the vagueness with which the concept of critical complex is encumbered. For the relatively small variations in water activity in question, the experimental data do not exclude the possibility that log $k + H_0 - \log a_{H_2O}$ rather than log $k + H_0$ is constant, although agreement is definitely less good for the former relation. It is also possible that there is some more or less accidental compensation between the factors a_{H_2O} and $f_{BH^+}f_S/f_Xf_B$ or that the hydration of the sucrose is a complicating factor.

It is to be noted that there is already evidence that some acid catalyses are not capable of correlation with the acidity function. Among these are the hydrochloric acid catalysis of the acetylchloroaminobenzene rearrangement,[10] and the hydrolysis of hydrogen cyanide recently studied by Krieble and Peiker.[11] In these cases there are large and specific effects of individual acids, and the trichloroacetic acid hydrolysis of sucrose can indeed be properly classified with them.

Summary

The rates of the acid catalyzed hydrolysis of sucrose, of ethyl acetate and of cyanamide in aqueous solutions of various strong acids in concentrations extending up to 7 molar can be closely correlated with the acidity function, H_0, which is to say with the measure of acidity given by a simple basic indicator, and with no other measure of acidity.

The variant behavior of trichloroacetic acid in the sucrose hydrolysis suggests the possibility of a general acid catalysis in the Brönsted sense, a catalysis by trichloroacetic acid molecules as well as by oxonium ion.

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[10] Harned and Seltz, THIS JOURNAL, **44**, 1475 (1922).

[11] Krieble and Peiker, *ibid.*, **55**, 2326 (1933).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Adsorption of Wool Violet (4BN) by Lead Sulfate and the Influence of the Adsorbed Dye on the Speed of Kinetic Exchange[1]

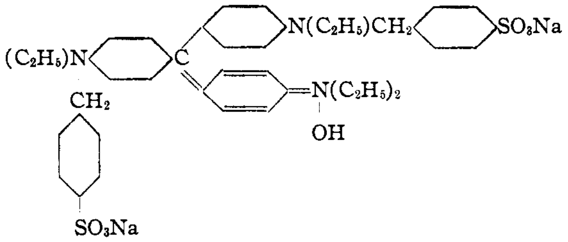
BY I. M. KOLTHOFF, W. VON FISCHER AND CHARLES ROSENBLUM

Ponceau 2R[2] and Ponceau 4R[3] have been used in a study of the adsorbent properties of lead sulfate. In the present work it appeared that wool violet 4BN has distinct advantages over the other dyes. The surface of lead sulfate is saturated with the wool violet at relatively small concentrations of the dye in the supernatant liquid; moreover, the lead salt of the dye is soluble enough to permit a study of the dye adsorption in the presence of a slight excess of lead ions in the solution. One cc. of a 0.5% solution of wool violet in water gives a colored precipitate when added to 5 cc. of 0.01 N lead nitrate, but remains clear with a 0.005 N solution.

Materials Used

Lead Sulfate.—This substance was prepared in a way similar to that described in a previous study,[4] and was used throughout in the air dried state.

Wool Violet 4BN.—A sample was obtained from the National Aniline and Chemical Company and purified by repeated recrystallizations. It was dissolved in alcohol, filtered and an equal volume of ether added to the filtrate. The crystalline precipitate was collected after several hours of standing, and the final product air dried. On heating in a vacuum oven at 65–70° for twelve hours the loss in weight was 0.5%. In Rowe's Colour Index (No. 698) the following formula of the wool violet is given: $C_{41}H_{44}N_3O_6S_2Na$. This corresponds to a molecular weight of 761 and a sodium content of 3.02%. The sodium content of the purified dye was determined according to the procedure of I. M. Kolthoff and J. Lingane[5] and was found to be 5.85 to 6.0%. This shows definitely that the wool violet is not a mono but a disodium salt to which we assign the formula: $C_{41}H_{45}N_3O_7S_2Na_2$, mol. wt. 801.



The nitrogen content of the dye was determined according to Kjeldahl and found to be 5.32, 5.31, 5.34% N. According to the above formula (disodium salt) the calculated percentage of sodium is 5.75 and of nitrogen 5.25.

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[1] Part of the material presented in this paper is taken from the master's thesis of William Von Fischer, University of Minnesota, 1933.

[2] F. Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 480 (1922).

[3] I. M. Kolthoff and Charles Rosenblum, THIS JOURNAL, **55**, 2664 (1933).

[4] Kolthoff and Rosenblum, *ibid.*, **55**, 2656 (1933).

[5] Kolthoff and Lingane, *ibid.*, **55**, 1871 (1933).

