5. Below a P_H of 5.1 and above 7.7 the results are much too low.

6. Solutions containing 5 to 10 g. of NH_4Cl, 10 cc. of 2 N $NaC_2H_3O_2$ and 10 cc. of 10% $(NH_4)_2HPO_4$ in 150 cc. have a P_H of 7.5 but automatically fall to a range of 6.4 to 6.9 on the water-bath when heated for two hours.

7. Washing of the precipitate with cold water seems to yield satisfactory results.

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[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 228]

THE QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN AZIDE

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Introduction

In a previous paper[1] it has been shown that gaseous hydrogen azide, HN_3, is decomposed by ultraviolet radiation of wave length less than 2200 Å. The products of the reaction were found to be hydrogen, nitrogen and ammonia (ammonium azide); no hydrazine was found.

The decompositions of aqueous solutions of HN_3 by ultraviolet radiation has been studied by Gleu[2] who found that here the products were largely hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.

The present paper is concerned with the quantum yields in the decomposition of gaseous HN_3 produced by monochromatic radiation, and with the effect of pressure on these yields.

Apparatus and Procedure

A diagram of the apparatus is shown in Fig. 1. Anhydrous gaseous HN_3, prepared as before[1] from sulfuric acid and NaN_3, was stored in the 1-liter bulb, A, which was attached to a vacuum system. Attached to the same system were a quartz reaction vessel, N, in which the HN_3 was irradiated, a McLeod gage, and a quartz fiber gage, H. With the mercury cut-off, C, and the cock K closed and with the cut-off M open, a desired quantity of HN_3 was admitted to the system with the aid of the doser, B. The HN_3 was frozen out by applying liquid air at P and any traces of non-condensable gas were pumped off. The cut-off M was then closed and the liquid air removed from P allowing the HN_3 to vaporize into the reaction cell, N. The pressure of the HN_3 was read from the difference in the mercury levels in the two arms of M. In those cases where the pressure of HN_3 was too small to be measured satisfactorily in this manner, this procedure was slightly modified to permit the measurement of the HN_3 pressure on the McLeod gage. The reaction cell, N, was a quartz cylinder 2.5 cm. in diameter and

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[1] Beckman and Dickinson, This Journal, **50**, 1870 (1928).

[2] Karl Gleu, *Ber.*, **61**, 702 (1928).

4.8 cm. long with flat windows fused on each end; it was attached to the rest of the apparatus through a graded seal.

After irradiation liquid air was again applied at P, the cut-off M opened and the non-condensed gas allowed to expand into the evacuated McLeod gage and quartz fiber gage. The McLeod gage reading gave the total pressure of hydrogen and nitrogen produced and this combined with the known volume of the gases (all mercury levels were held at definite marks) gave the total number of moles of nitrogen and hydrogen produced. The fiber gage readings were used to determine the mole fraction of hydrogen in the gas in the way already described.[1]

The source of radiation was an aluminum spark. Aluminum was used because it gives quite intense lines which are widely separated in the desired region, permitting the use of wide slits in the monochromator. The electrodes were 0.25 inch aluminum rods with the ends turned down to a diameter of 0.1 inch for a distance of $^3/_{16}$ of an inch. The small ends were essential to keep the spark from drifting about; the larger shanks were necessary to keep the tips from melting. As the electrodes eroded their separation was adjusted to a constant value of about 6 mm. during operation with the aid of an image of the spark projected upon a screen by a lens, in a manner similar to that described by Warburg.[3] The spark was operated from the 13,000 volt secondary winding of a transformer, the primary current being 40–60 amperes at 220 volts. A 0.1 mf. condenser was placed in parallel with the spark.

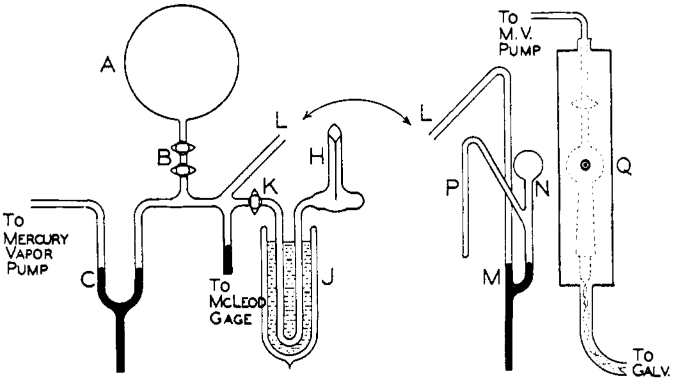

Fig. 1.—Schematic diagram of vacuum system.

