THE ESTIMATION OF ACETONE IN METHYL AND ETHYL ALCOHOL.

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During the examination of a number of commercial samples of "pure" methyl alcohol great difficulty was experienced in obtaining concordant results for the acetone content as determined by Messinger's method. Even when several precautions were adopted and fairly comparable values obtained, the results were higher than those expected. Further, when samples of methyl alcohol stated to be acetone-free and repurified in the laboratory with great care were examined, high values were obtained for their acetone content. It seemed evident, therefore, that the method itself was unreliable, and the following investigation was undertaken with a view to ascertaining the reason for the discrepancies.

Messinger's Method.—This method (*Ber.*, 1888, **21**, 3366) consists in treating the sample with sodium hydroxide followed by standard iodine solution, the sodium hypoiodite formed reacting according to the equation:—

$$CH_3.\ CO.\ CH_3 + 3\ NaOI = CH_3.\ COONa + 2\ NaOH + CHI_3.$$

After acidification, the excess of iodine is titrated with sodium thiosulphate, and the acetone content calculated from the quantity of iodine consumed.

The method has been examined by several investigators among whom may be mentioned Collischonn (*Z. anal. Chem.*, 1890, **29**, 562), Squibb (*J. Amer. Chem. Soc.*, 1896, **18**, 214), Geelmuyden (*Z. anal. Chem.*, 1896, **35**, 503). Denige (*Ann. Pharm. Bordeaux*, 1910), however, disagreed with the former authors. Marriott (*J. Biol. Chem.*, 1913, **16**, 218) explained some of the anomalous results previously obtained and showed that accurate values were obtainable except when the quantity of acetone was very minute. Goodwin (*J. Amer. Chem. Soc.*, 1920, **42**, 39) studied the effect of varying conditions upon the results and laid down several definite requirements for the manner in which the reaction should be conducted. He also drew attention to the fact that alcohols may react with the iodine solution, but gave no quantitative results. Rakshit (*Analyst*, 1916, **41**, 246) suggested the use of lime water instead of sodium hydroxide solution as a means of avoiding errors due to methyl alcohol. Bates, Mullaly and Hartley (*J. C. S.*, 1913, **123**, 401) examined the reaction in some detail, and found that sodium hypoiodite and methyl alcohol react to form iodoform and probably other products.

EXPERIMENTAL.

Preliminary experiments were conducted with aqueous solutions of acetone with the object of ascertaining the extent to which it is necessary to follow the somewhat rigorous conditions laid down by Goodwin. These are: (1) The excess of iodine must be at least equal to the amount which reacts; (2) the reaction must be conducted at 15–17°; (3) the solution should stand for 20 minutes; and (4) only just sufficient acid to make the solution acid should be added before titration. Condition (2) in particular is somewhat troublesome in the tropics and a higher temperature would be more convenient.

Pure acetone was prepared from the sodium iodide compound (Shipsey and Werner, *J. C. S.*, 1913, **103**, 1255), dried and redistilled. Solutions of different concentrations were prepared and 20 c.c. taken for each experiment. The following results were obtained:—

Acetone taken mg.	Acetone found mg.							
	A	B	C	D_5	D_{10}	D_{15}	D_{20}	E
16·10	16·05	16·13	16·13	16·07	16·05	16·06	16·06	15·99
8·05	8·15							
1·61	1·70	1·59	1·70	1·56	1·56	1·56	1·57	
0·40	0·40							0·40
0·10	0·09	0·10	0·09	0·10	0·10	0·10	0·10	

The figures under "A" are the mean of 5 values obtained under the standard conditions. The maximum variation observed in any one set of readings was 0.05 mg. between the extreme values. In B, only 20 per cent. excess of iodine was used and in C the temperature was 27–30°, other conditions being the same. The time of standing was then altered to 5, 10, 15 and 20 minutes at 15–17° and the results are shown under D. Finally, 1, 2, 3 and 5 c.c. of 1 N sulphuric acid were added in excess and identical figures as shown under E were obtained in all cases.

Experiments were next conducted with methyl alcohol. For these a sample of pure methyl alcohol purchased as acetone-free and the same material after treatment to remove acetone were employed. For purification, the alcohol was allowed to stand overnight with sodium hydroxide to which iodine solution had been added. It was then distilled and the density determined. The following are typical values obtained with 20 c.c. of the original alcohol treated with 25 c.c. of sodium hydroxide solution (1 N) and 25 c.c. of 0.1 N iodine solution observing Goodwin's conditions.

