the values to be 428.6 and 409.5° from surface tension measurements.[4]

The molal latent heats at the b. p. were calculated as well as the Trouton constant by the use of the Clausius–Clapeyron equation and by an equation suggested by Kistyakowsky.[5] The values are given in Table II, the values under 1 being those obtained from the former and those under 2 from the latter equation.

TABLE III

	Molal latent heats		Trouton constant	
	1	2	1	2
trans	9960	9614.9	21.7	20.9
cis	10210	9799.4	21.8	20.9

It is obvious from Fig. 1 that the latent heat is a linear function of the temperature only over a small range of temperature.

In conclusion, we wish to express our gratitude to the following for their assistance in this work: T. Pilkington, I. Rush, J. Leslie and H. Nemetz.

Summary

1. The vapor pressures of *cis*- and *trans*-decahydronaphthalene have been measured over a range of temperature from −30 to 223°.

2. The critical temperatures, latent heats and Trouton constant have been calculated from the data.

VANCOUVER, B. C., CANADA RECEIVED OCTOBER 5, 1944

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[4] C. H. Davenport, M.A.Sc. Thesis, University of British Columbia, 1939.

[5] Kistyakowsky, *Z. physik. Chem.*, **107**, 65 (1923).

Kinetics in Acid Media: The Correlation of Reaction Rates with Acidity Function

BY CHARLES W. DEANE

Recently, Lewis and Bigeleisen[1] presented an extension of available acidity function data into fuming sulfuric acid concentrations by a plot showing the effect of sulfur trioxide up to 100% sulfur trioxide concentration. Since Hammett and Deyrup[2] were able to correlate rates and acidity function up to 100% sulfuric acid, a test of the new data with related kinetic data is in order, and the quantitative results and interpretation of such a study for five organic acid decompositions are here presented.

Through assuming coincidence at 50 mole % sulfur trioxide with earlier results[2] upon sulfuric acid for concentrations up to 100% sulfuric acid, the acidity function has been presented by Lewis and Bigeleisen as a direct extension of the data of Hammett and Deyrup because the results of the latter are said[1] to be "more precise." Simultaneously to the publication of Lewis and Bigeleisen,[1] new kinetic data obtained in fuming sulfuric acid were presented and discussed,[3] and the variant effects of sulfur trioxide on organic acid decompositions in oleum published to date were given. A summary of these effects is here shown:

Organic acid	Influence of SO_3 on reaction rate
Oxalic[4]	Slight (increase to approx. 14% SO_3; decrease above)
Malic[5]	Marked inhibition
Citric[6]	Pronounced inhibition
Formic[7]	Acceleration (degree not measured)
o-Benzoylbenzoic[3]	Moderate acceleration

It was pointed out[3] that since organic oxygen compounds are highly ionized basically in strong sulfuric acid, acid–base catalysis is effective; because of the exceptional behavior of oxalic, malic, and citric acids, the reactions for these acids appear anomalous, and to be governed only incidentally by simple ionic factors.

To explain fully the reaction mechanism, an all-inclusive theory should cover all of these various phenomena. A mechanism should correlate known facts and predict new ones. Aimed to this end, Hammett and Deyrup[2] have developed a correlation showing a reasonable constancy in the sum of log k (reaction velocity constant) plus H_0 (acidity function) for the decompositions of six organic acids, and for acetophenone oxime, in sulfuric acid concentrations up to 100%.

The correlation of the velocity constants in the decomposition of *o*-benzoylbenzoic acid with the extension of the acidity function by Lewis and Bigeleisen is quite striking. Table I shows the constancy of the sum of H_0 and log k at various acid and oleum concentrations up to 28.8% sulfur trioxide concentration. Part of this table supersedes part A of Table IV of Hammett and Deyrup[2] which is based on an erroneous earlier plot of Gleason and Dougherty[8] wherein the sulfuric acid axis is 10% low throughout.