The spark was placed close to the entrance slit of a Bausch and Lomb quartz monochromator. To permit this, the regular slit mechanism was replaced by a more compact one covered by a micarta cap with a rectangular hole in front of the slit. Provision was also made for blowing the spark by a blast of air issuing from the hole in the micarta cap. A shutter was also built into the monochromator.

The flux of radiation was measured by the vacuum thermocouple Q (Fig. 1), which is shown in greater detail in Fig. 2. The thermo-elements were pure bismuth and an alloy of 95% bismuth with 5% tin. The junctions were cemented to the rear faces of two circular vanes of aluminum foil. The vanes were 5.5 mm. in diameter, just large enough to receive the entire beam of radiation which was converged onto the receiving vane by a quartz lens of 2.5 cm. focal length fastened to the monochromator just outside the rear slit. The front surfaces of the vanes were coated with lampblack from a sooty flame. To aid in alignment, a piece of fluorescent uranium glass was placed imme-

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[3] Warburg, *Sitz. Ber. Preuss. Akad.*, 216 (1912).

diately behind the vanes. When in use, the thermocouple vessel was continuously evacuated with a liquid-air trap placed between it and the pump. The thermocouple was connected with a Leeds and Northrup high sensitivity galvanometer; the thermocouple, galvanometer and leads were carefully shielded in a grounded metallic covering. The front windows of the thermocouple vessel and reaction cell were aligned horizontally and both located in a plane perpendicular to the exit beam of the monochromator. The monochromator, with the spark rigidly attached to it, was arranged to slide horizontally in V-grooves provided with stops so adjusted that when the monochromator was in one extreme position, the light was focused exactly on one receiving vane of the thermocouple and when in the other extreme position, the light was centered on the reaction cell. Reaction exposures were usually about fifteen minutes long. Ordinarily measurements of the energy flux were alternated with the reaction exposures and carried over about the same time interval; during this interval a number of galvanometer readings were made with the shutter open and closed and the deflections averaged. The mean values of several such sets of readings taken successively fluctuated about 10%. It would evidently be better so to arrange the apparatus that thermocouple readings could be made simultaneously with the reaction; apparatus is now being constructed which will permit this in the study of other reactions.

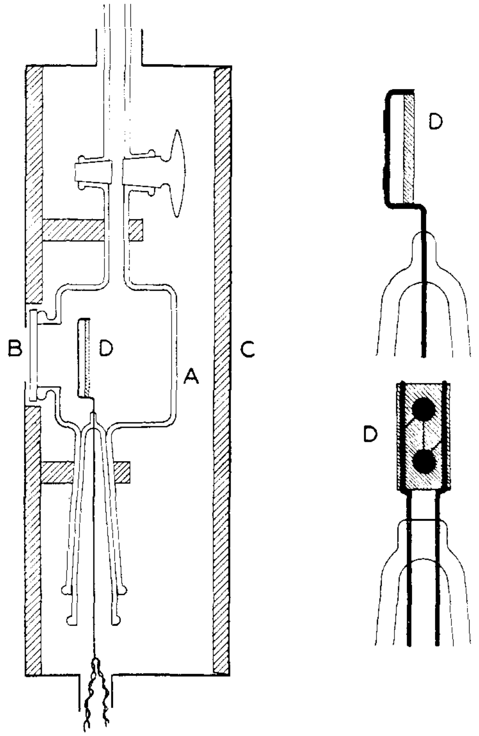

Fig. 2.—Side view of vacuum thermocouple. The thermocouple vessel, A, was of pyrex with a quartz window, B, fastened on with sealing wax. The rear side, C, of the metal-covered housing was removable for aligning. The thermocouple assembly and fluorescent screen, D, are shown in greater detail on the right.