Iodine absorbed (in c.c.):—10.55, 12.65, 8.7, 10.5, 11.8 and 13.9, the corresponding quantity of acetone ranging from 0.042 to 0.067 per cent. Similar discordant values from 0.033 to 0.050 were given by the purified alcohol.

It would be expected that if a reaction takes place between iodine and methyl alcohol, the effect would be less on dilution and this was confirmed by adding water to 20 c.c. of alcohol.

c.c. water added	0	50	100	150	300	400
c.c. iodine absorbed	13·7	9·20	7·12	5·82	4·50	3·80

The iodine absorption would also increase with time and this was found to be the case.

Time of standing in mins.	5	10	20	30	60	120
Iodine absorbed (in c.c)	7·4	10·9	16·6	19·4	22·6	23·5

In order to ascertain if it was possible to obtain zero iodine absorption, the methyl alcohol was treated with sodium hydroxide and iodine and re-distilled three times to ensure the absence of acetone. At each stage, 5 c.c. of alcohol was taken and diluted with 40 c.c. of water before estimation. 1.15 c.c. of iodine solution was used up in each case, corresponding with 0.022 per cent. of acetone. Since good quality samples of c.p. methanol should contain less than 0.02 per cent. of acetone, it is obvious that Messinger's method is unsuitable for the estimation.

The reaction between methyl alcohol and sodium hypoiodite.—Since the first stage in the production of iodoform from ethyl alcohol and sodium hypoiodite is considered to be the formation of acetaldehyde, it appeared likely that in the case of methyl alcohol, formaldehyde might be formed and subsequently oxidised to formic acid or even to carbon dioxide. On neutralising one of the experimental solutions after titration, evaporating to dryness and distilling with phosphoric acid, a solution was obtained which gave a precipitate with mercuric chloride showing that formic acid was present. The formic acid was estimated by Auerbach and Zeglin's method (*Z. physikal Chem.*, 1922, **103**, 166) by heating the solution with sodium acetate and mercuric chloride. Using 50 c.c. of pure methyl alcohol and 1 N sodium hydroxide, the amount of 0.1 N iodine which reacted was determined and the quantity of formic acid produced was calculated on the assumption that no secondary reactions occurred. The formic acid actually formed was then determined. The following mean results were obtained, the temperature in all cases being 28–30°.

	Time mins.	Iodine absorbed c.c.	Formic acid		
			calc. mg.	Found mg.	Per cent
30 c.c. I_2 and 20 c c. NaOH	5	24·7	28·0	23·8	85
Do. do.	10	27·0	30·9	26·6	86
50 c.c. I_2 and 50 c.c. NaOH	5	29·9	34·4	31·4	91

It is evident, therefore, that, with the quantities of reagents ordinarily used, formic acid is the main reaction product. Although in the last experiment the total quantity of iodine is greater relative to the methyl alcohol, its concentration (33.3 c.c. in 100 c.c.) is only slightly more and thus the quantity absorbed is not much greater than in the previous experiments. It may also be noted that the reaction takes place with considerable rapidity.

In order to examine the reaction in somewhat greater detail an experiment was made in which 100 c.c. methyl alcohol, 200 c.c. 1 N sodium hydroxide solution and 1050 c.c. water were mixed and maintained at 30°. 250 c.c. 0.1 N iodine solution were then added and samples were taken at intervals. A similar experiment was made with 100 c.c. of water instead of methyl alcohol and in this the sodium hypoiodite was estimated by Rupp's method (*Z. anal. Chem.*, 1918, **57**, 16), the solution being treated with hydrogen peroxide to decompose the hypoiodite, boiled to expel oxygen and the residual iodate determined. It has been shown by Schwicker (*Z. physikal. Chem.*, 1895, **16**, 303) that the reaction $3KIO = KIO_3 + 2KI$ is one of the second order in concentrated solutions when the alkali is in excess so that $(a-x)/xt = ka$ where x is the concentration of hypoiodite at time t and a the initial concentration. This equation was found to be approximately true until the reaction approached completion as may be seen from the following figures which show the number of milligrams of sodium hypoiodate in 150 c.c. of solution at different times and the corresponding values of $k\,a$:—

