[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XX. The Photochemical Decomposition of Acetone in the Schumann Region

BY WINSTON M. MANNING

The ultraviolet absorption spectrum of gaseous acetone falls into at least two distinct regions, one between 3400 Å. and 2200 Å.,[1] the other starting at about 2000 Å. and extending down at least as far as 1200 Å.,[2] the lower limit of measurements so far made. The decomposition of acetone by light in the region between 3400 Å. and 2200 Å. has already been studied.[3] The purpose of the present investigation is to study the decomposition produced by radiation of wave length below 2000 Å., and to compare the results with those obtained by using the longer wave length light, in so far as this may be done by analysis of the gaseous products of reaction in the two cases.

Some unsuccessful attempts were made to obtain a beam of light consisting only of wave lengths below 2000 Å. A fluorite prism monochromator would yield the desired type of radiation, but for this work there was not available a prism of sufficient size to give the necessary intensity. It was therefore decided to use a differential method in carrying out the decomposition studies, first exposing acetone to all the radiation transmitted by a fluorite window, using an aluminum spark in hydrogen as a light source, and then repeating the experiment, replacing the fluorite with a suitable filter to cut out wave lengths shorter than 2200 Å. Other conditions being the same in the two experiments, an accurate comparison of the total amount of decomposition in the two cases, when combined with an analysis of the decomposition products, should suffice to give a description of the reaction produced by the shorter wave length radiation.

Experimental

The acetone used in these experiments previously had been purified for use in solubility work in the laboratory of Professor Kraus. It was further purified by fractional distillation with liquid air, and stored over sodium iodide. Some of the acetone used in later experiments was dried over calcium chloride before being fractionally distilled.[3a]

The light source was a water cooled aluminum spark,[4] operated in a stream of hydrogen at pressures of about 0.9 atmosphere. The hydrogen was passed over hot copper to remove any traces of oxygen, and then dried over phosphorus pentoxide before being passed through the spark. The high-potential current was furnished by a 1 kilowatt 25,000 volt Thordarson transformer, with a 0.0045 microfarad capacity connected in parallel with the spark. In most runs a current of 8 amperes was passed through the primary (110 volt) line.

Two runs were made in which a Cooper-Hewitt quartz mercury vapor arc was used as a light source. It was operated at 120 volts and 3 amperes. Only the longer wave length ultraviolet light was desired in these cases, so the arc was placed parallel to the Pyrex tube leading to the reaction cell. In this way only light of wave length longer than 2900 Å. was permitted to act on the acetone.

The reaction vessel was a Pyrex tube 15 cm. long and 1.1 cm. in diameter. When radiation in the far ultraviolet was desired, the tube was fastened directly to the vessel containing the aluminum spark, with a fluorite window fixed between the two. The seal was made with "apiezon" wax. When it was desired to cut out radiation below 2200 Å., a cell containing a 2-cm. layer of 0.05 normal acetic acid was substituted for the fluorite window. The windows of the cell were optically plane pieces of fused quartz. A slow constant flow of acetic acid was maintained to avoid accumulation of decomposition products. With the fluorite window, the total distance from the spark to the nearest point of the reaction vessel was 13 cm.; with the acetic acid filter the distance was 15.5 cm.

Most reactions were run with initial acetone pressures either of the order of 100 mm. of mercury or in the neighborhood of 0.025 mm. of mercury. The higher pressures were measured with a mercury U-tube manometer, the lower pressures with a McLeod gage. In the former case, only a very small fraction of the acetone was decomposed, even with exposures as long as twenty hours. Consequently it was not possible during a reaction to detect any change in total pressure. In either case, the amounts of decomposition products were very small (from 1 to 10 cu. mm. at atmospheric pressure), so that it was necessary to employ a micromethod in their analysis.

(a) High Pressure Runs.[5]—After illumination of the acetone, liquid air was placed around a trap adjacent to the reaction cell and the residual gases transferred by means of a Toepler pump to a portion of the system containing a McLeod gage. After the pressure of the unknown gas mixture had been measured, the gases were

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[1] (a) Porter and Iddings, THIS JOURNAL, **48**, 40 (1926); (b) Norrish, *Nature*, **133**, 837 (1934).

[2] (a) Scheibe, Povenz and Linström, *Z. physik. Chem.*, **B20**, 283 (1933); (b) Noyes, Duncan and Manning, *J. Chem. Physics*, **2**, 717 (1934).