Experimental Methods.—In general the same procedures were followed as described in previous papers[3,4] unless otherwise stated.

Experimental Results

The Adsorption of Wool Violet by Lead Sulfate.—On shaking lead sulfate with solutions of the dye in various concentrations, adsorption equilibrium appeared to be established within half an hour. The amounts of dye adsorbed are given in Table I.

TABLE I

ADSORPTION OF WOOL VIOLET BY LEAD SULFATE FROM SATURATED SOLUTION IN WATER

(1 g. $PbSO_4$; 50 cc. solution)

Concn. of dye in mg. per liter Before ads.	After ads.	Dye adsorbed mg.	%
50	30.9	0.96	38.2
100	65.2	1.74	34.8
125	88.7	1.82	29.0
150	108.0	2.10	28.0
200	152.0	*2.40*	24.0
300	251.9	*2.41*	16.0
500	451.8	*2.41*	9.06
1000	952.2	*2.39*	4.78

The surface of the lead sulfate appears to be saturated with the dye at a final concentration of the latter of 150 mg. per liter. The same saturation value is reached at a smaller concentration if some lead nitrate is added to the solution (Table II) and at a larger concentration if the solution contains an excess of sodium sulfate (Table III, see also Fig. 1).

TABLE II

ADSORPTION OF WOOL VIOLET BY LEAD SULFATE FROM DILUTE LEAD NITRATE SOLUTIONS

(1 g. $PbSO_4$; 50 cc. solution)

Concn. of lead nitrate, N	Concn. of dye in mg. per liter Before ads.	After ads	Dye adsorbed mg. per 1 g.	%
5×10^{-4}	200	151	2.38	24.5
1×10^{-3}	50	21.8	1.41	56.4
1×10^{-3}	100	57.5	2.13	42.5
1×10^{-3}	200	150.4	*2.45*	24.8
1×10^{-3}	500	452.3	*2.38*	9.05
1×10^{-3}	700	651.1	*2.44*	6.10
1×10^{-3}	1000	952.8	*2.36*	4.72
5×10^{-3}	200	150.0	*2.44*	25.0

It was found that a larger adsorption of the dye resulted when a solution of the latter in water instead of in saturated lead sulfate solution was shaken for half an hour with the adsorbent (comp. curve 1 with 2 in Fig. 1). However, the adsorption curve obtained in the former case after twenty-four hours of shaking coincided exactly with the one obtained after half an hour of shaking when the dye solution was saturated with lead sulfate.

TABLE III

ADSORPTION OF WOOL VIOLET BY LEAD SULFATE FROM DILUTE SODIUM SULFATE SOLUTIONS

(1 g. $PbSO_4$; 50 cc. solution)

Concn. of sodium sulfate, N	Concn. of dye in mg. per liter Before ads.	After ads.	Dye adsorbed mg. per 1 g.	%
5×10^{-4}	200	154.6	2.27	27.7
10^{-3}	50	31.4	0.93	37.2
10^{-3}	100	69.9	1.51	30.1
10^{-3}	200	160.1	2.00	19.9
10^{-3}	500	455.0	2.25	9.00
10^{-3}	700	651.7	*2.41*	6.90
10^{-3}	1000	951.6	*2.42*	4.84
5×10^{-3}	200	170.6	1.47	14.7

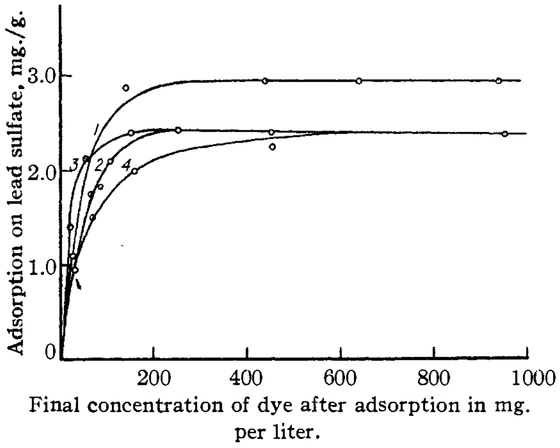

Fig. 1.—Adsorption isotherm for wool violet on lead sulfate at 25.5° with thirty minutes of shaking: 1, dye solution in water; 2, dye solution in saturated lead sulfate solution; 3, dye solution in excess lead ions; 4, dye solution in excess sulfate ions.

