Summary

1. A new oxidation–reduction indicator has been shown to be a satisfactory reagent for the detection of small amounts of oxygen.

2. A method of comparing the rates at which various reagents absorb oxygen from a stream of nitrogen has been described.

3. Chromous sulfate–sulfuric acid solutions have been shown to absorb oxygen from a stream of nitrogen at an unusually high rate under certain conditions. Adopting the results obtained with chromous sulfate reagents, as a standard, the relative oxygen-absorption rates as found in this same apparatus under similar conditions may be expressed as follows: potassium pyrogallate 2.3%, ammoniacal cuprous ammonium chloride 4%, alkaline sodium hyposulfite β-anthraquinone-sodium sulfonate 4%, and chromous sulfate–sulfuric acid reagent 100%.

LOS ANGELES, CALIF. RECEIVED JULY 15, 1936

[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF MARYLAND]

A Study of Promoter Action. The Oxidation of Aniline Sulfate by Hot, Concentrated Sulfuric Acid in the Presence of Copper and Mercury Sulfates[1]

BY M. M. HARING AND H. H. KAVELER

Oxidation by hot, concentrated sulfuric acid has many applications, of which one of the more important is the analytical method of Kjeldahl.[2] Numerous modifications of the method have been published, the use of copper and mercuric sulfate catalysts being emphasized. However, only Bredig and Brown[3,4] have made a study of the kinetics of the reaction and of the relation between catalytic effect and amount of the catalyst. They observed, among other things, that mixed copper and mercuric sulfates exhibited a catalytic effect greater than the additive value. However, they published only one set of data on mixed catalysts. It was the primary purpose of this investigation to study a wide range of catalyst ratios and total amounts.

Reagents.—Mercuric oxide was prepared by adding the calculated amount of sodium hydroxide to a solution of C. P. mercuric chloride heated to 70°. The precipitated red oxide was washed free of alkali and chlorides and dried at 100°.

Reagent copper sulfate pentahydrate was used without further purification.

The sulfuric acid used was reagent quality (sp. gr. 1.83–1.84) and was demonstrated to be free of the heavy metals.

The aniline sulfate was the purest obtainable. Analysis by the Kjeldahl method gave 9.77% nitrogen as against 9.86% theoretical.

Apparatus.—The apparatus used was similar to that described by Bredig and Brown.[3,4] The thermostat was modified to accord with modern practice. It maintained the experimental temperature of 275° to ± 0.1°. The reaction vessel and gas measuring apparatus are shown in Fig. 1, the volume of the reaction bulb being about 75 cc.

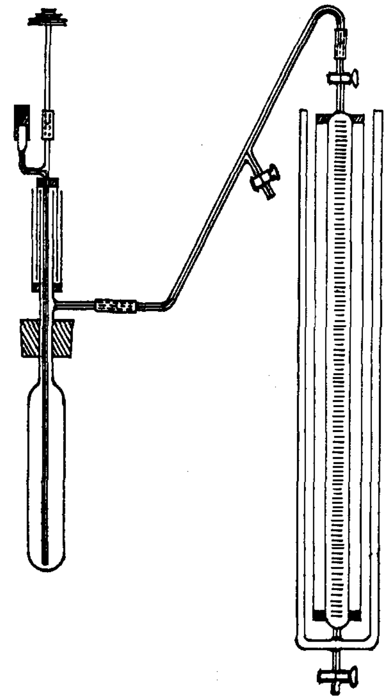

Fig. 1.

All weights and other measuring devices were checked for precision.

Procedure.—The desired quantity of the catalyst was introduced into the reaction flask through a long-stemmed funnel, followed by 50 cc. of sulfuric acid. After insertion in the bath, the mixture was stirred for one hour.

The stirring was stopped and the desired amount of a standard solution of aniline sulfate in sulfuric acid (about

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[1] Abstracted from a thesis submitted by H. H. Kaveler to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kjeldahl, *Z. anal. Chem.*, **22**, 366 (1883).

[3] Brown, Dissertation, Heidelberg, 1903.

[4] Bredig and Brown, *Z. physik. Chem.*, **46**, 502 (1903).

