of thio-urea, including the *sym.*-diethyl,[10] *iso*butyl,[11] *sym.*-butyl,[12] normal butyl,[12] *d-sym.*-butyl,[13] methyl *sym.*-propyl,[14] α,α'-dimethyl-β-ethyl,[15] and *unsym.*-diethyl[16] thio-ureas. In the thought that the tetramethylammonium salt might undergo transformation into tetramethyl thio-urea, several preliminary experiments have been performed. No evidence of such a molecular rearrangement has thus far been obtained.

Summary

Two new compounds, ammonium azido-dithiocarbonate, NH_4SCSN_3, and tetramethylammonium azido-dithiocarbonate, $N(CH_3)_4SCSN_3$, have been prepared and described. Both are white, crystalline solids, fairly stable at room temperature, but decomposing rapidly, and under certain conditions explosively, when heated. Both undergo a curious color change; the former when either heated or illuminated, the latter when illuminated at ordinary temperature.

Tetramethylammonium thiocyanate, a product of the thermal decomposition of the tetramethylammonium azido salt, has also been prepared and studied.

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

THE VOLUMETRIC DETERMINATION OF HYDRAZOIC ACID BY OXIDATION WITH CERIC SULFATE IN ACID SOLUTION

BY JEROME MARTIN

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Sommer and Pincas[1] developed a nitrometric method for determining hydrazoic acid which depends on its oxidation by a ceric salt in acid solution, and showed that the nitrogen evolved corresponds to the reaction $2Ce^{++++} + 2HN_3 = 3N_2 + 2Ce^{+++} + 2H^+$. In the present investigation an iodimetric method based on this reaction has been found to give satisfactory results. A measured quantity of a stock solution of ceric sulfate is added and the excess is determined iodimetrically. The writer is not aware of any other titration method which depends on the oxidation of hydrazoic acid.[2]

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[10] Hofmann, *Ber.*, **1**, 25 (1868).

[11] Hofmann and Reimer, *Ber.*, **3**, 755 (1870).

[12] Hofmann, *Ber.*, **7**, 508 (1874).

[13] Urban, *Arch. Pharm.*, **242**, 51 (1904), through *Chem. Zentr.*, **1904**, I, 997.

[14] Hecht, *Ber.*, **23**, 281 (1890).

[15] Billeter and von Pury, *Ber.*, **26**, 1681 (1893).

[16] Wallach, *Ber.*, **32**, 1872 (1899).

[1] Sommer and Pincas, *Ber.*, **48**, 1963 (1915).

[2] The volumetric method of West, *J. Chem. Soc.*, **77**, 705 (1900). Riegger [THIS JOURNAL, **33**, 1569 (1911)] depends on the distillation of hydrazoic acid and its titration with standard alkali.

Preparation of Solutions

The hydrazoic acid used in this work was prepared by the method of Browne.[3] From this a stock solution of sodium azide was made by neutralization with sodium hydroxide. This stock solution was standardized by the gravimetric method of Turrentine and Olin,[4] and the average value of five determinations was 0.1097 ± 0.1%.

Two different stock solutions of ceric sulfate were prepared and standardized iodimetrically.[5] Solution A was prepared by the electrolysis of cerous sulfate in 6 *N* sulfuric acid. Solution B was obtained by diluting with water a paste of ceric oxide and concd. sulfuric acid until the acid concentration was 2 *N*. The latter method is preferable since it is easier to carry out.

The thiosulfate solution was standardized against known potassium permanganate solution[6] which had been standardized against Bureau of Standards sodium oxalate.

The Standard Procedure is as follows. The air in a ground-glass stoppered flask is displaced by a current of nitrogen or carbon dioxide, and the neutral or slightly basic solution of hydrazoic acid added. A

TABLE I

DETERMINATION OF 0.1097 *M* HYDRAZOIC ACID WITH CERIC SULFATE

Expt.	Ceric sulfate soln. used	NaN_3 taken, cc.	Final volume, cc.	Approx. concn. of acid, *N*	Time, in min.	Vol. of thio. calcd. as 0.1 *N*	Vol. of Ce^{++++} calcd. as 0.1 *M*	Calcd. concn. of NaN_3
1	A	9.982	300	0.3	5	10.60	21.57	0.1099[a]
2	A	9.982	300	.3	5	10.62	21.57	.1097[a]
3	A	9.982	300	.3	5	10.60	21.57	.1099[a]
4	A	9.982	500	.2	5	32.16	43.14	.1100[a]
5	B	25.06	500	.12	5	0.84	28.33	.1097
6	B	25.06	500	.12	5	.87	28.33	.1096
7	B	25.06	500	.12	5	.85	28.33	.1097
8	B	25.06	500	.12	10	.87	28.33	.1096
9	B	25.06	500	.12	15	.85	28.33	.1097
10	B	25.06	500	.12	1	.95	28.33	.1092[a]
11	B	25.06	500	.12	1	.98	28.33	.1091[a]
12	B	25.06	500	.20	5	12.95	40.41	.1096
13	B	25.06	500	.20	5	12.93	40.41	.1097
14	B	25.06	500	.20	1	12.98	40.41	.1095[a]
15	B	25.06	500	$.12H^+$	5	0.87	28.33	.1096
16	B	25.06	500	.2M NH_4^+	5	.85	28.33	.1097

Av. 0.10965 ± 0.1%

[a] These values were not used in computing the average.