[3] (a) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933); (b) Norrish and Appleyard, *J. Chem. Soc.*, 874 (1934); (c) see Noyes, *Rev. Mod. Physics*, **5**, 280 (1933) for a review.

[4] The author wishes to express his appreciation to Dr. A. B. F. Duncan, who designed this spark.

[5] This method of analysis resembles in certain respects one described by Ryder, THIS JOURNAL, **40**, 1656 (1918).

again transferred, by means of another Toepler pump, to a tube containing copper oxide, which was maintained in an electric furnace at a temperature of about 190°. About six hours at this temperature was sufficient, at the low pressures under which this work was carried out, to convert completely into water and carbon dioxide, respectively, any hydrogen and carbon monoxide,[6] while leaving undisturbed the other gases which may have been present, *viz.*, methane, ethylene and ethane. Liquid air was then placed on a trap adjacent to the copper oxide tube in order to condense the carbon dioxide and water; the other gases were pumped off and returned to the McLeod gage, where the pressure was read and subtracted from the initial pressure to give the sum of the original carbon monoxide and hydrogen pressures. After the other gases were analyzed and pumped out, the liquid air bath on the trap by the copper oxide tube was replaced by solid ammonia (temperature −78°) and the carbon dioxide pumped off and measured, which gave directly the amount of carbon monoxide originally present. The amount of hydrogen originally present could then be calculated. The mixture of methane, ethylene and ethane was determined by combustion in the presence of a short platinum filament (length, 30 mm.; diameter 0.1 mm.) heated to a dull red heat. Pressures were measured with the McLeod gage already mentioned. Oxygen was added to the mixture by means of a modified form of Toepler pump, in which the volume of gas cut off from the oxygen storage system at each operation of the pump was small, about 1 cc. A trap immersed in solid ammonia served to keep mercury vapor away from the vicinity of the platinum filament, and also condensed water vapor formed during combustion. Knowing the amount of gas to be analyzed, the amount of oxygen used, and the amount of carbon dioxide formed, it was possible to calculate the amounts of methane, ethylene and ethane originally present.

(b) Low Pressure Runs.—In this case it was possible to decompose the acetone nearly completely within a reasonable length of time. Hence for these runs the analysis of the reaction products was extended to those gases condensed by liquid air in the trap near the reaction vessel. After completion of the rest of the analysis, these gases were transferred to the portion of the system containing the McLeod gage and platinum filament and determined by combustion with oxygen.

Several analyses have been made on known mixtures of the various gases involved, and the results indicate that by this method of analysis it is possible to analyze samples containing 1 or 2 cu. mm. at atmospheric pressure with an accuracy of about 5%, and larger samples with a somewhat smaller error. The determination of carbon monoxide is probably the most accurate; the simultaneous determination of the three hydrocarbons by combustion is the least accurate. Table I shows the results obtained with some known mixtures.

At room temperature copper oxide absorbs carbon dioxide very strongly, so that when performing an analysis involving carbon monoxide it is necessary to prevent the copper oxide temperature from falling much below 190° while the carbon dioxide formed is in contact with it.

TABLE I

RESULTS OF ANALYSES OF KNOWN MIXTURES

	Introduced, %	Found, %
(a) Total press., 76.5×10^{-3} mm.		
H_2	29	30
CO	33	34
CH_4	..	..
C_2H_4	25	23
C_2H_6	14	13
(b) Total press., 23.5×10^{-3} mm.		
H_2	63	63
CO	..	..
CH_4	..	3
C_2H_4	37	34
C_2H_6	..	..
(c) Total press., 86.5×10^{-3} mm.		
H_2	18	19
CO	23	23.5
CH_4	18	19.5
C_2H_4	19	17
C_2H_6	23	21

Under some conditions hydrogen and ethylene combine in the presence of copper to form ethane, and it appeared possible that this reaction might take place to a considerable extent during the time a gas sample was in contact with the copper oxide, since any hydrogen or carbon monoxide present would at once cause the formation of small amounts of free copper. Such, however, appears not to be the case, since an analysis performed on a known mixture of hydrogen and ethylene in which the two gases were in contact with copper oxide for six hours, gave no evidence of ethane formation (see Table Ib).

