01	1.1
	.8228	1.0145	.873	.0479	9.72	6.14	6.17	-.5
	1.2341	1.0448	1.286	.0487	9.66	7.64	7.60	.6
	1.4398	1.0595	1.492	.0491	9.50	8.45	8.43	.3
.10	0	.9574	.093	.0925	9.66	7.27	7.61	-4.7
	.2057	.9721	.299	.0929	9.91	8.49	8.24	3.0
	.4114	.9869	.506	.0933	9.84	9.29	8.91	4.1
	.8228	1.0172	.919	.0942	9.66	10.4	10.4	-.5
	1.2341	1.0476	1.332	.0950	9.70	12.0	12.2	-1.7
	1.4398	1.0623	1.538	.0955	9.72	13.3	13.2	.9
.20	0	.9639	.185	.1848	9.80	14.9	15.2	-2.0
	.2057	.9777	.392	.1852	9.73	16.2	16.1	.7
	.4114	.9933	.598	.1856	10.05	17.6	17.0	3.5
	.8228	1.0236	1.012	.1865	9.62	18.8	18.9	-.8
	1.2341	1.0531	1.425	.1875	9.68	20.7	21.1	-1.7
	1.4398	1.0678	1.632	.1880	9.64	22.6	22.3	1.5
1.00	0	1.0071	.924	.9232	9.70	94.5	96.1	-1.7
	.2097	1.0219	1.130	.9236	9.74	103	102	.5
	.4194	1.0366	1.336	.9241	9.77	111	109	1.9
	.8388	1.0660	1.749	.9252	9.62	123	123	.1
	1.2582	1.0936	2.162	.9263	9.40	138	139	-1.1
	1.4679	1.1083	2.369	.9269	9.48	149	148	.2

¹Total concentration of the solvated proton including the contribution of secondary ionization.

²Based on the experimental value.

³Nominal acid molarity at 24° C. All other molarities at temperature indicated.

of the xylose, hydrogen ion, and intermediate complex respectively; C_H is the concentration of hydrogen ion (gram equivalent per liter); and k_o is the rate constant in the infinitely dilute solution.

By employing the extended Debye-Hückel equation for the activity of the ionic species and the typical exponential salt-effect for the activity coefficient of a nonelectrolyte, equation (5) becomes:

$$\ln(k/C_H) = \ln k_o + B\mu \quad (6)$$

where μ is the total ionic strength (gram equivalent per liter) and B a constant.

A more detailed explanation of the steps involved in the derivation of equation (6) may be found in texts treating the subject (8, 13). It should be noted, however, that molar activity coefficients and molar concentrations have been used; thus, the derivation of equation (6) assumes the molar activity coefficient to be directly proportional to the rational activity coefficient. Molar units have been used because they reflect the effect of temperature, and the data correlated by equation (6) was slightly better when these units were used. Although the extended equation for the ion activity coefficients is not expected to hold for wide ranges of electrolyte concentration, equation (6) has been successfully used to correlate data for salt concentrations as high as 4 molars (15). Lack of knowledge of the behavior of ionic species in concentrated solutions precludes any theoretical justification for extending the application of the above equations to solutions more concentrated than 0.1 molar; nevertheless, they have been used in the past and are a convenient starting point for correlating data.

The application of equation (6) requires a knowledge of the hydrogen-ion concentration and the ionic strength at reaction conditions. The total hydrogen-ion concentration (C_H) consists of the first hydrogen from sulfuric acid, this entire quantity being available, plus an additional small amount from the dissociation of the bisulfate ion, less that associated as 2,4 dimethylbenzenesulfonic acid. It is necessary to have the ionization constants for the bisulfate ion and xylene-sulfonic acid. No data are available for the latter, but on the basis of data for the isomer, 2,5 dimethylbenzenesulfonic acid (11) and other struc-

turally related acids (1, 2, 5), it was assumed to be entirely dissociated at reaction conditions. Measurements on the bisulfate system have been made by Lietzke, Stoughton, and Young (14) for temperatures as high as 275° C. and ionic strengths to 4.0 molal. Their results are expressed by the following equations:

$$\log Q = \log K + 4S \sqrt{I} / (1 + 0.4\sqrt{I}) \quad (7)$$

$$\ln K = \frac{1283.108}{T} + 12.31995 - 0.0422322T \quad (8)$$

where T is the absolute temperature (°K), I the molal ionic strength, K the thermodynamic equilibrium constant, Q the concentration dissociation constant (molal units), and S the Debye-Hückel limiting slope for a singly charged ion.