TABLE I
NO CATALYST

	1	2	3	*V*	*K*
45	0.4	...	...	..	...
60	.5	...	...	..	...
90	.8	...	...	..	...
120	1.0	...	1.1	1.05	0.554
150	1.3	...	1.4	1.35	.553
180	1.6	1.6	1.5	1.57	.563
240	2.1	2.1	2.0	2.07	.557
300	2.6	2.6	2.6	2.60	.553
360	3.1	3.3	3.1	3.17	.569
				Av.	.558

TABLE II
MERCURIC OXIDE CATALYST

	1 unit		2 units		4 units		8 units	
t	*V*	*K*	*V*	*K*	*V*	*K*	*V*	*K*
5	0.5	6.45	0.5	6.45	0.9	11.52	0.8	10.14
10	1.0	6.45	1.1	6.91	1.8	11.52	1.7	10.82
15	1.5	6.45	1.8	7.68	2.8	11.98	2.7	11.52
25	2.4	6.17	3.1	7.92	4.8	12.46	5.7	14.84
45	4.5	6.50	6.2	8.96	9.2	13.46	12.9	19.14
60	6.1	6.60	8.8	9.63	12.8	14.20	18.8	21.30
90	9.4	6.86	14.5	10.82	21.8	16.68	29.2	22.98
120	13.1	7.28	20.2	11.53	29.5	17.41	39.5	23.55
150	..	..	25.9	12.09	36.1	17.50	47.9	24.39
180	20.6	7.84	31.6	12.55	42.3	17.53	..	...
		Av. 6.65		9.80		14.78		21.14

TABLE III
COPPER SULFATE PENTAHYDRATE CATALYST

	1 unit		2 units		4 units		8 units	
t	*V*	*K*	*V*	*K*	*V*	*K*	*V*	*K*
5	0.2	2.30	0.5	6.45	0.7	8.75	1.1	13.81
10	0.6	3.68	1.2	7.60	1.4	8.98	1.8	11.52
15	1.0	4.30	1.8	7.68	2.5	10.75	2.6	11.05
25	2.0	5.16	3.4	8.85	4.2	10.87	4.7	12.16
45	4.7	6.76	7.2	10.44	8.5	12.39	10.5	15.40
60	7.1	7.71	10.5	11.55	12.3	13.62	15.5	17.43
90	11.5	8.47	16.9	12.70	19.7	14.97	25.4	19.73
120	15.9	8.94	22.7	13.07	26.4	15.41	34.4	20.72
150	20.1	9.18	27.7	12.99	32.7	15.64	42.0	20.86
180	23.9	9.21	31.7	12.59	38.5	15.70	48.0	20.78
		Av. 7.65		11.56		13.66		17.52

8% by weight) was run from a weight buret into the well on the side-arm of the stirrer. This was followed immediately by 1.0–1.5 cc. of sulfuric acid and the run started. The pressure was maintained at the atmospheric value throughout a run. 0.05–0.09 g. of aniline sulfate was used in all experiments. The weights of catalyst used were always 0.0305 g. of mercuric oxide and 0.0351 g. of copper sulfate pentahydrate or integral multiples thereof. These unit weights are in the same ratio as the molecular weights. The maximum amount of catalyst used in any experiment was a very small fraction of the solubility in sulfuric acid.[5]

Data and Calculations

For comparison purpose, all gas volumes were reduced to a weight of 0.0500 g. of aniline sulfate by proportion. Bredig and Brown[3,4] showed this procedure to be valid. All volumes likewise were corrected to standard conditions. From two to nine runs (in most cases four) were made for each quantity of catalyst. The volumes for each case were averaged at corresponding times, plotted on a large scale and the best smooth curve drawn. All data given below, save Table I, were obtained in this manner. Table I shows all the data. The variation in volumes from the mean for corresponding times for the different members of a series was seldom in excess of 5% and usually much less. In the following tables *t* is for times in minutes, *V* is the average volume in cc. and *K* is the monomolecular reaction constant for times in minutes, as obtained from $K = (2.303/t) \log (C_0/C)$. Purity of the aniline sulfate was considered in calculating C_0. The amount of catalyst is expressed in terms of unit weights as defined previously. The average *K* is based on the values at 45, 60 and 90 minutes. Early values for *K* for catalyzed reactions are too unsteady to give a good comparison. All values of *K* are included in the average for the uncatalyzed reaction. *K* values in all tables are $\times 10^4$.

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(5) See "International Critical Tables," Vol. IV, p. 42.

Table IV gives the ratios between the average velocity constants catalyzed and uncatalyzed.

TABLE IV

MERCURIC OXIDE CATALYST

1 unit	2 units	4 units	8 units
11.7	17.5	26.4	37.8

COPPER SULFATE PENTAHYDRATE CATALYST

1 unit	2 units	4 units	8 units
13.7	20.7	24.2	31.4

The data of Tables I, II and III are portrayed graphically in Figs. 2 and 3.