Results

(a) High Pressure Runs.—A summary of the data obtained from high pressure runs is given in Table II. For those runs in which the aluminum spark was used as the light source it will be noticed that reaction apparently took place only when the fluorite window was used. Hence it is assumed that practically all of the reaction is due to that portion of the radiation lying below 2000 Å. This is not surprising in view of the nature of the weak light source and the fact that the absorption by acetone in the region below 2000 Å. is very much stronger than its absorption in the near ultraviolet.[2b] The effective radiation lies mostly in the region of the Lyman bands (<1700 Å.). The runs made with water replacing the 0.05 normal acetic acid indicate further that radiation between 1900 and 2000 Å. is not effective in producing reaction with the acetone at pressures near 100 mm. of mercury. The transmission of the acetic acid filter was

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[6] See Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1923, Vol. III, p. 137.

TABLE II

ANALYSIS OF PRODUCTS FOR HIGH PRESSURE RUNS

Pressures in mm. of mercury

Run number	1	2	3	4	5	12	14	16	19[a]
Filter[b]	F	F	F	F	F	Q + A	Q + W	Q + W	P
Initial pressure	95	96	89	92	89	90	91	83	98
Time, min.	1300	400	1320	62	110	375	190	588	215
Press. of prod. not cond. with liq. air	0.176	0.0533	0.210	0.0157	0.0241	0.0004	0.0002	0.0002	0.0179
Products after CO and H_2 are removed	.0836	.0241	.102	.0049	.0078				.0105
O_2 used in combustion	.276	.0729	.332	.0152	.0236				.0327
CO_2 formed in combustion	.156	.042	.193	.0090	.0137				.0185
Press. of CO_2 formed in CuO tube	.0817	.0262	.0982	.0090	.0140				.0074
Proportions of analyzed products									
CO, %	46	49	47	57	58				41
H_2, %	6	6	5	12	10				..
CH_4, %	6	11	5	5	8				14
C_2H_4, %	..	8	8	9	7				4
C_2H_6, %	42	26	35	17	17				41

[a] Mercury arc was used as light source in run 19. [b] Abbreviations: F, fluorite window; Q + A, acetic acid filter with quartz windows; Q + W, water filter with quartz windows; P, Pyrex.

estimated by photographing through it the light from a quartz mercury vapor arc. Nearly all of the radiation above 2400 Å. was transmitted; below 2400 Å. absorption was increasingly noticeable, becoming complete at about 2200 Å.

The run with a mercury arc light source was made in order to obtain reaction at the longer wave lengths, for comparison purposes.

The variation of percentages of products found for different reactions is very large. In most cases the larger portion of the variation is probably a real one, and not due to errors in the analysis. Time of exposure seems to be one factor producing variation in the relative amounts of products, particularly in the case of carbon monoxide and ethane. This is surprising, since in no case does the measured pressure of the products exceed 0.25% of the amount of acetone present. Small amounts of impurities, such as water, may also have a marked effect.[3a] Undoubtedly some of the products are condensed at liquid air temperatures and hence not measured.

In run 19, where a mercury arc was used as a light source, the analysis agrees approximately with that reported by Damon and Daniels.[3a] In another similar run, where the amount of decomposition product was too small to permit a significant analysis of the hydrocarbon gases, the following results were obtained: CO, 49.6%; H_2, 1.7%; hydrocarbons, 48.6%.

One important conclusion may be drawn from a comparison of the composition of the products formed in the different spectral regions: the amount of hydrogen formed is considerably greater in the case of the short wave length reactions. The relative amount of hydrogen seems if anything to decrease as the concentration of reaction products increases, which indicates that it is formed by a primary rather than by a secondary reaction. The formation of hydrogen necessarily involves the breaking of a carbon-hydrogen bond, which appears more probable with the type of vibration excited in the acetone molecule by absorption of radiation in the Schumann region than in the case of absorption in the near ultraviolet.[2b]

(b) Low Pressure Runs.—Table III summarizes the data obtained from low pressure runs. Except in one run, not listed in the table, no reaction was observed when the acetic acid filter was used, but reaction did occur when the acetic acid was replaced with water (run 13). Hence it appears that in contrast with the high pressure runs, reaction is produced by radiation between 1850 or 1900 Å. and 2000 Å. However, a further investigation of the reaction in this region, using monochromatic radiation, needs to be made before definite conclusions can be drawn.