Employing a trial and error procedure, equations (7) and (8), in conjunction with the equation defining the ionic strength,

$$I = (\text{acid}) + (\text{salt}) + 2(\text{sec } H^+) \quad (9)$$

were solved for the total hydrogen-ion concentration and the ionic strength in molal units. These were then converted to molar units by using the solution density at room temperature (table 1), and assuming the solutions to have the same coefficient of expansion as water. Values of C_H , μ , and ρ thus obtained are listed in table 2.

The data group for each acid and temperature level was correlated using equation (6). Table 3 lists the resulting values of the slope, B, and intercept, k_o , while the general character of the correlation is illustrated by the data for 140° C. given in figure 2.

The last columns of table 2 show the value of the rate constant calculated from equation (6) using the appropriate values of B and k_o from table 3, and the deviation of the calculated value from the experimental value. Apparently the form of the Bronsted-Debye-Hückel equation can adequately represent the experimental data. However, the variation of the slope and intercept with acid concentration would not be expected, and it is evident that the acid concentration has an effect other than what was accounted for by the assumed functional form for the activity coefficients in equation (5) or by consideration of the secondary salt effect on the bisulfate equilibrium.

It is possible to advance a variety of theories

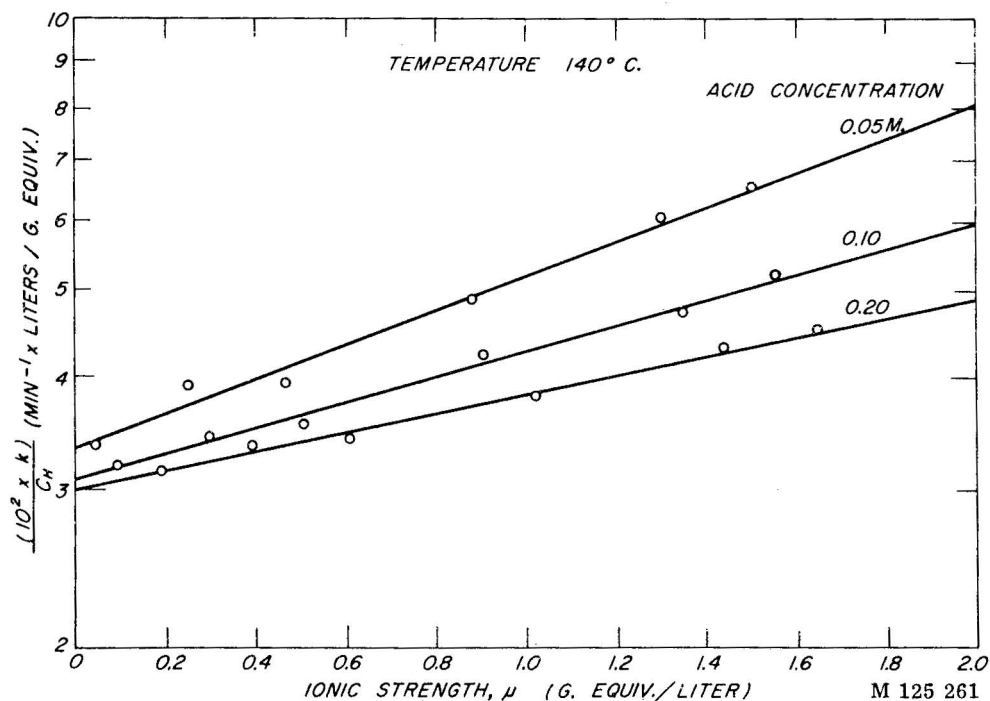


Figure 2.--Influence of ionic strength on the rate of decomposition of xylose.

hinging about equation (5) that might explain this effect of acid; for example, assuming the activity coefficient of the neutral molecule or hydrogen ion is dependent upon acid concentration. Attempts to use the Guggenheim extension of the Debye-Hückel theory, where only those ions of opposite sign to the reacting ion are considered to influence the ionic-activity coefficients, failed to yield true constants in the resulting equation for the reaction rate. Other assumptions as to the functional form of the activity coefficients might be made, but without independent experimental knowledge of them, any allocation of the effect remains arbitrary. Furthermore, the experimentally-measured reaction rate undoubtedly includes contributions from other modes of xylose disappearance that complicate any interpretation. To some extent these effects may be reflected in the values for k_0 which decrease slightly with acid concentration at each temperature.