The thermocouple–galvanometer combination was calibrated with the aid of a carbon lamp which had itself been calibrated by the Bureau of Standards. The procedure was as follows: with the aid of a Moll thermopile the transparency of a quartz plate for radiation from the standard lamp was measured and found to be 90.6%. The vacuum thermocouple was then assembled using this quartz plate as a window, and evacuated. A hole 4.50 mm. in diameter (area, 15.87 mm.^{2}) was made in a thin sheet of metal. The hole was placed in front of the thermocouple window in such a position that light from the standard lamp passing through the hole was entirely intercepted by the receiving vane; the scale deflection was 4.766 cm. (average). From the calibration of the standard lamp, the intensity of radiation at the hole was known to be 7.04 ergs per mm.^{2} per sec. Accordingly 1 cm. of scale deflection corresponded to $7.04 \times 15.87 \times 0.906/4.766 = 21.25$ ergs per second of radiation falling on the receiving vane. An exactly similar plate of quartz was used for the front window of the reaction cell. Hence, in using the thermocouple to measure ultraviolet radiation, no correction for the transmission loss at the front window of the reaction cell was necessary, *i. e.*, 1 cm. of scale deflection was taken to indicate 21.25 ergs per second entering the reacting substance. To test the integrating ability of the thermocouple vane, a beam of light about 0.5 mm. in diameter was directed onto the center and then onto regions near the edge of the vane, and the deflections were noted. The deflections differed from each other by less than 1%.

Light Absorption Coefficients.—In the determination of the quantum yields it was necessary to know the absorption coefficient of HN_3 for the radiation used. Absorption coefficients were determined photographically by a method substantially the same as that described by Winther.[4] This consisted in photographing on the same plate with a quartz spectrograph a series of exposures of the radiation from the aluminum spark. The exposures were all of the same length and in every case the radiation passed through the reaction vessel. In half the exposures the reaction vessel contained HN_3 at a measured pressure; in the alternate exposures, the reaction vessel was empty, and calibrated wire screens of known transmission were interposed in the optical path. The plates were photometered using the microphotometer of the Mount Wilson Observatory. The resulting absorption coefficients, α, defined by the equation $I/I_0 = e^{-\alpha l}$ where I/I_0 is the fraction of radiation transmitted by a thickness of l cm. of gas at 0° and 1 atm., are shown in Fig. 3. The absence of any systematic variation of α with the pressure is evidence that Beer's law holds here at least approximately.

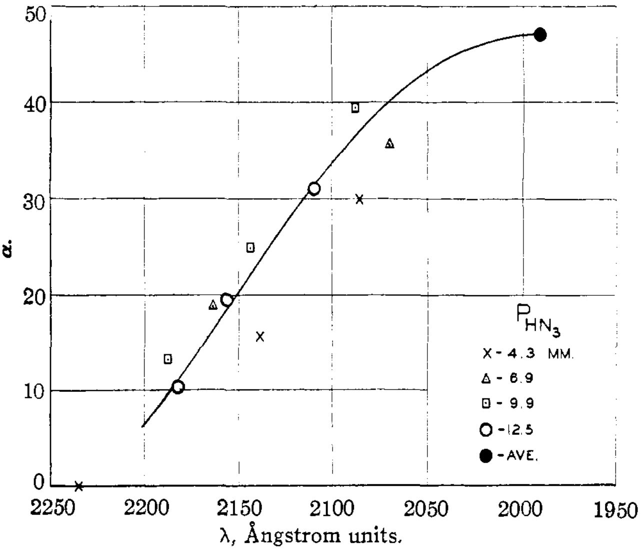

Fig. 3.—Light absorption coefficients, α, of HN_3 at various wave lengths, λ.

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[4] Winther, *Z. wiss. Phot.*, **22**, 125 (1923).