Time in mins.	0	1·5	3	5	10	20	30	45	60	120
mg. NaOI	414	232	162	113	61	35	22	13	9	2
$k\,a$		0·52	0·52	0·53	0·58	0·54	0·59	0·68	0·75	1·7

Since the alcohol concentration does not alter appreciably, the experimental error towards the end of the series is large and the increasing values for $k\ a$ have no significance. In the reaction between methyl alcohol and sodium hypoiodite, since the concentration of alcohol does not vary appreciably, the rate of reaction at different times depends only on the quantity of hypoiodite present. Assuming that this rate is directly proportional to the concentration of hypoiodite x, $dy/dt = kx$, where y is the quantity of alcohol decomposed at time t. Since the quantity of hypoiodite used up by the alcohol is found to be small in comparison with the amount which decomposes spontaneously, it is sufficiently accurate to assume $x = a/(1 + akt)$, as can be derived from the equation already given. On substituting for x and integrating, $ky = Kln\ (l + akt)$. Assigning to ak the value 0.53, deduced from the decomposition experiments, and putting $K = 0.00139$, a mean value, the values of y may be calculated and compared with those experimentally obtained. The following figures show the amount of iodine, expressed as c.c. of 0.1 N solution, absorbed by 10 c.c. of methyl alcohol at different times, and also the calculated values:—

Time in mins.	1·5	3	6	10	20	30	45	60	120
c.c. absorbed	0·60	1·15	1·60	2·00	2·60	3·10	3·70	4·05	4·50
c c. calculated	0·63	1·03	1·55	2·00	2·66	3·07	3·49	3·79	4·52

The agreement is as good as can be expected from the nature of the experiment and suffices to confirm the correctness of the assumptions upon which the equation was based.

OTHER METHODS OF ESTIMATION.

Tonescu, Spirescu, and Popescu (*Bull. Soc. Chem., Roumania,* 1923, **5**, 15) have suggested the precipitation of acetone with mercuric sulphate as $Hg_2SO_4 . 3HgO . 4(CH_3.CO.CH_3)$ and subsequent titration of the mercury. It was found, however, that the reagent gave a precipitate with even the most carefully purified samples of methyl alcohol and thus it appeared unsuitable. Morasco (*Ind. Eng. Chem.,* 1926, **18**, 701) liberated hydrochloric acid from hydroxylamine hydrochloride by acetone and titrated the free acid using methyl orange as indicator. On trying this method it was found that the end point was not very sharp and thus it could not be used for small quantities of acetone. An examination was next made of the process of Scott-Wilson as modified by Marriott (*J. Physiol.,* 1911, **42**, 444; *J. Biol. Chem.,* 1913, **16**, 284), in which acetone is precipitated as $CO.C_2(HgCN)_4\ Hg$ by means of mercuric cyanide. The reagent is prepared by dissolving 10 g. of mercuric cyanide and 180 g. sodium hydroxide in 1200 c.c. water and adding 400 c.c. of 0.72 per cent.

silver nitrate solution. 30 c.c. of this reagent correspond to one milligram of acetone. This reagent gave no precipitate with purified methyl alcohol but on the addition of 0.1 mg. of acetone to 10 c.c. of the alcohol, a very distinct precipitate resulted.

The actual method adopted was to add the sample to the freshly filtered reagent and to allow the mixture to stand for 20 minutes with occasional shaking. The precipitate was filtered through a Gooch crucible, washed with water and dissolved by boiling with 10 c.c. of a mixture of 5 c.c. sulphuric acid, 40 c.c. nitric acid and 55 c.c. water. Asbestos was removed by filtering through a second Gooch crucible and the mercurous salt oxidised by adding permanganate to the boiling solution until a brown precipitate formed. This was dissolved by adding a few drops of fuming nitric acid and the mercury was titrated with 0.01 N ammonium thiocyanate, using 2 c.c. of a saturated solution of ferric-alum as indicator. According to the formula, 1 c.c. of ammonium thiocyanate should correspond to 0.061 g. of acetone, but Marriott gives the figure 0.0644 and this was found to yield more accurate results.

