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

The Iodine-Sensitized Decomposition of Methyl Alcohol

BY G. K. ROLLEFSON AND WARREN GARRISON

Some years ago it was found by Bairstow and Hinshelwood[1] that the rates of decomposition of a number of simple organic compounds were greatly increased by the addition of iodine and in some cases the nature of the products was changed. Later, Rollefson and Faull[2] found that under the experimental conditions prevailing in these experiments the concentration of free iodine is extremely low during most of the reaction but returns to its original value as the decomposition of the organic compound approaches completion. They also showed that in mixtures of acetaldehyde or propionaldehyde with iodine the decomposition is the net result of a reaction of the iodine with the aldehyde to give carbon monoxide, hydrogen iodide, and alkyl iodide followed by the reaction of the alkyl iodide with hydrogen iodide to form the corresponding hydrocarbon and iodine. The latter reaction is the rate determining step. In this paper we wish to present a study of the iodine-sensitized decomposition of methyl alcohol which differs from that of the aldehydes in that the products are not the same as are obtained in unsensitized decomposition. In this case also we have found that the action of the iodine can be expressed in terms of ordinary chemical reactions.

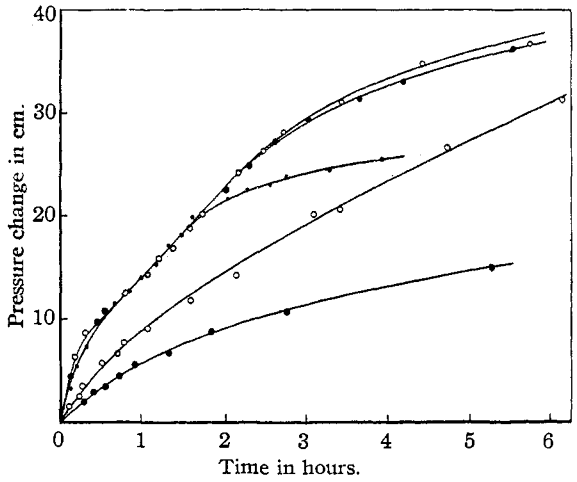

Fig. 1.—Pressure change *vs.* time curves. The composition of the reaction mixtures for the various curves is:

Curve	Iodine added, mole	Alcohol added, mole
1	1.67×10^{-4}	29.4×10^{-4}
2	2.66	29.4
3	4.00	20.0
4	4.00	28.6
5	4.00	30.9

In order to obtain the maximum amount of information concerning conditions which affect the rate, it is desirable to have the iodine concentration measurable during the course of the reaction. Preliminary tests showed that at 325° the unsensitized decomposition was negligible and the sensitized reaction proceeded at a convenient rate with appreciable amounts of free iodine present at all times. All of the quantitative measurements were made at this temperature.

The reaction vessel was made of Pyrex, cylindrical in shape, and of approximately 250 cc. capacity. It was connected through a click gage to a mercury manometer and through another tube, which was sealed off during the reaction, to vacuum pumps and a supply of methyl alcohol. The vessel was mounted in an electric furnace which was kept within a degree of the desired temperature by hand regulation. The temperature was measured by a chrome–alumel thermocouple placed in a small glass tube which was sealed into the reaction vessel.

The alcohol was distilled over anhydrous potassium carbonate; the middle fraction with a boiling range of less than one degree was used (boiling range, 64.0–64.6°). The iodine was resublimed Merck reagent.

The procedure followed in filling the reaction vessel was to introduce sufficient alcohol vapor to give the desired pressure at 325°, and seal the reaction vessel off from the vacuum system and alcohol supply. The temperature of the system was raised to 325° and then a bulb containing a weighed quantity of iodine was broken in the vessel. The curves obtained by plotting the pressure against the time were found to be very reproducible and showed no anomalies which might be attributed to slowness of mixing of the iodine and alcohol vapors. A few typical curves are shown in Fig. 1.

It was found that the pressure–time curves were quite reproducible for any given mixture.

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(1) Bairstow and Hinshelwood, *Proc. Roy. Soc.* (London), **A142**, 77 (1933); *J. Chem. Soc.*, 1147 (1933).

(2) Rollefson and Faull, THIS JOURNAL, **58**, 1755 (1936); **59**, 625 (1937).