The adsorption of wool violet was also determined in the presence of small concentrations of nitric acid. In all cases the acid was shaken with the lead sulfate for two hours in order to saturate the solution with adsorbent, before the dye was added. Under these conditions adsorption equilibrium was attained within half an hour of shaking, and the same adsorption values were obtained after this time as after twenty-four hours of shaking. The dilute acid changes the color of the dye solution from blue violet to a more reddish violet. Therefore, in the colorimetric analysis, the standards were prepared with the same amount of nitric acid as the solutions to be analyzed contained.

From Table IV it is evident that the adsorption of the dye increases considerably in the presence of nitric acid.

TABLE IV

ADSORPTION OF WOOL VIOLET FROM DILUTE NITRIC ACID SATURATED WITH LEAD SULFATE

(1 g. $PbSO_4$; 50 cc. solution)

Concn. HNO_3, N	Concn. of dye in mg. per liter Before ads.	Concn. of dye in mg. per liter After ads.	Dye adsorbed mg. per 1 g.	Dye adsorbed %
10^{-3}	100	70.1	1.49	29.9
10^{-3}	200	151.9	2.40	24.1
10^{-3}	300	233.2	3.34	22.3
10^{-3}	400	315.0	4.25	21.2
10^{-3}	500	414.9	4.26	17.0
10^{-2}	100	69.8	1.51	30.2
10^{-2}	200	150.1	2.50	25.0
10^{-2}	300	217.5	4.13	27.5
10^{-2}	400	288.0	5.60	28.0
10^{-2}	500	386.6	5.67	22.7

Exchange between Dye Ions and Sulfate Ions in the Surface of Lead Sulfate.—Ten grams of lead sulfate was shaken for four days in a thermostat at 25° with 225 cc. of wool violet solution, containing 100 mg. of the dye per liter. After this time the suspension was centrifuged and a 200-cc. sample analyzed for lead. The lead concentration was found to be 2.69×10^{-4} N. The dye concentration after the shaking was found to be 42.6 mg. per liter. In another set of experiments 225 cc. of a solution containing 40 mg. of dye per liter (which is the wool violet concentration found at the end of the previous experiment) was shaken with 0.1 g. of lead sulfate for four days at 25°. The lead concentration was found to be 3.1×10^{-4} N.

Comparison of the results of the two sets of experiments shows that the adsorbed wool violet exchanges with sulfate ions in the surface of the adsorbent

$$\underset{\text{surface}}{PbSO_4} + \underset{\text{solution}}{\text{Wool Violet}} \longrightarrow \underset{\text{surface}}{\text{Pb Wool Violet}} + \underset{\text{solution}}{SO_4^{=}}$$

The solution thereby becomes supersaturated with lead sulfate and a small amount of the latter precipitates. This explains why the lead concentration in the first type of experiment is found to be smaller than in the second one. By making sodium determinations in dye solutions before and after adsorption, it was found that no sodium was adsorbed, although in some cases more than 50% of the dye was removed from the solutions. This confirms the above result that we are not dealing with an equivalent adsorption, but with an exchange between the dye ions and the sulfate ions in the surface of the lead sulfate. The adsorption of the dye ions in the presence of an excess of lead in the solution is also the result of an exchange, an amount of lead equivalent to the amount of dye adsorbed is removed from solutions by precipitation. Even in the presence of nitric acid, when the adsorption of the dye was much greater than in neutral medium (compare Tables I and IV) no sodium was found to be removed from the solution.

Effect of Wool Violet on the Speed of Kinetic Exchange and upon the Speed of Recrystallization of Lead Sulfate.—The distribution of thorium B between a solution and the surface of lead sulfate was determined according to the procedure described in a previous paper.[4] In the first place it was shown that adsorbed wool violet inhibits the kinetic exchange of lead between the surface of lead sulfate and a saturated solution of the latter in water. In this respect wool violet behaves in the same way as does ponceau;[6] therefore, only a few results will be given. The specific surface of the lead sulfate used in all of the experiments was found to be equal to 1.20 mg. of lead per gram after one hour of shaking with Th B in a saturated solution in water at 24°, and 1.31 mg. of lead per gram after two hours of shaking (the speed of shaking in all the following experiments was 400 cycles per minute). When the lead sulfate was shaken first with a solution containing 200 mg. of wool violet per liter of saturated lead sulfate and then one hour with Th B, the specific surface was found to be 0.90 mg. of lead per gram, thus showing the inhibiting effect of the dye upon the kinetic exchange. When the lead sulfate suspension was shaken first for one hour with Th B and then the dye added and shaken for another hour, a specific surface of 1.68 mg. was found. This high value is explained by the fact that the exchange adsorption between the dye and sulfate ions takes place in the presence of thorium B; consequently some of the radioactive lead disappears by precipitation of active lead sulfate.

