soluble salt without decomposing it, the mixture of salt and platinum was thoroughly dried and analyzed, the amount of platinum in the sample being determined by weighing the boat after the analysis.

Analysis. Calc. for $C_{34}H_{25}O_4N_2$: C, 76.1; H, 6.7. Found: C, 75.7; H, 6.8.

Both the pure hydrochloride and the pure oxalate were decomposed with alkali in the hope of getting a solid pyrrolidine, but the product in each case was a colorless oil.

Summary

1. When γ-nitro ketones are reduced with hydrogen in the presence of Loew's platinum black there is a succession of reduction and condensation reactions that overlap to such a degree that the rate at which the hydrogen is absorbed is represented by a smooth curve.

2. The principal reduction products are the amino ketone, hydroxypyrroline and pyrrolidine, corresponding to the nitro ketone that is reduced.

3. These products do not represent successive stages in the reduction; they are formed, simultaneously, along different routes.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, AND THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, TULANE UNIVERSITY SCHOOL OF MEDICINE]

DETERMINATION OF FORMALDEHYDE IN PRESENCE OF SUBSTANCES FOUND IN FORMALIN

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Received June 15, 1923

The object of this paper is to present the results of a study of certain methods for the determination of formaldehyde in the presence of some of the organic substances that may be present in a formalin solution. The substances whose effect will be noted are methyl alcohol, ethyl alcohol, sodium formate, acetone and methylal.

The methods chosen are (1) iodimetric, (2) "alkali-peroxide" and (3) neutral sulfite.[1] These methods have been studied in previous work,[2] and as the procedure used in this work is the same no detailed explanation of the procedure will be given.

The paraformaldehyde used is the same as in previous work, and gave by the Liebig combustion method 96.8% of formaldehyde and 3.2% of water. Sodium formate was

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[1] The determination of formaldehyde, methyl alcohol, and sodium formate in the same solution was attempted by the oxidation with permanganate and the absorption of the carbon dioxide produced. The method used is that suggested by Messinger [*Ber.*, **21**, 2910 (1888)]. By this method the purity of the methyl alcohol was determined to be 95.35% and the sodium formate 100%; 0.2466 g. of paraformaldehyde and 0.7510 g. of sodium formate produced 0.8284 g. of carbon dioxide; calc., 0.8352 g.; 0.1170 g. of paraformaldehyde, 0.2722 g. of sodium formate and 0.2270 g. of methyl alcohol produced 0.6448 g. of carbon dioxide; calc., 0.6397 g.

[2] Borgstrom and Horsch, THIS JOURNAL, **45**, 1493 (1923).

used as a source of formate ion due to the ease of purification. The methyl alcohol was acetone-free but no attempt was made to have it absolute. The ethyl alcohol was absolute but no special purification was attempted to free it from traces of aldehydes. The acetone used was from the bisulfite compound. The methylal was used as purchased. From the odor of iodoform given off during use in the iodimetric method it may have had a trace of either acetone or ethyl alcohol and because of this no extensive investigation was made with it.

The substance whose effect was to be studied was added to the weighed paraformaldehyde.[3] With liquids, especially with methyl alcohol and methylal, the materials to be added were sealed in small tubes of known weight. Most of the work was done by weight except in a few cases in which a micro-buret calibrated to 0.02 cc. was used.

Iodimetric Method.—No difference could be detected in the ratio of iodine to thiosulfate due to the presence of sodium formate in amounts ranging from 0.003 to 0.044 molecular equivalent.