Since the intercept value, k_0 , is the reaction rate constant in infinitely-dilute solution, it cannot be measured directly but can only be approximated by extrapolation of measurements taken at low ionic strengths. In this work, the solutions of lowest ionic strength are those which contain

no sodium xylenosulfonate. Restricting consideration of the effect of ionic strength to these solutions, the effect appears as the reverse of that obtained by the addition of salt to solutions of fixed acid composition. This is clearly demonstrated by the three points on the left side of figure 2. A possible explanation of this behavior is the occurrence of concurrent base reactions that were not considered in the derivation of equation (6). Although this explanation is substantiated only in part by consideration of the data presented here, it is supported by more recent experimental work done at the Laboratory. Thus, the increase in the value of the intercept for the 0.05 and 0.1-molar acid solutions over that of the 0.2-molar acid solution can be ascribed entirely to the presence of concurrent base reactions. The value of the intercept for more acidic solutions than 0.2 molar would not be expected to decrease perceptibly as the hydroxyl-ion concentration rapidly becomes insignificant. This is verified for the 1.0 molar at 150° C., where the value of the intercept (table 3) is shown to agree, within experimental error, with that measured for the 0.2-molar solution.

When the presence of concomitant reactions is recognized, a probable explanation for the variation of the slope B with acid concentration

Table 3.--Slope and intercept values for the correlating equation, $\log (k/C_H = \text{Log } k_0 + Bu)$

Temperature	Acid concentration ¹	Slope	Intercept
°C.	Molarity	Molarity ⁻¹	Minutes ⁻¹
120	0.05	0.178	4.42
	.10	.140	4.13
	.20	.100	4.07
130	.05	.182	12.5
	.10	.138	11.8
	.20	.105	11.2
140	.05	.194	33.2
	.10	.144	30.8
	.20	.106	30.0
150	.05	.205	86.0
	.10	.156	79.7
	.20	.109	78.7
	1.00	.129	79.2

¹Nominal acid molarity at 24° C.

arises, since it would be expected that these reactions would respond differently to a change in ionic strength than the acid-catalyzed reaction. In addition to the difference in the primary salt effects, it is likely that increasing the ionic strength results in an increase in hydroxyl-ion because of an increase in the dissociation of water (10), which would enhance the effect of increasing the slope with decreasing acidity.

Introduction of a term for the base reaction makes it apparent that, except for the case of equal salt effects for the acid and base reactions, the plot of $\log k/C_H$ will deviate from linearity.

By taking the contribution of the base reaction to the total reaction rate to be negligible at 0.2-molar acid and above, it is possible to demonstrate that the deviation from linearity is so small it is experimentally imperceptible at the 0.05 and 0.1-molar acid concentrations. The reason for this, of course, is the relatively small part of the reaction rate that is due to base reactions at these acid levels. Additional support for the above explanation is derived from the 1.0-molar acid data given in table 3 where the slope, B, is practically the same as that for 0.2 molar. This fact is in agreement with the assumption of a negligible base reaction above 0.2 molar.

The energy of activation for the acid-catalyzed

reaction was calculated using the relationship,

$$E_a = RT^2 \frac{d(\ln k)}{dT} \quad (10)$$

Only the data (intercepts in table 3) for 0.2-molar acid were used because lack of information on the concurrent reactions prevents calculation of a value for k_0 which would weigh all the points.

By this method a value of 32,630 calories per gram mol was calculated for the acid-catalyzed reaction. This can be compared to values of 33,560 and 32,000 calories per gram mol (6) reported for temperature ranges of 160°-280° C. and 100°-200° C. respectively.

All of the experimental reaction rates (k) were well correlated by the Arrhenius equation, and the results are given in table 4 for all of the experimental conditions. The average activation energy of all the values reported in table 4 is 32,068 calories per gram mol. The small difference between this value and the activation energy for the acid-catalyzed reaction, as calculated above, indicates that either the activation energy for the base-catalyzed reaction is near that for the acid-catalyzed reaction, or that it accounts for only a small part of the total reaction rate under these conditions.