A few sets of experiments were then made in 0.01 N nitric acid saturated with lead sulfate as a solvent. The solubility of the lead sulfate in 0.01 N nitric acid was determined at 24° and found to be equal to 2.77×10^{-4} moles per liter,[7] this figure being used in the calculations of the specific surface. In the following experiments 1 g. of lead sulfate was used and the volume of the solution was 29.88 cc. The temperature in all cases was kept constant at 24°.

[6] See Ref. 3, Tables V and VI.

[7] The method used was similar to that of H. H. Willard and J. L. Kassner, THIS JOURNAL, **52**, 2402 (1930).

Table V gives the specific surface found after shaking the thorium B for various times with the lead sulfate suspension in 0.01 *N* nitric acid (saturated with lead sulfate).

TABLE V

SPECIFIC SURFACE OF LEAD SULFATE IN 0.01 *N* NITRIC ACID CONTAINING Th B AT 24°

(1 g. $PbSO_4$; volume 29.88 cc.)

Time of shaking with thorium B, hours	Thorium B adsorbed, %	"Specific surface" in mg. of lead per 1 g. of $PbSO_4$
$^1/_6$	49.0	1.64
0.5	57.5	2.32
1	62.5	2.86
2	76.1	5.48
4	88.1	12.7
6	93.3	23.7

It is evident that the figures reported under the heading "specific surface" are much greater than correspond with the amount of lead ions in the surface. A recrystallization of the lead sulfate takes place whereby radioactive lead is removed from the solutions and is incorporated in the newly formed crystals. This is clearly shown by comparison of the figures of Table V with those of Table VI. In the latter case the lead sulfate was shaken for various times with its saturated solution in 0.01 *N* nitric acid, and then for one hour after addition of thorium B. After eight days of shaking the speed of recrystallization is markedly decreased and the specific surface found after that time is smaller than that after one hour of shaking of the original product with its saturated solution in water.

TABLE VI

LEAD SULFATE SHAKEN FOR VARIOUS TIMES IN 0.01 *N* NITRIC ACID, THEN SHAKEN FOR ONE HOUR WITH Th B

(t = 24°; 1 g. $PbSO_4$; volume 29.88 cc.)

Time of shaking before addition of thorium B, hours	Thorium B adsorbed, %	"Specific surface" in mg. of lead per 1 g. of $PbSO_4$
1	55.2	2.11
2	59.3	2.50
24	50.6	1.76
8 days	39.2	1.11

Since it had been found that wool violet adsorbed on lead sulfate inhibits the speed of kinetic exchange, it was to be expected that it would inhibit its speed of recrystallization as well. The experiments in Table VII (compare with the figures in Table V) show that the adsorbed dye virtually prevents the recrystallization of lead sulfate in 0.01 *N* nitric acid. Another experiment was made in which the lead sulfate was shaken for eleven and one-half hours with a solution of the dye in 0.01 *N* nitric acid, and then one hour with thorium B. A specific surface of 0.82 mg. of lead per gram was found, thus confirming the above conclusion.

TABLE VII

LEAD SULFATE SHAKEN FOR THIRTY MINUTES WITH WOOL VIOLET SOLUTION (0.785 G. PER LITER) IN 0.01 *N* HNO_3, THEN Th B ADDED AND SHAKEN

(25°; 1 g. $PbSO_4$; volume 29.88 cc.)

Time of shaking with Th B, hours	Thorium B adsorbed, %	"Specific surface" in mg. of lead per 1 g. $PbSO_4$
$^1/_6$	31.24	0.78
0.5	33.87	0.88
1	37.00	1.01
2	40.67	1.17
4	41.53	1.22
12	45.27	1.42

From the figures in Tables I, II and III, it follows that at a certain dye concentration in the solutions with a neutral reaction, the surface becomes saturated with wool violet. The saturated surface contains 2.40 mg. of dye per 1 g. of lead sulfate, this saturation value being reached at a lower dye concentration in the solution in the presence of an excess of lead nitrate, and at a higher concentration in the presence of an excess of sodium sulfate. The amount of dye in the saturated surface corresponds to 1.8×10^{18} wool violet ions per 1 g. of lead sulfate, whereas from the specific surface determination after one hour of shaking with thorium B in neutral medium it is computed that there are 2.8×10^{18} lead and sulfate ions in the surface of 1 g. of lead sulfate. This means that there is one dye ion absorbed per 1.5 lead ions in the surface.

In the case of ponceau only one dye ion per 6 lead ions was found to be adsorbed[3] in the saturated state. Wool violet is very suitable for the determination of the specific surface of aged lead sulfate preparations in neutral medium. Experiments are now under way to find out whether it can be used for the determination of the surface of other slightly soluble precipitates such as barium sulfate, silver halides, and calcium oxalate.