Run 7 was made with mercury vapor removed by means of solid ammonia (−78°) placed around a trap between the reaction cell and the rest of the system. No significant change was observed in reaction rate, so it may be concluded that the presence of mercury vapor under these conditions has very little if any influence on the reaction.[7]

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[7] Bates and Taylor have reported on the mercury-sensitized decomposition of acetone, THIS JOURNAL, **49**, 2438 (1927).

TABLE III

ANALYSIS OF PRODUCTS FOR LOW PRESSURE RUNS

Pressures in microns (10^{-3} mm.)

Run number	6	7	10	11	13	18
Filter[a]	F	F	Q + W	Q + A	Q + W[b]	Q + A
Initial pressure	27.5	21.2	21.3	21.6	24.7	26.8
Time, min.	1008	1257	455	900	117[b]	150
Final total pressure	89	66.5	34.4	21	37.4	27
Pressure of products not condensed with liquid air	80.8	64.9	22.9	0.4	17.3	0.4
Pressure of remaining product after CO and H_2 removed	1.3	2.9	3.7		1.9	
O_2 used in combustion	2.6		7.0		4.6	
CO_2 formed in combustion	1.5		3.4		2.7	
Pressure of CO_2 formed in CuO tube	27.1	19.5	10.2		9.3	
Pressure of reaction products condensed with liquid air	2.7	2.4	11.0		17.4	
O_2 used in combustion of these products	5.7		40.8		68.3	
CO_2 present after combustion, observed	5.5		32.1		51.9	
CO_2 present after combustion, calculated	5.5		31.4		51.6	
Proportions of analyzed products						
CO, %	32	29	30		27	
CO_2, %	1.6		2.4		0.9	
H_2, %	63	63	27		18	
CH_4, %	2		10		3	
C_2H_4, %	..		..		2	
C_2H_6, %	..		..		Trace	
Acetone, %	2		30		49	

[a] Abbreviations as in footnote *b*, Table II. [b] Part of run 13 was made with acetic acid filter (see Fig. 1). Time was counted only when acetic acid filter was removed.

One run in which the acetic acid filter was used gave anomalous results; decomposition of the acetone took place, though at only about one-fourth of the rate which was observed with fluorite. Very small amounts of impurities may have caused the deviation noted in this run.

From the analysis it appears that the gas condensed by liquid air at the close of a run consists of acetone and carbon dioxide. The value for the calculated amount of carbon dioxide present after combustion of this gas is obtained by subtracting one-fourth of the oxygen used in combustion (representing the acetone present) from the total amount of condensed gas, and adding to this difference three-fourths of the oxygen used in combustion (representing carbon dioxide formed by combustion of acetone). From Table III it will be seen that the value thus obtained agrees very closely with the observed amount of carbon dioxide formed.

In the four runs in which complete or partial analyses were made, secondary reactions undoubtedly played an important part. It will be noted that the amount of hydrogen increases greatly as reaction approaches completion, and that the amount of hydrocarbons, principally methane, is always small. In all cases much of the hydrogen and carbon in the decomposed acetone remains unaccounted for, as shown in Table IV. Slightly more than the theoretical amount of oxygen is present as CO and CO_2.

TABLE IV

PRESSURES IN MICRONS (10^{-3} MM.)

Run number	13	10	6	7
Initial press. acetone	24.7	21.3	27.5	21.2
Press. of acetone dec.	7.6	11.1	26.1	20.2[a]
Press. of products:				
CO	9.3	10.2	27.1	19.5
H_2	6.1	9.0	52.4	42.5
CO_2	Trace	0.8	1.3	1[a]
CH_4	1.0	3.6	1.4	3[a]
C_2H_4	0.6	..	..	..
C_2H_6	Trace	..	..	..
Acetone dec., %	30.8	52.1	94.9	95[a]
C from dec. acetone not found in gas phase, %	47.4	56.2	61.9	61[a]
H_2 from dec. acetone not found in gas phase, %	57.4	51.4	29.5	19[a]

[a] Estimated from comparison of figures in runs 6 and 7 (see Table III).

The excess may possibly come from the walls of the reaction vessel, which could not be flamed when evacuated because of the wax seal. The percentage of carbon unaccounted for increases as reaction goes toward completion, while at the same time the percentage of hydrogen unaccounted for decreases. A reasonable explanation is that during reaction some of the products condense on the cell window to form non-volatile hydrocarbons, possibly cuprene or a similar substance,[8] the relative amount of this condensation increasing as the acetone concentration decreases; that furthermore the condensed product is slowly decomposed by the radiation to give hydrogen and either free carbon or a less saturated hydrocarbon. No darkening of the window was observed, but since only about 2 × 10^{-7} g. of carbon would be involved, the results would hardly be expected to be observable.