On testing the method with aqueous acetone solutions containing 3.14 mg. in 10 c.c. and 1.26 mg. in 20 c.c., the weights found (mean of 4 and 5 determinations) were 3.18 and 1.26 mg. respectively, the individual values not varying by more than 1 per cent. With methyl alcohol solutions the following results were obtained (mean of 3 to 5 values) :—

MeOH c.c.	Acetone taken mg.	Acetone found mg.	Extreme values	
50	8·05	8·01	7·98	8·06
30	4·85	4·82	4·78	4·88
20	3·23	3·23	3·21	3·24
10	1·61	1·63	1·61	1·65
10	0·40	0·37	0·36	0·37
10	0·10	0·10	0·097	0·10

Variations in the conditions of precipitation were then examined. Allowing the precipitate to stand for various periods upto 80 minutes was found not to affect the results, but a 20-minute period of standing was found necessary as the precipitate required some time for coagulation and could not be filtered until this occurred. Filtration difficulties were also experienced if the precipitate was too bulky, and it was found desirable to restrict the quantity of acetone in any one determination to 8 mg.

Dilution of the reagent with varying amounts of water upto 3 times its original volume did not appreciably affect the results. The most dilute solution examined contained only 3 mg. of acetone in 400 c.c. and the quantities found were accurate to 0.05 mg.

The standard quantity of reagent is 9 times the amount required theoretically and experiments were made to see if this large excess was necessary. The following values were obtained with 20 c.c. of methyl alcohol containing 3.23 mg. of acetone, 100 c.c. of reagent being the normal amount:—

Reagent c.c.	100	50	30
mg. acetone found	3·20	2·91	2·66

It is thus evident that it is not desirable appreciably to reduce the quantity of reagent.

While making these estimations it was observed that the acetone content of some of the solutions decreased on standing. A solution containing 3.20 mg. in 20 c.c. of methyl alcohol was kept in a stoppered bottle in a well-lighted laboratory and samples of 20 c.c. withdrawn at intervals. The acetone content varied as shown below, each figure being the mean of two concordant determinations:—

Time in days	0	3	6	9	11
mg. acetone	3·22	2·54	1·83	1·89	1·88

The same solution, when stored in sealed brown glass tubes, was found to be unchanged after 3 and 6 days. The reaction thus appears to be a photochemical one, and from the fact that no change takes place in the illuminated solution after 6 days, it seems that an equilibrium is established. Further investigation is required regarding the exact nature of the reaction.

Estimation in ethyl alcohol solutions.—Ethyl alcohol free from acetone was prepared by refluxing it with sodium hydroxide, distilling and adding excess of the mercury cyanide reagent to the distillate. The precipitate was filtered and the filtrate distilled from calcium chloride yielding a 93 per cent. product which gave no precipitate with the reagent. On adding known amounts of acetone and conducting the estimation, values very similar to those in presence of methyl alcohol were obtained and the method is thus suitable for estimations in ethyl alcohol solutions.

SUMMARY.

1. Messinger's method gives accurate results when determining acetone in aqueous solution even in concentrations as low as 0.5 mg. in 100 c.c., under conditions much more variable than those laid down by Goodwin as being necessary.

2. In presence of methyl alcohol, high and irregular values are obtained owing to the reaction between sodium hypoiodite and methyl alcohol. The main product of this reaction is formic acid which is formed to the extent of 80–90 per cent. of the amount theoretically possible.

3. Assuming that the rate of oxidation of methyl alcohol is proportional to the concentration of hypoiodite at any time, a logarithmic equation has been derived for the total quantity oxidised, and the calculated results agree with those obtained experimentally.

4. Of other methods for estimating acetone, that of Scott-Wilson modified by Marriott has been found the most suitable. This gives accurate results in presence of methyl and ethyl alcohol and the reagent is capable of detecting 0.1 mg. in 100 c.c. According to Marriott, 1 c.c. of 1 N ammonium thiocyanate corresponds to 6.12 mg. of acetone as compared with 5.80 mg. required by theory. The present experiments show that the factor recommended by Marriott yields good results. The method should not, however, be employed for precipitating more than about 8 mg. of acetone at a time. The precipitate must be allowed to stand for at least 20 minutes to coagulate, and a large excess, 8–9 times the theoretical amount of reagent, must be used.

Our best thanks are due to Professor H. E. Watson for his keen interest and valuable suggestions during the progress of this investigation.

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[Received, 21–6–1935.]

1330-35.—Printed at The Bangalore Press, Bangalore City by T. Subramania Aiyar, Superintendent.