Experimental Results

The results of the quantum yield determinations made with the aluminum line λ1990 are given in Table I. In the first column is given the initial pressure of HN_3 in the reaction chamber; in no case was more than 1.7% of the HN_3 decomposed. In the second column is A, the fraction of the incident radiation absorbed, calculated from the absorption coefficient $\alpha = 47.0$, assuming Beer's law to hold and allowing for reflection at the *rear* window of the reaction cell. The exposure time, t, is given in seconds in the third column. The variability of the galvanometer deflection, d, given in the fourth column arises in part from the fact that the slit widths and spark lengths were not the same in all experiments. The volume of the gas during the reaction was 25.3 cc. in all experiments. The volume of the products when expanded into the gages was larger, and is given in Col. 6; this volume is an effective one determined by air expansion with liquid air at P as in the measurement of the non-condensable gas pressures. The pressure of the non-condensed products given in Col. 7 came directly from McLeod gage readings. From these and the values of $\Sigma p\sqrt{M}$ determined with the quartz fiber gage, the mole fractions of hydrogen given in Col. 8 were computed. These mole fractions are, in the present case, very sensitive toward small errors in the readings of either gage. Since the measured pressures are small, we do not feel certain that the rather considerable variability of these mole fractions is real; fortunately, the quantum yields are not sharply dependent upon them. In the ninth column, the number of quanta of radiation absorbed by the HN_3 was computed from the relation

$$N_Q = \frac{21.25 \cdot d \cdot t \cdot A}{hc/\lambda} = 2.150 \cdot 10^{12} \cdot d \cdot t \cdot A$$

the factor 21.25 being the number of ergs per second of radiation entering the gas for a galvanometer deflection of 1 cm. In the tenth column is given N_{HN_3}, the number of molecules of HN_3 decomposed; this was calculated from the following equation which may be simply obtained from the perfect gas law and the consideration that the number of gram atoms of hydrogen and nitrogen in the products (H_2, N_2 and HN_3) must equal the number of gram atoms of hydrogen and nitrogen in the decomposed HN_3

$$N_{HN_3} = \frac{N \cdot p_{H_2 + N_2}\, v}{760RT} (3/4 - x_{H_2})$$

Here N is the Avogadro number, and R has the value 82.1-cc. atm. per degree.

The quantum yield tabulated in the last column is the ratio of the number of molecules of HN_3 decomposed to the number of quanta absorbed, *i. e.*, N_{HN_3}/N_Q. The yield at the lowest pressure is regarded as less reliable than the others, partly on account of the comparatively small pressure of the products; any uncertainty in the absorption coefficient would also have its greatest effect in this run. If this run be left out of account, there remains certainly no considerable variation of yield with pressure over the range from 2 to 130 mm. The mean of all the yields excluding the first is 2.97 ± 0.45.

TABLE I

QUANTUM YIELDS FOR THE WAVE LENGTH λ1990

Pressure of HN_3 p_{HN_3}, mm.	Fraction of light abs., A	Exposure time, t, sec.	Galv. defl., d, cm.	Temp. of prods., T, °A.	Vol. of prods., $V_{H_2+N_2}$, cm.^{3}	Press. of prods., $p_{H_2+N_2}$, mm.$\times 10^3$	Mole fraction of H_2, x_{H_2}	No. of quanta abs., N_Q $\times 10^{-15}$	Molecules of HN_3 decomp., N_{HN_3} $\times 10^{-15}$	Quantum yield, Y
0.328	0.096	2430	4.58	298	165.0	1.22	0.152	2.26	3.92	1.74
1.93	0.441	1620	6.68	295	174.2	8.05	.161	10.15	27.2	2.68
3.26	0.620	1290	5.12	298	165.0	4.67	.110	8.71	16.1	1.84
9.4	0.934	900	7.46	295	174.2	11.17	.180	13.35	36.5	2.74
24.2	1.00	900	4.74	299	165.0	6.27	.102	9.08	21.9	2.41
27.5	1.00	900	4.92	295	174.2	7.47	.123	9.40	26.9	2.86
39.5	1.00	600	4.51	299	165.0	5.30	.080	5.75	19.1	3.32
42.0	1.00	900	5.88	295	174.2	8.62	.157	11.25	29.4	2.62
58.0	1.00	900	4.71	295	174.2	10.18	.150	9.02	35.1	3.89
71.0	1.00	900	4.63	297	165.0	8.34	.067	8.86	30.7	3.47
72.5	1.00	600	4.51	299	165.0	4.97	.052	5.75	18.6	3.23
101.0	1.00	900	4.74	299	165.0	8.58	.077	9.08	31.0	3.41
131.0	1.00	900	4.74	300	165.0	7.99	.075	9.08	28.9	3.18