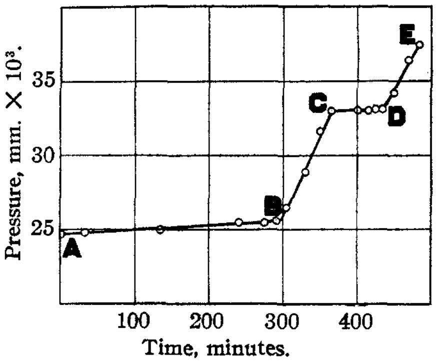

Fig. 1.—A to B, acetic acid filter; B to C, water filter; C to D, acetic acid filter; D to E, water filter.

In run 13, the acetic acid filter was used for the first 280 minutes. The acetic acid was then replaced with water for 85 minutes, after which acetic acid was again used for 75 minutes and then once more replaced with water. Figure 1 shows the change in total pressure with time during this run.

Figure 2 shows typical curves of total pressure and pressure of gas uncondensed by liquid air as a function of the time. Before reading the pressure of uncondensed gases, a mercury cut-off was raised between the McLeod gage and the trap surrounded by liquid air, and a Toepler pump used to transfer all the volatile gases into the gage portion of the system. This precaution was taken because ethane and ethylene have vapor pressures less than 0.01 mm. at liquid air temperature. The pressure as read was corrected for the consequent change in volume of the system and the gases then allowed to remix. The curve at the bottom of Fig. 2 represents the difference of the other two curves.

Table V shows for run 7 the ratio of amount of acetone decomposed to the amount of uncondensed products formed. In calculating these ratios it is assumed that the pressure of carbon dioxide at any time is proportional to the amount of acetone decomposed. This assumption probably is not quite correct, but the ratios are changed only slightly if the small amount of carbon dioxide formed is neglected. The increase with time of this ratio gives some indication of the extent of secondary reactions taking place, though the increasing fraction of carbon condensed, as shown in Table IV, represents an opposing factor.

TABLE V

INITIAL ACETONE PRESSURE, 21.2 × 10^{-3} MM.

Fraction of acetone decomposed, %	Ratio $\left(\frac{\text{uncondensed products}}{\text{acetone decomposed}}\right)$
15	2.78
28	2.75
41	2.80
62	2.98
79	3.10
84	3.30
95	3.19

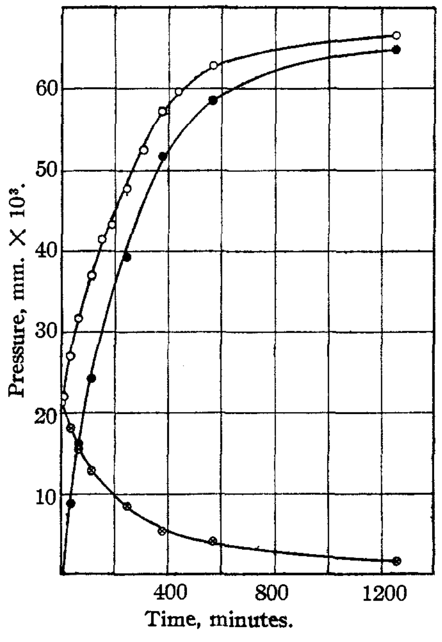

Fig. 2.—○, total gas; ●, gas uncondensed by liquid air; ⊗, acetone + carbon dioxide

A further discussion of the results given here must be withheld until additional work has been done on this and related phases of the acetone problem.

The author wishes to express his appreciation for a Grant-in-aid obtained from the National Research Council which was of material assistance in carrying out this investigation.

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(8) Bates and Taylor, Ref. 7; Lind and Livingston, THIS JOURNAL, 54, 94 (1932).