Owing to the widely variant behavior in fuming acid indicated in the introduction, certain questions concerning correlation above 100% sulfuric acid arise: (1) whether *o*-benzoylbenzoic acid, as previously suggested,[3] is more ideal when the earlier correlation method[2] is applied? (2) Would data on some other studied organic acid serve better?

To test these points, calculations with the new data of Lewis and Bigeleisen have been made, to-

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[1] Lewis and Bigeleisen, THIS JOURNAL **65**, 1144 (1943).

[2] Hammett and Deyrup, *ibid.*, **54**, 2721 (1932).

[3] Deane with Huffman, *Ind. Eng. Chem.*, **35**, 684 (1943).

[4] Wiig, THIS JOURNAL, **52**, 4737 (1930).

[5] Dittmar, *ibid.*, **52**, 2746 (1930); Whitford, *ibid.*, **47**, 953 (1925).

[6] Wiig, *ibid.*, **52**, 4729 (1930).

[7] Deright, private communication.

[8] Gleason and Dougherty, THIS JOURNAL, **51**, 310 (1929).

Table I

Showing the Constancy of [log $k + H_0$] for the Decomposition of *o*-Benzoylbenzoic Acid in Sulfuric Acid and Oleum of Various Concentrations at 75 and 85°

% H_2SO_4	% Free SO_3	H_0 at 25°	Log k at 75°	Log k at 85°	Log $k + H_0$ at 75°	Log $k + H_0$ at 85°
86		− 7.34	−4.06	....	−11.40	.....
89		− 7.74	−3.53	....	−11.27	.....
91		− 8.01	−3.23	....	−11.24	.....
93		− 8.20	−2.89	....	−11.09	.....
96		− 8.67	−2.32	....	−10.99	.....
98		− 8.95	−2.11	−1.64	−11.06	−11.59
100	0	−10.70	−1.93	−1.47	−12.63	−12.17
100.4	1.8	−10.71	−1.90	−1.43	−12.61	−12.14
101.8	8.0	−10.73	−1.89	−1.42	−12.62	−12.15
103.2	14.0	−10.94	−1.87	−1.42	−12.81	−12.36
104.5	20.0	−11.04	−1.84	−1.38	−12.88	−12.42
105.4	24.0	−11.16	....	−1.36	.....	−12.52
105.9	26.2	−11.22	−1.77	−1.34	−12.99	−12.56
106.5	28.8	−11.45	....	−1.32	.....	−12.77

gether with the reaction rate data measured on *o*-benzoylbenzoic acid in fuming sulfuric acid. The following summary, comparing the results with those earlier presented, indicates that the correlation for *o*-benzoylbenzoic acid is definitely more consistent than other organic acids (except formic, below 100% sulfuric acid concentration) which appear to be correlated by this method.[2] In Table II, it will be noted the organic acids have been arranged in the order of their best agreement, or constancy, for the total range of sulfuric acid concentration over which data have been obtained. Due to the inhibition in oleum pointed out above for malic, oxalic, and citric acids, however, it is evident that this correlation, or the explanation of catalysis by acidity function in fuming sulfuric acid, does not cover these cases and that other factors predominate.

Table II

Comparison of Deviations Obtained by Acidity Function Correlation for Various Organic Acid Decompositions

Organic acid	Sulfuric acid concn. range, %	^{a}Range of variation from midpoint of log $k + H_0$	$\left[\frac{^a\text{Range}}{\text{acid concn. range, \%}}\right]$
Formic	85.0 to 98.9	0.29	0.021
o-Benzoylbenzoic	100 to 106.5 (= 0 to 28.3% free SO_3)	.16	.025
o-Benzoylbenzoic	86.0 to 100%	.40	.029
Malic	97.1 to 98.7	.13	.081
Citric	94.8 to 99.0	.505	.120
Oxalic	97.0 to 99.4	.30	.125
Triphenylacetic	95.9 to 98.3	.41	.171
*(Acetophenone oxime)	(93.6 to 98.7)	(0.055)	(0.009)

* Although not an organic acid, this compound is included in the table since it correlates log k plus H_0 even better than the organic acids listed above.