The average net consumption of 0.0803 *N* iodine was 0.140 cc. per g. of methyl alcohol. Using this value, one mole of methyl alcohol reacts with an iodine equivalent of 0.0066 g. (or 0.00022 mole) of formaldehyde. This means that when both are present in the same concentration the determination will be 0.022% high.[4]

To show the actual effect of sodium formate and methyl alcohol nine determinations with a ratio of moles of HCOONa to moles of HCHO ranging from 1.24 to 4.26 gave an average value of 96.72% with an average deviation of 0.28. Seven determinations with the ratio of moles of CH_3OH to moles of HCHO ranging from 4.9 to 46.1 gave an average value of 97.0% with an average deviation of 0.18. Twelve determinations with a ratio of moles of HCOONa to moles of HCHO of 2.72, 8.84, 3.64, 5.65, 1.07, 3.55, 2.73, 4.78, 4.16, 4.19, 3.69 and 2.82 and the corresponding ratio of moles of CH_3OH to moles of HCHO of 20.6, 11.4, 14.1, 21.7, 16.2, 11.1, 7.0, 13.9, 31.7, 11.2, 7.8, 23.0, gave the percentage of formaldehyde as 96.90, 97.52, 96.47, 96.79, 96.23, 96.80, 97.19, 97.00, 97.39, 96.83, 96.86, and 97.25, respectively, with an average value of 96.93 and an average deviation of 0.28. This shows that the concentration of methyl alcohol and sodium

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[3] A paper by F. Mach and R. Herrmann has just appeared [*Z. anal. Chem.*, **62,** 104 (1923); *C. A.*, **17,** 945 (1923)] on "A Comparison of the Most Useful Methods for the Determination of the Formaldehyde Content of Formalin Solutions." The conclusions drawn by them differ somewhat from the results found in the present work and may be due to the fact that they used a formalin solution, while in this work paraformaldehyde was used as a standard.

[4] L. F. Goodwin [THIS JOURNAL, **42,** 44 (1920)] has found that "0.5 cc. methyl alcohol causes an error of nearly 0.5 cc. in the amount of 0.1 *N* iodine solution used." This value is higher than that found by the author and may be explained by the difference in quality of the methyl alcohol. If the alcohol be very carefully purified and used when fresh it probably will have no reaction or but very slight with alkaline iodine solutions.

formate in an ordinary formalin solution has no effect on the titration by the iodimetric method.

As both acetone[5] and ethyl alcohol[6] react rapidly with an alkaline iodine solution, error in the results would be dependent upon the concentration of these present and, therefore, no further work was done in connection with this method.

With methylal there was a reaction with the alkaline-iodine solution, and a strong odor of iodoform developed and in some cases even a precipitate. This may be due to either ethyl alcohol or acetone. The consumption of iodine (0.0759 N) per gram of the methylal was 11.07 cc. as an average for 5 trials. Because of this no direct determinations were made with methylal present.

Hydrogen Peroxide Method.—The previous work was repeated; 7 determinations gave an average value of 96.86% with an average deviation of 0.23%. An attempt was made to use cresol red (*o*-cresol-sulfonphthalein) as an indicator in place of litmus but the results were 98.71 and 98.01%, showing that under this condition this indicator was not satisfactory. When litmus was used as an indicator and the solution allowed to stand for an hour as recommended by Mach and Herrmann[3] the purity found was 97.34% (5 determinations) with an average deviation of 0.20%. When cresol red was used under the same conditions the average value was 96.92% (7 determinations) with an average deviation of 0.21%.

When 5 cc. of methyl alcohol (calculated to be about 3.93 g.) was heated for 5 minutes, the net consumption of 1.0 N sodium hydroxide solution as calculated for per mole of methyl alcohol was 0.250 cc. or a negligible error. When 5 cc. was heated for 10 minutes the calculated consumption per mole was 2.304 cc. of N alkali. Mole for mole the error would not be over 0.25% even if the methyl alcohol were heated for 10 minutes.

When 1.9883, 1.4544, 1.1735 and 2.2280 g. of ethyl alcohol were heated with "alkaline peroxide" the net consumption of N alkali per mole of alcohol was 0.16, 1.53, 4.48 and 7.92 cc. for time of heating 5.5, 6, 8.5 and 27.5 minutes, respectively. The error is very small when the solution is molar, in formaldehyde and ethyl alcohol, and time of heating 5 minutes but with 8 minutes' heating the error is about 0.5%.