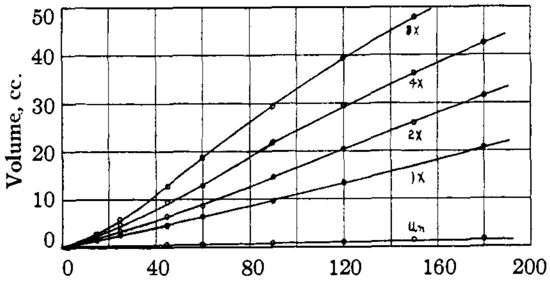

Fig. 2.—Mercuric oxide catalyst: x, units of catalyst; Un, uncatalyzed.

The data for mixed catalysts are given in the following tabulation. The various mixtures are identified thus: 1Hg–8Cu means one unit weight (0.0305 g.) of mercuric oxide and eight unit weights (0.2808 g.) of copper sulfate pentahydrate; and so on. Other symbols have the same significance as before.

TABLE V

	3Hg–3Cu		5Hg–1Cu		2Hg–4Cu		4Hg–2Cu	
	V	*K*	*V*	*K*	*V*	*K*	*V*	*K*
5	1.7	21.7	2.6	33.2	2.0	25.8	2.5	32.2
10	4.7	30.4	5.1	32.9	4.6	29.7	5.0	32.5
15	7.0	30.4	7.9	34.4	7.2	31.3	8.3	36.2
25	13.8	36.9	14.1	37.8	12.4	34.9	15.0	40.4
45	27.2	42.5	26.6	41.4	24.8	38.4	29.4	46.3
60	36.2	43.9	35.9	43.5	33.4	40.1	39.8	48.9
90	52.2	45.2	51.8	44.7	49.5	42.3	55.0	48.2
	Av.	43.9		43.2		40.3		47.8

	1Hg–1Cu		8Hg–8Cu		4Hg–1Cu		1Hg–4Cu	
t	*V*	*K*	*V*	*K*	*V*	*K*	*V*	*K*
5	1.1	13.8	3.2	41.0	2.2	28.1	1.5	19.3
10	2.5	16.1	8.3	53.5	4.0	26.0	3.0	19.4
15	3.7	16.0	14.6	65.4	6.1	26.4	4.8	20.7
25	6.8	17.3	29.9	84.9	10.9	28.8	8.6	22.6
45	13.8	20.5	53.6	93.4	22.5	34.5	17.6	26.5
60	19.2	21.8	65.8	91.1	30.2	35.8	25.0	28.4
90	29.4	23.1	82.0	82.6	44.6	37.4	39.8	32.6
	Av.	21.8		89.0		35.9		29.2

	1Hg–8Cu		8Hg–1Cu		4.5Hg–4.5Cu	
t	*V*	*K*	*V*	*K*	*V*	*K*
5	1.9	24.4	2.8	35.9	3.1	39.6
10	4.4	28.6	6.8	44.2	6.8	44.2
15	7.2	31.3	12.1	53.6	11.2	49.4
25	13.1	35.0	25.8	72.2	21.9	60.3
45	27.6	43.1	43.8	73.1	39.3	64.3
60	37.8	46.1	54.6	71.6	51.1	66.0
90	54.3	47.4	70.3	66.4	67.2	62.4
	Av.	45.6		70.4		64.3

The fact that the effect of mixed catalysts is more than additive is demonstrated by calculating the promotion factor. This is obtained by dividing the average *K* for a mixed catalyst (less *K* uncatalyzed) by the sum of the *K* values for the appropriate units of the pure catalysts (less 2 *K* uncatalyzed). Wherever these values had not been directly determined they were obtained by graphic interpolation. The promotion factors are given in Table VI.

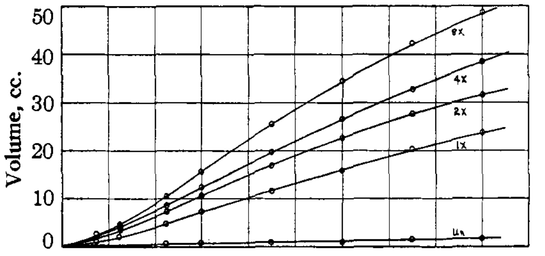

Fig. 3.—Copper sulfate pentahydrate catalyst, x, units of catalyst; Un, uncatalyzed.

TABLE VI

3Hg–3Cu	5Hg–1Cu	2Hg–4Cu	4Hg–2Cu
1.80	1.84	1.78	1.87
1Hg–1Cu	8Hg–8Cu	4Hg–1Cu	1Hg–4Cu
1.62	2.36	1.66	1.49
1Hg–8Cu	8Hg–1Cu	4.5Hg–4.5Cu	
1.95	2.52	2.22	

The effect is more apparent when graphically portrayed. This is given for the series containing six units of mixed catalyst. In Fig. 4 the volumes of gas liberated at 24, 45, 60 and 90 minutes are plotted against the Hg/Cu mole ratio. Values for six units of pure catalyst were obtained by graphic interpolation.