A consideration of the following reversible equilibria is presented to bring out the relation between the decomposition of *o*-benzoylbenzoic acid and the other organic materials studied to date

$$\overset{\text{I}}{\text{XCOOH}} + \text{H}^+ \rightleftharpoons \overset{\text{II}}{\text{XCOOH}_2^+} \rightleftharpoons \overset{\text{III}}{\text{XCO}^+} + \text{H}_2\text{O}$$

where XCOOH is the organic acid; in fuming sulfuric acid, H^+ can be replaced by the free sulfur trioxide.

Whether it is ion II or ion III that reacts is in this discussion not too important, but it may be better to consider that III determines the reaction rate. It follows that

$$\log k = -H_0 + \text{const.}$$

This is found true for the *o*-benzoylbenzoic; when fully studied, it may also hold for formic acid. In certain other organic materials, a more complicated situation is found when a second type of reaction occurs at some high value of $-H_0$. For simplicity of example, this is regarded as the removal of another OH^- from a di- or polyhydroxylic substance. This reaction yields a new substance which may inhibit the reaction, and in certain of the cases given, evidently does.

In support of the acidity function theory, the exact mechanism is of interest. The original *o*-benzoylbenzoic acid, which must remain in a plane, has some molecules with a carboxyl group next to the oxygen; and in others, next to the benzene of the ring. These two sets may be pictured in rapid equilibrium with each other, with the latter in condition to react directly in accord with Newman's step III.[9] In the case of *o*-benzoylbenzoic acid the reaction appears to be of such directness and simplicity that nearly perfect yields of anthraquinone occur.

Summary

The data and discussion above lead to these conclusions:

1. The new data[1] on acidity function *vs.* % sulfur trioxide are highly consistent with reaction rate findings upon *o*-benzoylbenzoic acid,[3] in fuming acid concentration when an earlier correlation[2] is applied.
2. In fuming sulfuric acid, the *o*-benzoylbenzoic acid decomposition corroborates the correlation method of Hammett and Deyrup.[2]
3. A general quantitative method of correlating the rate of *o*-benzoylbenzoic acid condensation in oleum to 28.3% free sulfur trioxide concentration is presented.
4. From the demonstrated close correlation of kinetic behavior from 0 to 28% free sulfur trioxide concentration, it is predicted at higher sulfur trioxide concentrations, that the rate of *o*-benzoylbenzoic acid condensation—at a given temperature—will increase up to 55% free sulfur trioxide (80 mole %); beyond (for concentrations of 55 to 100% sulfur trioxide) only slightly.
5. No such simple means seem to explain the inhibition by sulfur trioxide observed in the decompositions of malic, oxalic and citric acids. Possible mechanisms to explain this are discussed.
6. It is demonstrated that the acidity function correlation explains the kinetics for the decomposition of acetophenone oxime better than

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(9) Newman, This Journal, 64, 2324 (1942).

for any of the organic acid decompositions studied to date.

7. A new means for measuring the acidity function of oleum up to 28.3% free sulfur trioxide concentration, by kinetic measurements with *o*-benzoylbenzoic acid, is shown to have experimental basis and proof.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Poisoning of Nickel Hydrogenation Catalysts by Water Vapor[1,2]

BY W. B. BURFORD, III, AND J. C. W. FRAZER[3]

During some experiments on the hydrogenation of ethylene over nickel catalysts anomalous results were observed which indicated that traces of water vapor might be acting as a catalyst poison. The following experiments, which were performed to detect the limit of such action, showed that the effect could be observed at a pressure of water vapor as low as 10^{-4} mm.

A similar poisoning effect by oxygen or water vapor was observed by Normann[4] for palladium hydrogenation catalysts, and Woodman and Taylor[5] have shown that water vapor causes a decrease in rate of hydrogenation over zinc chromite catalysts, although in this case the amount of water vapor was much larger.