Table 4.--Activation energy for experimentally measured reaction rates

Acid concentration	Salt concentration	Activation energy
C _a	C _s	E _a x 10 ⁻³
Molarity	Molarity	Calories per gram mol
0.05	0	31.9
	.223	32.5
	.446	32.0
	.892	32.1
	1.34	31.5
	1.563	32.1
0.1	0	31.7
	.223	32.3
	.446	32.4
	.892	32.0
	1.34	31.6
	1.563	32.0
0.2	0	32.1
	.223	32.3
	.446	32.5
	.892	32.0
	1.34	31.5
	1.563	32.5

Average activation energy 32.1 x 10³

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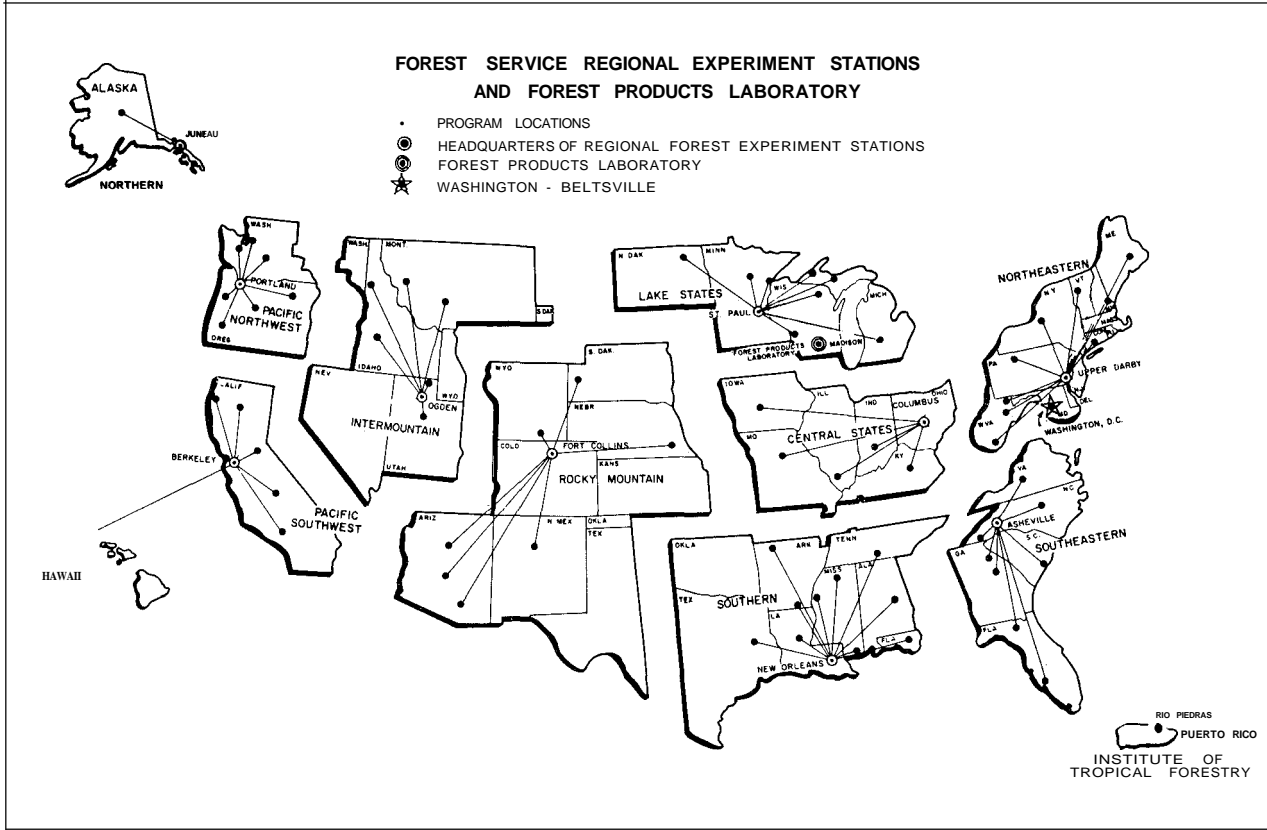


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