Three trials were made with methylal using 0.2379, 0.1799 and 0.2789 g. heated for 5 minutes and then cooled rapidly. The ratio of the acid and alkali used in these experiments was 1.1672, with an average deviation of 0.0005 in 8 trials. The trials with methylal showed a difference from this mean of 0.0017, 0.0003 and 0.0011 or an average of 0.0010. This is twice the error found without methylal. There is a trace of acetone or ethyl

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[5] Messinger, *Ber.*, **21**, 3366 (1888).

[6] Luben, *Ann. Spl.*, **7**, 218, 377 (1870).

alcohol in the methylal (as shown by the iodimetric method) and this probably accounts for the difference. The actual difference as found is —0.04, +0.01, —0.02 cc. for the three runs. In one trial in which 0.4137 g. of methylal was allowed to stand for 45 minutes and gradually cool after heating for 5 minutes, the result was a net consumption of 0.11 cc. of *N* alkali; if both methylal and formaldehyde were molar the results on this account would be 2% high.

The action of alkaline peroxide on acetone is greater than on methyl or ethyl alcohol. When the mixture was heated for 5 minutes and then rapidly cooled the consumption of *N* alkali was 0.10, 0.05 and 0.15 cc. for 0.270, 0.320 and 0.410 cc. of acetone. Using the density of 0.7863[7] for acetone one mole reacted, therefore, with 27.32, 11.53 and 26.93 cc. of *N* alkali, respectively, giving thus an error of 2.7, 1.15 and 2.7%, respectively, if the concentration of each is molar.

Table I shows the actual effect of these substances on the determination of formaldehyde by the peroxide method. No attempt was made to cool

TABLE I

EFFECT OF ADDED SUBSTANCES ON THE DETERMINATION OF FORMALDEHYDE IN PARAFORMALDEHYDE BY THE PEROXIDE METHOD

Paraformaldehyde G.	$\frac{\text{Moles HCOONa}}{\text{Moles HCHO}}$	$\frac{\text{Moles CH}_3\text{OH}}{\text{Moles HCHO}}$	$\frac{\text{Moles C}_2\text{H}_5\text{OH}}{\text{Moles HCHO}}$	$\frac{\text{Moles acetone}}{\text{Moles HCHO}}$	% CH_2O
0.4104	1.145	. .	. .	. . .	96.34
.4212	1.12	. .	. .	. . .	96.77
.3922	1.85	. .	. .	. . .	96.69
.3639	1.31	2.59	. .	. . .	97.22
.4003	0.64	1.98	. .	. . .	97.65
.3525	1.19	3.79	. .	. . .	97.73
.3742	1.65	5.14	. .	. . .	97.59
.4258	1.11	3.18	. .	. . .	96.94
.3917	. .	0.280	. .	. . .	97.10
.5754	. .	.304	. .	. . .	96.75
.5989	. .	.261	. .	. . .	96.56
.4589	. .	.390	. .	. . .	96.50
.3460	0.71	. .	2.73	. . .	97.14
.4169	. .	. .	2.65	. . .	97.21
.4271	. .	. .	1.51	. . .	96.99
.3106	. .	. .	1.11	. . .	97.20
.3807	. .	. .	2.88	. . .	96.82
.4183	. .	. .	2.38	. . .	97.17
.4562	. .	0.369	.279	. . .	97.33
.5390	. .	.162	.104	. . .	97.31
.4710	. .	.170	.103	. . .	96.70
.4546	. .	. .	. .	0.161	97.34
.4847	. .	. .	. .	.140	97.46
.4517	. .	. .	. .	.098	97.23
.2981	. .	. .	. .	.115	97.42
.2839	. .	. .	. .	.197	97.69

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[7] Krug and Elroy, *Z. anal. Chem.*, **32**, 106 (1893).

Runs 5, 6 and 7, while 8 was placed in water at about 20° for cooling. Runs 22 and 26, inclusive, show the effect of acetone. Evidently, if present in traces acetone should not have an effect when this method is used. Omitting Runs 5, 6 and 7, and 22 to 26, inclusive, the average value obtained was 96.94% with an average deviation of 0.20%, or about 0.1% higher than that found in the absence of these materials.