Consequently we found it more convenient to carry out most of the determinations of the composition of the reaction products at different degrees of completion of the reaction by heating a mixture of alcohol and iodine vapors for various definite times in sealed bulbs identical in size and shape with the one used in the pressure measurements. When the bulbs had been heated long enough to bring the reaction to the desired degree of completion the bulbs were removed from the furnace and cooled rapidly. Different rates of cooling were tried but were not found to affect the results appreciably. In order to analyze the reaction mixture the tip of the reaction vessel was broken under the surface of a known volume of potassium iodide solution and this solution was used to force the gases into an Orsat gas analyzer. A sample of the iodide solution was titrated for iodine using 0.05 *N* thiosulfate solution. The hydrogen ion concentration was determined by adding excess of potassium iodate to the same sample of the iodide solution and titrating again with the thiosulfate. The gases were analyzed for carbon monoxide, carbon dioxide, hydrogen and methane by conventional methods. Carbon dioxide and hydrogen were found to be negligible. The amounts of carbon monoxide and methane present at various states of the reaction are shown in Table I.

TABLE I

METHANE AND CARBON MONOXIDE PRESENT DURING THE REACTION

CH_3OH added = 25 × 10^{-4} mole. I_2 added = 3.9 × 10^{-4} mole.

	Moles × 10^4		
Hours	CH_4	CO	CH_4/CO
0.75	2.40	3.40	0.71
.75	2.30	3.40	.68
1.25	4.20	4.50	.93
1.25	4.25	4.30	.99
2.5	8.30	6.00	1.38
2.5	8.45	6.15	1.37
3.0	9.30	6.76	1.38
3.0	9.30	6.70	1.39
4.25	13.40	7.30	1.84
4.25	13.60	7.45	1.83
5.5	15.10	7.50	2.01
5.5	15.0	7.50	2.00
9.0	15.8	7.56	2.08
9.0	15.9	7.56	2.10
18.0	16.0	7.60	2.10

The condition of the iodine during that part of a run corresponding to the relatively straight section of the pressure–time curve is shown by the data in Table II.

TABLE II

DISTRIBUTION OF IODINE DURING A REACTION

I_2 added = 1.67 × 10^{-4} moles. CH_3OH added = 25.0 × 10^{-4} moles.

Hours reacted	I_2 × 10^4 mole	HI × 10^4 mole	Other iodides × 10^4 mole
1	0.314	0.340	2.38
1.5	.348	.360	2.228
2	.308	.340	2.38
3	.394	.368	2.20

The presence of hydrogen iodide was demonstrated by shaking water and carbon tetrachloride in a bulb filled with the gases to be analyzed. In this way hydrogen iodide and iodine were extracted from the gases. The water and carbon tetrachloride were separated, the water layer extracted again with carbon tetrachloride and then titrated for hydrogen and iodide ions. The iodide was found to be about 1% higher than the hydrogen ion but this slight discrepancy was attributed to incomplete removal of the iodine by the carbon tetrachloride.

The data which have been obtained show that the net over-all reaction may be represented by the equation

$$3CH_3OH = 2CH_4 + CO + 2H_2O \qquad (1)$$

Additional support for this equation is found in that the total pressure change observed in reaction mixtures which were run to completion was two-thirds the original methyl alcohol pressure. However, the variation of the methane–carbon monoxide ratio in the course of the reaction shows that this net reaction must be the resultant of two parallel reactions, one an oxidation of the alcohol to carbon monoxide, the other a reduction to methane. Iodine is the oxidizing agent for the first and hydrogen iodide the reducing agent for the second. The equations representing the changes are

$$CH_3OH + 2I_2 = CO + 4HI \qquad (2)$$

$$CH_3OH + 2HI = CH_4 + I_2 + H_2O \qquad (3)$$

The preponderance of carbon monoxide in the early stages of the reaction is caused by the first of these reactions proceeding faster than the second until the steady state is reached. During the steady state the methane and carbon monoxide are formed in the proportions of two to one as required by the over-all reaction as written above. In the final stages of the reaction when the iodine is regenerated methane is produced thus compensating for the excess carbon monoxide produced in the initial stage. This behavior is apparent from an inspection of the data in Table I.

The formation of methyl iodide in the reaction mixture can be accounted for by

$$CH_3OH + HI = CH_3I + H_2O \qquad (4)$$

which may be one of the steps in the mechanism of (3). The net change in the reaction mixture from the time of mixing is given by a combination of the equations (2), (3), (4). When the reaction is carried to completion the contribution from (4) is zero and the net effect is the combination of (2) and (3) so as to give (1).