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[3] Browne, THIS JOURNAL, **27**, 551 (1905).

[4] Turrentine and Olin, *ibid.*, **37**, 1118 (1915).

[5] Brauner, *Z. anorg. Chem.*, **34**, 207 (1903).

[6] Bray and Miller, THIS JOURNAL, **46**, 2204 (1924).

measured excess of a standard ceric sulfate solution is quickly added, the flask stoppered, shaken vigorously, and allowed to stand for five minutes. An excess of potassium iodide is then added and the liberated iodine titrated with 0.1 *N* thiosulfate solution, using starch as an indicator. A solution of 0.01 *N* iodine may be used to determine the end-point more exactly.

The experimental results are shown in Table I.

Discussion of Experimental Results

Expts. 1–4 in which Solution A was used cannot be given much weight since the high acid concentration would accentuate the oxygen error, due to a trace of residual oxygen, either in the standard procedure or in the standardization of the stock ceric sulfate solution.

The reaction is complete in five minutes under the conditions employed, but Expts. 10, 11 and 14 show that it is not complete in one minute.

That the excess of ceric salt does not affect the results is shown by comparing Expts. 12–13 with Expts. 5–9. This indicates that the reaction is smooth, and free from side reactions.

That ammonium ion has no effect on the ceric ion-hydrazoic acid reaction is shown by Expts. 15 and 16 which differed from the standard procedure only in that 5 g. of ammonium sulfate was dissolved in the solution of sodium azide before the ceric sulfate was added. Additional experiments showed that ammonium ion is slowly oxidized at boiling temperature when the acid concentration is high (about 20 *N*), but not under other conditions.

The method cannot be used in the presence of hydrazine since it is oxidized rapidly by ceric salt, the products being nitrogen and ammonium ion. More nitrogen is evolved than corresponds to the equation,[7] $2Ce^{++++} + 2N_2H_5^+ = N_2 + 2NH_4^+ + 2Ce^{+++} + 2H^+$. However, the hydrazoic acid can be distilled from the acid solution of hydrazine.

The two sources of error are the volatility of the hydrazoic acid in acid solution, and the catalytic effect which cerous ion exerts on the oxygen-iodide reaction. When the acid concentration is low, the latter error may be rendered negligible by using oxygen-free water and sweeping out the reaction flask with nitrogen. The effect of the volatility of the hydrazoic acid was reduced by adding the ceric sulfate quickly, stoppering the flask and shaking vigorously.

The author wishes to thank Professor William C. Bray for his suggestions and interest in this work.

Summary

Hydrazoic acid has been determined volumetrically by a method which depends upon the oxidation of hydrazoic acid to nitrogen by ceric sulfate

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[7] Benrath and Ruland, *Z. anorg. Chem.*, **114**, 267 (1920).

in acid solution. The method is accurate to within 0.1% if care is taken to eliminate the oxygen-iodide error and if the loss of hydrazoic acid by volatilization is prevented. Hydrazoic acid cannot be determined in the presence of hydrazine, but the two can be readily separated. Ammonium ion has no effect on the method.

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[CONTRIBUTION NO. 36 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE ADSORPTION OF HYDROGEN AND ETHYLENE ON A COPPER CATALYST POISONED WITH CARBON MONOXIDE

BY CARROLL W. GRIFFIN

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Some years ago Taylor and Burns[1] in studying the adsorption of gases on metallic catalysts found that catalytically active copper adsorbed ethylene strongly at low temperatures and hydrogen less strongly. Later Pease[2] took up the study of the hydrogenation of ethylene using copper as the catalyst. He pointed out the apparent correlation of catalytic activity and strong or low-pressure adsorption of reactants in view of the fact that either mercury poisoning or heat treatment of the copper caused a simultaneous and marked decrease of both of these properties. This was followed by a study by Pease and Stewart[3] of the effect of carbon monoxide as a poison to the reaction. They showed that less than 0.05 cc. of carbon monoxide reduced by 88% the activity (towards an ethylene-hydrogen mixture) of a copper catalyst which adsorbed at less than one mm. pressure approximately 1 cc. of hydrogen, 2 cc. of ethylene or 5 cc. of carbon monoxide. Their conclusion was that the copper surface owed 88% of its catalytic activity to less than 1% of the centers active in adsorption, thus emphasizing the existence on the copper surface of centers of different degrees of activity. The adsorption of the reactants on the catalyst poisoned with carbon monoxide had not been measured and it was suggested to the writer by Dr. R. N. Pease that such measurements be made.

Procedure

The apparatus, the method of preparation of the catalyst, of the hydrogen and of the ethylene, as well as the taking of measurements and the limit of accuracy, were as Pease[4] has previously described. Pure carbon monoxide was obtained by the decomposition of formic acid and passage of the gas over phosphorus pentoxide and soda lime. The 63.42 grams

[1] Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921).

[2] (a) Pease, *ibid.*, **45**, 1196 (1923); (b) **45**, 2296 (1923).

[3] Pease and Stewart, *ibid.*, **47**, 1235 (1925).

[4] Pease, Refs. 2 and 3.