Experimental Part

Catalyst.—To make the catalyst as sensitive to poisoning as possible it was prepared with a small, highly active surface area. This was done by etching C. P. nickel pellets of 1 to 3 mm. diameter with aqua regia to produce a mat, after which they were oxidized in a stream of oxygen at 550 to 700° for sensitization. Batches of about 70 g., occupying about 25 ml., were then placed in the catalyst chamber and reduced *in situ*. These catalysts had an activity sufficient to convert 150 ml. per minute of ethylene–hydrogen mixture practically completely at temperatures above 75°, but only about 30% at room temperature.

Reagents.—The ethylene was "anesthetic" grade, with listed impurities of 0.35%. It was purified by passage first through a pre-catalyst tube containing finely divided nickel reduced from carbonate which was maintained at a slightly higher temperature than the main catalyst tube. The gas next passed through a trap cooled with Dry Ice in acetone and then through a large tube of phosphorus pentoxide free from phosphorus trioxide.

The hydrogen was a commercial grade prepared electrolytically and contained about 1.8% oxygen. It was purified by passage over platinized asbestos at 350° with subsequent drying in the same manner as for the ethylene.

Apparatus and Procedure.—Known mixtures of the purified gases were prepared and measured by flow meters patterned after a design by Bruun,[6] and were then led to the catalyst bulb, part of the hydrogen being by-passed through the humidifying train and returned to the main stream. In the experiments cited the gas was generally mixed in the ratio 3 hydrogen to 1 ethylene at a total flow of 200 ml. per minute.

In the by-pass humidifying line the hydrogen first picked up water vapor from a trap at room temperature, after which the excess moisture was frozen out in a condenser cooled with Dry Ice in acetone. Temperatures as low as −106° were obtained by evacuating the vessel containing the Dry Ice.

The gases coming from the catalyst chamber were analyzed in a standard gas analysis apparatus. Ordinarily analyses were made only for ethylene by absorption in fuming sulfuric acid, though a few check determinations of the other constituents were also carried out. Sample analyses agreed with flowmeter readings within one half per cent.

The operating technique was to cool the catalyst chamber in boiling water immediately after reduction of the catalyst until the thermocouple within the catalyst bed showed 108°. At this point the gas mixture, which had been flowing to waste under operating conditions for some time to sweep out the system, was admitted to the catalyst tube. The heat of reaction was great enough to maintain the reaction vessel at 106 to 108° when the vessel was immersed in boiling water. Samples were taken at numerous time intervals beginning at two minutes and continuing for several hours.

Results

Using the catalyst which gave complete hydrogenation with pure gases above 75°, it was found that at 107° the presence of 3×10^{-4} mm. of water vapor was sufficient to cause a decrease of 5% in the amount of hydrogenation after a reaction period of forty minutes. With higher amounts of water vapor—about 10^{-3} mm.—the drop in activity was more pronounced and it required less time for a noticeable effect to occur. With pressures of 0.1 mm. of water vapor the activity dropped ultimately to about 30% of its normal value.

One attempt to find an effect of water vapor at a pressure of 5×10^{-5} mm. gave negative results after an hour at 107°, so that 10^{-4} mm. is presumably the lowest pressure at which poisoning can be detected under these conditions. However, since the catalyst is not as sensitive to poisoning at 107 as at 74°, the lowest temperature at which it attains complete conversion, it is possible that some retardation might be observed for smaller water vapor pressures at the lower temperature.

Effects with such small amounts of water vapor were probably made possible by the extremely sensitive form of catalyst used. The surface

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(2) Abstract of part of a dissertation submitted to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Original manuscript received January 27, 1943.

(3) This manuscript is published after the death of Professor J. C. W. Frazer on July 28, 1944. His part in the work and the preparation of the original manuscript of this article was too considerable to permit its publication without acknowledgment.

(4) W. Normann, *Ber.*, **55**, 2193 (1922).

(5) J. O. Woodman and H. S. Taylor, THIS JOURNAL, **62**, 1393 (1940).

(6) Bruun, *Ind. Eng. Chem., Anal. Ed.*, **11**, 655 (1939).