Neutral Sulfite Method.—No color change was noted on the addition of 1.5 g. of anhydrous sodium formate to 25 cc. of 4 *N* sulfite solution neutralized to rosolic acid by 0.498 *N* sulfuric acid.

In 3 experiments the average alkalinity produced on the addition of 5 cc. of methyl alcohol to 25 cc. of neutralized sulfite solution was 0.41 cc. of 0.498 *N* sulfuric acid, using rosolic acid as an indicator. Assuming 5 cc. of methyl alcohol to be about 0.12 mole, the same amount of formaldehyde would require 240 cc. of 0.498 *N* acid for the neutralization of the base liberated by the reaction. This shows that for equal concentrations methyl alcohol causes an error of 0.16% when *no correction* is made for the effect of dilution.

The values given in Table II show that methylal, ethyl alcohol and methyl alcohol have no appreciable effect in the determinations by the neutral sulfite method.

TABLE II

DETERMINATION OF FORMALDEHYDE IN PARAFORMALDEHYDE 4*N* IN SODIUM SULFITE SOLUTION, 1.169 *N* IN SULFURIC ACID, USING ROSOLIC ACID AS INDICATOR

Paraformaldehyde G.	Ethyl alcohol G.	Methyl alcohol G.	Methylal G.	CH_2O found, %
0.4787	...	0.2255	...	96.90
.3682	0.1457	.0780	...	96.85
.4258	.1422	.1555	...	96.92
.3155	.1500	.2333	...	96.80
.4488	.1104	.2178	...	97.02
.3563	.1419	...	...	96.74
.4357	.1143	...	...	96.97
.4385	.1498	...	...	96.99
.5551	...	...	0.1579	96.83
.3216	...	...	.1210	96.61
				Av. 96.86
				Av. dev., 0.10

Acetone and neutral sulfite react, liberating alkali just as formaldehyde does. Assuming the density of acetone to be 0.8, the amount of base liberated per mole of acetone was 407.5, 410.0 and 408.0 cc. as determined by neutralization with *N* sulfuric acid, working with samples of 0.235, 0.310 and 0.135 cc., respectively. This substance, then, would cause an error of 40% if the concentration of formaldehyde and acetone were the same.

Paraformaldehyde in the presence of acetone, as determined by this method, gradually decreased in purity with increased time of contact before neutralization of the alkali liberated. With the addition of 0.060 cc. of acetone to samples of paraformaldehyde of 0.45 to 0.52 g. the purity determined was 97.66, 97.03, 96.27, 96.00 and 93.70% with time intervals of 5, 10, 15, 20 and 30 minutes, respectively. When 0.4466, 0.5283 and 0.5194 g. were mixed with 0.250, 0.235, and 0.240 cc. of acetone, respectively, the purity determined was 101.34, 95.23 and 94.45% with time intervals of 5, 10 and 15 minutes, respectively.

These data show that the determinations when made within 5 minutes' time may be high but not additive. The larger the amount of acetone, the greater will be the error. The cause of the change may be due to (1) the addition of sodium sulfite to the acetone and resultant liberation of sodium hydroxide; (2) the condensation of acetone and formaldehyde under the influence of the base present, thus freeing 2 molecules of sodium sulfite; or (3) the reaction of formaldehyde with the base, forming sodium formate and methyl alcohol. The first cause would be responsible for the first increase, and the second and third causes would tend to lower the values with time, as found. No attempt was made to determine the actual cause of this variation.

Summary

1. The iodimetric method can be used for the determination of formaldehyde in the presence of methyl alcohol and formic acid. Methylal, if pure, should have no effect. When acetone and ethyl alcohol are present this method cannot be used.

2. The peroxide method as outlined can be used for the determination of formaldehyde in the presence of methyl alcohol, ethyl alcohol, formic acid and methylal. When acetone is present in equal concentrations, the determination will be about 2% high.

3. The neutral sulfite method can be used for the determination of formaldehyde in the presence of methyl alcohol, ethyl alcohol, formic acid and methylal. Acetone introduces an error that cannot be readily corrected.

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