Discussion

The data of Tables II and III reveal that copper is a better catalyst than mercury at the lower concentrations but a poorer catalyst at the higher concentration, on a mole for mole basis. The catalytic effect increases with concentration of the catalyst, but is not directly proportional as claimed by Bredig and Brown.[3,4] However, examination of their data does not support their contention. Mixtures of the two catalysts show the same general proportionality. The mixtures with a high mercury content are better catalysts than those with a high copper content. Figure 4 shows that the most active mixture is approximately two moles of mercury to one of copper.

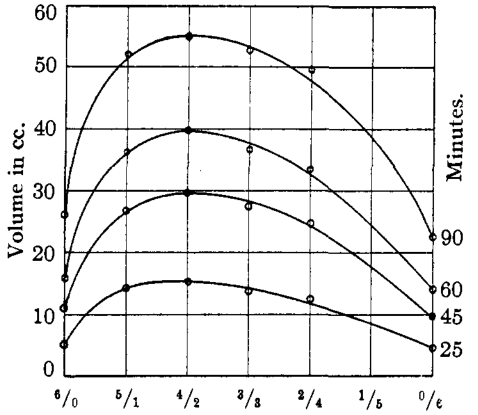

Fig. 4.—Variation of promoter effect with catalyst composition ratio and time.

Since both metals are good catalysts and all mixtures, as shown in Table VI, have activities far greater than the additive value, it is clear that this is a case of coactivation. A very interesting observation is that the promoter effect drops off with time.

Bredig and Brown[3,4] claimed this reaction to be monomolecular. The results of this study, particularly the data on the uncatalyzed reaction, support their contention. The values of *K* for the catalyzed reactions are far from constant, although they become more so, in most cases, after about an hour. Examination of Figs. 2 and 3 reveals that all curves have an inflection at about forty minutes. The curves of Bredig and Brown show the same inflection. This might be explained in four ways. (1) The cooling effect of introducing the sample might slow up the reaction for a brief interval. (2) The sample, due to inadequate stirring, might not be uniformly distributed immediately. (3) An undisturbed rate of gas evolution might not be obtained while the gas concentration in the mixture increased to saturation. (4) The inflection is real and due to a series of consecutive reactions of differing velocity. (1), (2) and (3) would be errors inherent in the method. As such they would be subject to variation. That two groups of investigators working entirely independently should duplicate these factors is highly improbable. Explanation (4) is almost certainly correct. Heated to 275°, a solution of aniline sulfate in sulfuric acid slowly darkens, going to green, then to black and finally to yellow, thus indicating numerous successive reactions. The equation for the reaction given by Bredig and Brown is

$$(C_6H_5NH_2)_2{\cdot}H_2SO_4 + 28H_2SO_4 = 12CO_2 + 28SO_2 + (NH_4)_2SO_4 + 32H_2O$$

which is evidently only the sum of a series. Of course, with excess sulfuric acid this reaction would be pseudomonomolecular, but the evidence is against a single step. The data do not permit more than a guess at the probable path. Aniline blacks, sulfonated products and quinone are almost certainly produced. In fact the yellow needles of quinone were observed to crystallize out in several of the mixtures after cooling. However, the very good constancy of *K* uncatalyzed shows that, in the first stages, the reaction is monomolecular or at least pseudomonomolecular.

As to the mechanism of the catalysis and coactivation, the data afford little evidence. Aniline has been shown to form numerous complexes with mercuric and other metallic salts.[6,7,8]

Mercuriated aryls are also formed with aniline.[9]

The copper compounds are less easily prepared and are not as stable[9] (p. 774).

Such complexes might react to produce a compound more readily oxidized than aniline itself. A parallel case has been studied.[10]

The work of Bohnson and Robertson[11,12] on the decomposition of hydrogen peroxide by mixtures of copper and iron ions affords a possible explanation of the coactivation.

In this case it was shown that one metal continually regenerates the other in active form. Some support for this suggestion is found in the work of Germuth,[13] who showed that the rate of oxidation of mercurous to mercuric ion by atmospheric oxygen is appreciably increased by traces of cupric ion.

Summary

1. Copper and mercury sulfates are excellent

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[6] "International Critical Tables," Vol. IV, p. 199.

[7] Spacie and Ripan, *Bull. Soc. stiinte Cluj*, **1**, 542 (1922); see also *C. A.*, **18**, 1442 (1924) and **19**, 1995 (1925).