Summary

The photochemical decomposition of acetone has been studied, using two different pressure ranges, and the decomposition products have been analyzed. The method of analysis is described. More hydrogen is produced by decomposition in the Schumann region than when light in the near ultraviolet is used. The low pressure reaction differs considerably from the one at high pressures, both in rate and in products formed.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Decomposition of Ammonium Amalgam

BY ALDEN J. DEYRUP[1]

The decompositions of ammonium and the substituted ammoniums offer a possibility of comparison of reaction kinetics in such widely different solvents as liquid metals and non-metals. Of reactions in mercury solution the decomposition of ammonium is most accessible to interpretation because properties of ammonium amalgam have been already investigated. The similarity to amalgams of the alkali metals has been shown with respect to electrode potential,[2] molal freezing point depression,[3] and photoelectric effect.[4] The products of the decomposition are well established[5]

$$NH_4 \longrightarrow NH_3 + {}^1/_2H_2$$

The reverse reaction is negligible. The free energy change of the process

$$NH_3\ (g.,\ 1\ atm.) + {}^1/_2H_2\ (g.,\ 1\ atm.) \longrightarrow NH_4\ (1\ molal\ soln.\ in\ mercury)$$

may be calculated from the e. m. f. of the aqueous cell

$$\begin{array}{c} NH_3\ (g.,\ 1\ atm.) \\ \updownarrow \\ Pt,\ H_2\ (g.,\ 1\ atm.)\ |\ NH_4^+,\ 1\ m.;\ NH_3\ |\ NH_4, \\ (1\ molal\ solution\ in\ mercury) \end{array}$$

The electrode potential of ammonium amalgam is not known exactly but is approximately the same as that of sodium amalgam.[2] Hence only a provisional value can be calculated for the free energy change, $\Delta F^\circ = 30$ Cal.[6]

Experimental Method and Preparation of Materials

Ammonium amalgams were prepared by electrolyzing an aqueous solution of ammonium acetate saturated with ammonia gas between mercury electrodes at about $-38°$ Ammonium acetate was prepared from freshly distilled acetic acid and ammonia gas. Mercury was purified by distillation in a current of air under reduced pressure. The cathode was kept partially frozen and was stirred during the electrolysis. Electrical connection was made by iron wires dipping into the mercury but not in contact with the electrolyte. The kinetic effect of iron dissolved, if any, was found to be negligible by a series of experiments in which connections to cathode and anode were made by mercury-filled siphons. Ammonium amalgams after preparation were filtered rapidly and kept frozen at $-78°$, at which temperature no decomposition is detectable.

A method for analysis of ammonium amalgams (and other alkali metal amalgams) is based on the reduction of iodate ion to iodide in neutral solution

$$6H_2O + IO_3^- + 6NH_4 = 6NH_4^+ + I^- + 3H_2O + 6OH^-$$

followed by acidulation, distillation of the liberated iodine and titration with thiosulfate. A sample was shaken with a 0.5 molar solution of iodide-free lithium iodate in 60% ethyl alcohol (free from aldehyde) at about the freezing point of mercury. The solution was separated from the mercury, since iodic acid oxidizes mercury, and rinsed into an all-glass still. Excess acetic acid was added and the liberated iodine was distilled into potassium iodide solution in a receiver cooled to about 0° and protected by a trap containing potassium iodide solution to prevent possible loss of iodine. Acetic acid was used in the distillation because strong acids cause a gradual reduction of iodate ion by the ethyl alcohol which had been used to lower the freezing point of the iodate solution. Blanks were made on all reagents used. The following experiments were made to establish the accuracy of the method and the rapidity and completeness of the initial reduction of iodate ion by ammonium amalgam. A solution of sodium in mercury was analyzed by this method and also acidimetrically using B. of S. potassium hydrogen phthalate as primary standard. The respective mean results by the two methods were 0.0646 and 0.0648 molal. To determine the completeness and rapidity of the reduction of iodate ion use was made of a test depending on the minimum concentration of alkali metal amalgam which will give a clearly discernible hydrogen evolution with dilute acid. This minimum concentration was found, by dilution of a sodium solution with mercury, to be about 0.0002 molal. When

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(1) National Research Fellow in Chemistry.

(2) G. McP. Smith, THIS JOURNAL, **29**, 844 (1907).

(3) Rich and Travers, *J. Chem. Soc.*, **89**, 872 (1906).

(4) Sander and Nitsche, *Z. Elektrochem.*, **34**, 244 (1928).

(5) J. W. Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., Vol. IV, p. 1005.

(6) The formation of ammonium amalgam from mercury, ammonia, and atomic hydrogen appears, however, to be thermodynamically possible.