The conclusion that the quantum yield is largely independent of the pressure is borne out by the results of some rate experiments made at lower pressures. In these experiments the monochromator was removed. The cell was exposed to the full radiation of the spark which was placed at a distance of 40 cm. from the cell. The spark length was controlled as before. A series of 2-minute exposures was made at various HN_3 pressures of from 0.06 to 0.5 mm. The HN_3 pressures were measured on the McLeod gage. It was found that the manipulation of the gage produced traces of decomposition; consequently, after HN_3 had been admitted to the McLeod gage and the reaction cell, the trap M (Fig. 1) was just closed and the gas in the McLeod gage pumped off after the HN_3 pressure measurement. After exposure, liquid air was applied at P, and the pressure of the non-condensed gas measured with the McLeod gage. It was also found that illumination of the reaction cell with the full radiation of the spark produced gas pressure at the rate of 6×10^{-5} mm. per minute even when the cell was empty. Consequently 12×10^{-5} mm. was subtracted from the measured pressures. The results are shown in Fig. 4 in which the abscissas are the HN_3 pressures and the ordinates the total corrected pressures of non-condensed gas. The curve has been drawn as a straight line through the origin and is evidently reasonably representative of the points.

In these rate experiments the absorption of λ1990 was sufficiently low (13%) at even the highest pressure, so that it could be taken as proportional to the pressure. If this is true also of such shorter wave-length radiations from the spark as may have reached the reaction cell, then the linearity of rate with pressure is evidence in favor of constancy of quantum yield down to those lower pressures.

Discussion

The first question involved in the consideration of the mechanism of photochemical HN_3 decomposition is the nature of the primary process, *i. e.*, whether light absorption is accompanied by the production of an HN_3 molecule in an excited electronic state or is accompanied by dissociation of the absorbing molecule. Unless we have to deal here with unusually large molecular diameters or with an electronic state of considerably longer life than that usually assumed ($\sim 10^{-7}$ sec.), the experiments are decidedly in favor of primary dissociation; taking a collision diameter of 5×10^{-8} cm., the mean time between collisions is readily calculated from the usual kinetic theory formula to be about 7×10^{-7} sec. at a pressure of 0.1 mm. so that a decided falling off in rate could be expected at even higher pressures, were the primary process one of excitation.

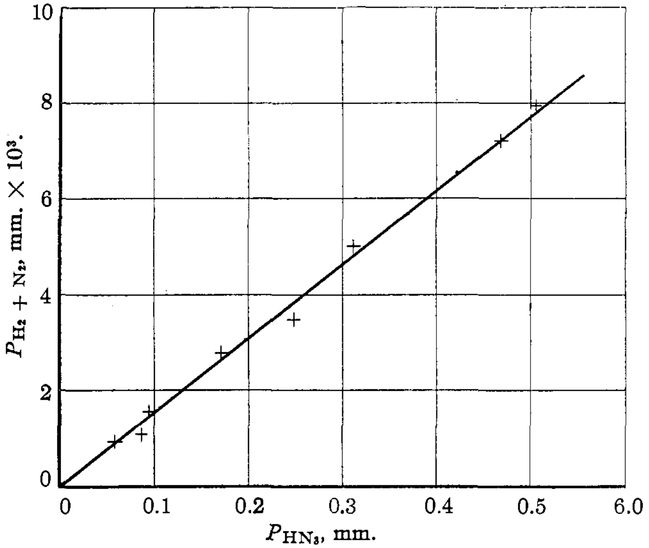

Fig. 4.—Rate of production of non-condensable gas at low HN_3 pressures.

The energy available for primary dissociation is large; a quantum of wave length λ1990 corresponds to 143,000 cal. per mole and in addition HN_3 is itself endothermal to the extent of 54,500 cal. per mole.[5] Because of the high heat of dissociation of nitrogen,[6] 219,000 cal. per mole, the

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[5] According to Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, p. 334, the heat of formation of HN_3 in aqueous solution is −61,600 cal. while the heat of solution is −7080 cal.

[6] R. T. Birge, *Nature*, **122**, 842 (1928).

available energy is not sufficient for complete dissociation of HN_3 into atoms, but is sufficient for dissociation into H, N and N_2 or, it seems reasonable to suppose, into other configurations such as HN and N_2.

The fact that NH_3 is produced from HN_3 seems to require either (1) the occurrence of multiple collisions involving an active configuration (such as a collision of $2HN_3$ with one H), or (2) the transient occurrence of intermediate compounds. In the first case we should expect the amount of ammonia produced (as compared with the amount of hydrogen produced) to fall off greatly with decreasing pressure. As this appears not to be the case, we are disposed to accept the second alternative.