The adsorption of the dye from acid medium (see Table IV) is much greater than from neutral medium and increases with the acidity. The maximum adsorption in 0.01 *N* nitric acid amounts to 5.7 mg. of the dye per gram, corresponding to 1.5 dye ions per lead ion in the surface. Since the dye is chemically affected by the acid it is not possible now to give an exact interpretation of this phenomenon. In dilute acid the adsorption is more than monionic, and there may be an adsorption of the dye acid itself together with the exchange adsorption.

Summary

1. Wool violet is very suitable for the determination of the specific surface of lead sulfate. In the saturated state 1 dye ion is adsorbed per 1.5 lead ions in the surface of lead sulfate when the supernatant liquid is neutral. The dye adsorption increases in acid medium.

2. Wool violet gives an exchange adsorption on the surface of lead sulfate. The sulfate ions in the surface are replaced by an equivalent amount of dye ions, thus causing the precipitation of some lead sulfate from the supernatant liquid and yielding a solution containing sulfate in excess of lead.

3. Adsorbed wool violet inhibits the speed of kinetic exchange of lead ions at the interface lead sulfate–solution, and virtually prevents the recrystallization of lead sulfate from 0.01 *N* nitric acid at room temperature.

4. On shaking a coarsely crystalline product of lead sulfate in 0.01 *N* nitric acid a recrystallization takes place.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 11, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Thermal Decomposition of Nitrogen Pentoxide at Low Pressures[1,2]

BY E. F. LINHORST AND J. H. HODGES

Introduction

The generally accepted theory of the mechanism of unimolecular reaction was proposed in 1922 by Lindemann, and elaborated in succeeding years by others.[3] It is a consequence of this theory that at sufficiently low pressures, when the mean interval between collisions has increased until it is of the same order of magnitude as the mean interval between the activation of a molecule and its decomposition, the specific reaction rate will decrease as the pressure is lowered. If the activation process depends on the collision between two molecules, the reaction should approach a second order process at very low pressures. Experimental confirmation of this predicted decrease in the specific reaction rate has been obtained in a number of cases, which have been summarized by Ramsperger.[4]

The results of previous work on the rate of decomposition of nitrogen pentoxide at low pressures are somewhat discordant. Hunt and Daniels[5] find the specific reaction rate essentially constant down to 0.01 mm., though the value at their lowest pressure is slightly lower than at higher pressures. Hirst and Rideal[6] find the specific reaction rate to increase at pressures below 0.26 mm., but no other work has indicated an increase at low pressures. Hibben[7] finds no decrease in the specific reaction rate from 0.2 mm. down to 0.03 mm. Sprenger[8] concludes that the reaction slows down and stops before all the nitrogen pentoxide has decomposed, but these conclusions are supported by no other work. Schumacher and Sprenger[9] report a decrease in the specific reaction rate becoming apparent at pressures below 0.06 mm. Ramsperger and Tolman[10] report careful measurements at pressures down to 0.001 mm. showing a decrease in the specific reaction rate evident below 0.05 mm., but giving no indication that the reaction during any given experiment deviates appreciably from the first order even at their lowest pressures. Preliminary results obtained in the present research[11] using comparatively small reaction vessels and working at the temperature of 35° indicated a

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[1] From a dissertation submitted by E. F. Linhorst to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

[2] Presented in part at the Buffalo meeting of the American Chemical Society, September, 1931.

[3] (a) Lindemann, *Trans. Faraday Soc.*, **17**, 598–99 (1922); (b) Rodebush, THIS JOURNAL, **45**, 606 (1923); (c) Hinshelwood, *Proc. Roy. Soc.* (London), **A113**, 230 (1926); (d) Fowler and Rideal, *ibid.*, **A113**, 570 (1926); (e) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); (f) Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928); (g) Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, 1932.

[4] Ramsperger, *Chem. Rev.*, **10**, 27 (1932).

[5] Hunt and Daniels, THIS JOURNAL, **47**, 1602 (1925).

[6] Hirst and Rideal, *Proc. Roy. Soc.* (London), **A109**, 526 (1925).

[7] Hibben, THIS JOURNAL, **50**, 940 (1928).

[8] Sprenger, *Z. physik. Chem.*, **136**, 49 (1928).

[9] Schumacher and Sprenger, *Proc. Nat. Acad. Sci.*, **16**, 129 (1930).

[10] Ramsperger and Tolman, *ibid.*, **16**, 6 (1930).

[11] Hodges and Linhorst, *ibid.*, **17**, 28 (1931).