No mechanisms which we have devised for the reactions (2) and (3) will account for all the experimental observations. The possibility that methane is formed from methyl iodide and hydrogen iodide was considered. Assuming that the iodine not in the form of hydrogen iodide or free iodine was all methyl iodide, we calculated the rate of formation of methane from Ogg's data. The observed rate during the steady state was 12.6×10^{-7} mole/cc./hr. and the calculated rate was 18.5×10^{-7} mole/cc./hr. The agreement is not sufficiently good to warrant the conclusion that the methane must be formed by this reaction but it seems to be a reasonable possibility at these temperatures. The constancy of the rate of formation of methane during a large percentage of the reaction could be accounted for by this reaction since the concentrations of methyl iodide and hydrogen iodide are constant over the same range.

Summary

The iodine sensitized decomposition of methyl alcohol has been studied at 325°. It has been shown that although the net effect in systems in which the reaction was carried to completion may be represented by the equation $3CH_3OH = 2CH_4 + CO + 2H_2O$ this is the resultant of two other reactions. One of these is the oxidation of the alcohol to carbon monoxide by the iodine, the other the reduction of the alcohol to methane by hydrogen iodide.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 6, 1939

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 747]

The Diliturates (5-Nitrobarbiturates) of Some Physiologically Important Bases

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The qualitative or quantitative isolation of basic compounds from natural sources is, in general, most satisfactorily accomplished when the base in question can be obtained as the salt of a suitable acid.[1] Of the acidic reagents that have been employed in the past, it is certain that compounds such as picric acid, styphnic acid, picrolonic acid, nitranilic acid[2] and 3-nitrodiketohydrindene[3] have found the greatest application and it is noteworthy that all of these compounds are characterized by the presence of a contiguous nitrophenolic (or enolic) array in an ensemble of atoms capable of forming a resonating system.

We have found that dilituric acid (5-nitrobarbituric acid) surpasses the above nitro-enolic compounds as a reagent for the isolation of many naturally occurring bases and it is the purpose of this communication to call attention to the properties of some of the salts of this acid and their use in isolation problems.

Dilituric acid[4] prepared by the direct nitration of barbituric acid[4b,c,f,h,i] is readily purified. The solubility of the acid, in millimoles per liter of solution at 25°, in methanol is 99; in 95% ethanol, 85; in water, 63; in absolute ethanol, 35; in acetone, 25; in ethyl ether, 0.9; and in benzene, 0.4. Dilituric acid behaves like a strong monobasic acid and from the electrometric titration of a 0.00904 *N* aqueous solution it appears that the acid strength of dilituric acid is intermediate between that of picric acid and hydrochloric acid.[5]

Examination of Table I reveals that dilituric acid is a satisfactory reagent for the separation of potassium from binary mixtures containing so-

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[1] (a) M. Bergmann and C. Niemann, *J. Biol. Chem.*, **122**, 577 (1937); (b) W. H. Stein, C. Niemann and M. Bergmann, THIS JOURNAL, **60**, 1703 (1938); (c) M. Bergmann and W. H. Stein, *J. Biol. Chem.*, **128**, 217; **129**, 609 (1939); (d) H. R. Ing and M. Bergmann, *ibid.*, **129**, 603 (1939).

[2] B. W. Town, *Biochem. J.*, **30**, 1833 (1936).

[3] (a) G. Wanag, *Ber.*, **69**, 1066 (1936); (b) G. Wanag and A. Lode, *ibid.*, **70**, 547 (1937).

[4] (a) A. Schlieper, *Ann.*, **56**, 23 (1845); (b) A. Baeyer, *ibid.*, **127**, 209 (1863); **130**, 140 (1864); (c) M. Grimaux, *Ann. chim.*, (5) **17**, 278 (1879); (d) M. Ceresole, *Ber.*, **16**, 1134 (1883); (e) R. Bartling, *Ann.*, **339**, 39 (1905); (f) A. F. Holleman, *Rec. trav. chim.*, **16**, 168 (1897); (g) H. Biltz and K. Sedlatscheck, *Ber.*, **57**, 339 (1924); (h) *Org. Syntheses*, **12**, 58 (1932); (i) H. Fredholm, *Z. anal. Chem.*, **104**, 400 (1936).

[5] P. A. Trübsach, *Z. physik. Chem.*, **16**, 718 (1895).