A possible mechanism of the reaction is the following, the first step of which is identical with that assumed by Gleu[2] to account for the formation of hydroxylamine in aqueous solution.

$$h\nu + HN_3 = HN + N_2 \quad (1)$$
$$HN + HN_3 = H_2N_2 + N_2 \quad (2a)$$
$$HN + HN_3 = H_2 + 2N_2 \quad (2b)$$
$$H_2N_2 + HN_3 = NH_3 + N_2 \quad (3)$$

If Reaction 2a went three times as often as Reaction 2b the quantum yield would be 2.75 HN_3 decomposed per quantum and the mole fraction of hydrogen in the non-condensed gas would be 0.08; the averages of the observed values are 2.97 ± 0.45 and 0.111 ± 0.036, respectively. However, we do not care to stress this particular mechanism; indeed, we regard the *ad hoc* invention of intermediate compounds as a pastime usually indulged in with more entertainment than profit.

We would finally draw attention to the fact that in spite of the very high concentration of energy involved in the primary process and the highly explosive character of HN_3, there is no discernible tendency toward chain reaction even at a pressure of 130 mm. This behavior is, however, not entirely unprecedented, for low quantum yields have been found in the decomposition of the gaseous compounds chlorine monoxide[7] and azomethane,[8] both of which are explosive.

Summary

Using monochromatic radiation of wave length λ1990, quantum yields in the decomposition of gaseous HN_3 have been measured over a pressure range of from 2 to 130 mm.; the quantum yield was found to be substantially constant over this range with the average value 3.0 ± 0.5 molecules of HN_3 decomposed per quantum absorbed. At pressures of from 0.06 to 0.5 mm., the rate of decomposition produced by the full radiation from an aluminum spark was found to be proportional to the HN_3 pressure, indicat-

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[7] E. J. Bowen, *J. Chem. Soc.*, **123**, 2328 (1923); Bodenstein and Kistiakowsky, *Z. physik Chem.*, **116**, 371 (1925).

[8] H. C. Ramsperger, THIS JOURNAL, **50**, 123 (1928).

ing constancy of yields also over this pressure range. Some features of the mechanism of the reaction are discussed.

PASADENA, CALIFORNIA

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

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XI. THE OXIDATION OF ORGANIC ACIDS

BY H. H. WILLARD AND PHILENA YOUNG

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Introduction

The permanganate oxidation method for a number of organic acids[1] such as tartaric, malic, malonic, etc., is not entirely satisfactory, due to the fact that formic acid, which is one of the oxidation products, is, in turn, slowly oxidized by permanganate in acid solution. If a direct titration of any of these acids with standard permanganate in hot solution is attempted, the end-point is unsatisfactory, and if even a slight excess of standard permanganate is added, followed by excess of standard oxalic acid and back titration with permanganate, some formic acid is oxidized, the amount depending on such factors as concentration of the formic acid, amount of permanganate in excess and time of its action, temperature and acidity of solution. Therefore, even fairly accurate results can be obtained only when experimental conditions are closely controlled. To avoid the error caused by oxidation of formic acid, the complete oxidation of a number of these acids to carbon dioxide and water has been proposed, first in acid, then in alkaline solution, using standard permanganate, followed by addition of sulfuric acid, excess of standard oxalate and back titration with permanganate.

Hatcher and West[2] found that formic acid was an intermediate oxidation product in the oxidation of complex organic acids and that the rate of its oxidation by permanganate was inversely proportional to the hydrogen-ion concentration of the solution.

Benrath and Ruland[3] studied the velocity of reaction of ceric sulfate with a number of organic compounds. They were interested in determining the course of the reactions, however, rather than in an analytical method for these acids. They stated that sulfuric acid retarded the velocity of oxidation by ceric sulfate, and that a solution containing ceric

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[1] Representative references are given under the individual acids. It is obvious, however, that space is not available for complete lists of oxidation methods for determining these acids. The authors have made no attempt to prepare such a bibliography, which would be beyond the scope of the present paper.

[2] Hatcher and West, *Trans. Roy. Soc.*, **21**, 269 (1927).

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