[8] Mathews and Benger, *J. Phys. Chem.*, **18**, 263, 667 (1914); Mathews and Spero, *ibid.*, **21**, 402 (1917); Hahn and Wolf, *Z. anorg. Chem.*, **144**, 128 (1925).

[9] Houben–Weyl, "Die Methoden der Org. Chem.," Georg Thieme, Leipzig, 1924, Vol. IV, pp. 921–945.

[10] Davis, Worrall, Drake, Helmkamp and Young, THIS JOURNAL, **43**, 594 (1921).

[11] Bohnson and Robertson, *ibid.*, **45**, 2512 (1923).

[12] Robertson, *ibid.*, **47**, 1299 (1925).

[13] Germuth, *Am. J. Pharm.*, **102**, 263 (1903).

catalysts for the oxidation of aniline sulfate by sulfuric acid, mercury being the better. The effect is not strictly proportional to the amount of the catalyst.

2. Together the two catalysts give effects much greater than the additive value. This is, accordingly, a case of coactivation. Mercury and copper in the ratio of two moles to one give the most pronounced effect.

3. The reaction is monomolecular or pseudomonomolecular in the first stages.

COLLEGE PARK, MD. RECEIVED SEPTEMBER 17, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 148]

Condensations by Sodium. VIII. Solvent Exchange Reactions, Preparation of Phenylmalonic Acid, and Comments on Some Mechanisms of Reactions which Employ Sodium

BY AVERY A. MORTON AND INGENUIN HECHENBLEIKNER

When benzene or a mixture of benzene and ligroin was used as the solvent for the preparation of amylsodium from amyl chloride and sodium by the recently described[1] synthesis of organo-metallic compounds, the product after carbonation was benzoic instead of caproic acid. Exchange of phenyl for the amyl radical was complete and the yield of benzoic acid, calculated on the basis of a molecule of acid for every one of amyl chloride used, was as high as 78%. Toluene, dimethylaniline, anisole, diphenylmethane and fluorene, when used similarly either as solvents or as diluents in a ligroin solution, shared this interesting property so that the monocarboxylic acids formed as products of carbonation were phenylacetic, N-dimethylanthranilic, *o*-methoxybenzoic, diphenylacetic and diphenyleneacetic acids in yields of 40, 18, 20, 14 and 18.5%, respectively (see Table II). No attempt was made to obtain the maximum yields.

In order to illustrate the possibilities of extending this solvent exchange type of synthesis beyond the preparation of acids we have prepared phenylsodium by interaction of amyl chloride, sodium and benzene and then brought about its reaction with propyl chloride. Propylbenzene was found in substantial quantity. In a like manner phenylsodium was induced to react with ethylene oxide yielding β-phenylethyl alcohol as one of the products.

Syntheses of this type continued to show promise of use in the preparation of malonic acids. A notable example was the formation of phenylmalonic in addition to phenylacetic acid from the reaction in toluene solution. With amyl chloride in a mixture of toluene and ligroin a yield of 33% of phenylmalonic acid was obtained from the same run which yielded 40% of phenylacetic acid. With isobutyl chloride the yields were 20% of phenylmalonic and 11% of phenylacetic acid. When the addition of toluene was delayed until after all reactions between amyl chloride and sodium had ceased, the yields of phenylmalonic and phenylacetic acids were 28 and 5%, respectively. The method is therefore a far more convenient source of this compound than has hitherto been available. It is especially interesting to note that the yield of the malonic acid is often considerably in excess of that for the monocarboxylic acid.

Mechanism of Exchange Reactions.—Our work has now progressed to a point where we have assurance as to the manner in which some of the products are formed. The monosubstitution product, benzoic acid, arises from metathesis of the sodium compound with the hydrocarbon according to equation 1.

$$C_5H_{11}Na + C_6H_6 \longrightarrow C_5H_{12} + C_6H_5Na \qquad (1)$$

Important evidence of the correctness of this view was furnished by (a) reserving the addition of benzene in experiments 3 and 4 until after the free radicals had disappeared and the formation of amylsodium had been completed, a condition which resulted in the entire replacement of caproic by benzoic acid among the products of carbonation and (b) by carrying out, as in experiment 6, an exchange reaction in the presence of carbon dioxide to remove amylsodium as fast as it was formed and thereupon failing to find any benzoic acid. Neither was this acid found in six experiments made under pressure of carbon dioxide. We therefore conclude that the free radi-

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(1) Morton and Hechenbleikner, THIS JOURNAL, 58, 1697 (1936).