Summary

1. The oxidation of carbon monoxide catalyzed by nitrogen dioxide has been measured at 527°. The rate-determining reaction at low concentrations of the catalyst appears to be a chain mechanism, and at higher concentrations to be the trimolecular oxidation of nitric oxide.

2. The rate is first order with respect to oxygen at high concentrations of the catalyst and at low concentrations it is proportional to the oxygen and also to the second power of the carbon monoxide.

3. The initial rate is approximately proportional to the square of the hydrogen pressure and is infinite with the hydrogen greater than 0.53 mm.

4. The effect of water has been found.

5. The oxidation of nitric oxide at 527° has been discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Solubility of Ammonium Oxalate in Water

BY ARTHUR E. HILL AND EDGAR F. DISTLER[1]

The figures on the solubility of ammonium oxalate in water as given in "International Critical Tables,"[2] cover the range from 0 to 50°; they are based upon a small number of individual determinations[3] and lead to a curve with an estimated variation of ±3%. The present investigation was undertaken to extend the temperature range and to improve the probable accuracy.

For the experimental work, analyzed ammonium oxalate was recrystallized, giving a product which agreed upon analysis with the formula for the monohydrate. Samples were enclosed with water in glass-stoppered Pyrex vessels and rotated in thermostats; equilibrium was reached in a few hours with good stirring. The 0° temperature was obtained in an ice-bath, temperatures up to 45° in a water-filled thermostat, and higher temperatures in a glycerol-filled thermostat; the temperature variation was not greater than ±0.05° at the lower temperatures, about ±0.1° at 60 and 75° and about ±0.2° at 87 and 100°; the thermometer was compared with a standard and corrected for emergent stem. Samples for analysis were withdrawn through cotton and paper filters into pipets at the lower temperatures, and aspirated through heated tubes at the higher temperatures; the oxalate was determined by titration with 0.1 *N* potassium permanganate solution, using the method of McBride;[4] the permanganate was standardized with a sample of sodium oxalate from the Bureau of Standards.

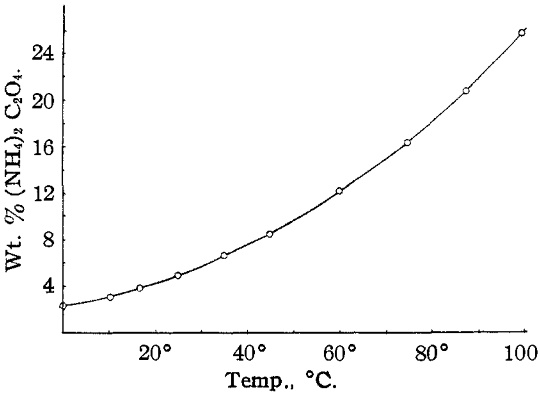

Fig. 1.

The results are shown in Fig. 1 and Table I. The curve shows no break to indicate the existence

TABLE I

SOLUBILITY OF AMMONIUM OXALATE IN WATER

T, °C.	Wt. per cent. found Undersatn.	Supersatn.	Average
0.0	2.264	2.275	2.269
10.3	3.107	3.107	3.107
16.78	3.897	3.887	3.892
25.0	4.995	4.976	4.985
34.97	6.627	6.634	6.630
44.75	8.617	8.621	8.619
60.3	12.28	12.31	12.30
74.8	16.43	16.44	16.44
87.7	20.82	20.91	20.86
99.8	25.80	25.79	25.79

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(1) The material of this paper is from the thesis of Edgar F. Distler, offered in partial fulfilment of the requirements for the degree of B.S. in Chemical Engineering at New York University, 1935.

(2) "International Critical Tables," New York City, 1928, Vol. IV, p. 219.

(3) Engel, *Ann. chim. phys.*, [6] **13**, 348 (1888); Foote and Andrew, *Am. Chem. J.*, **34**, 153 (1905); Woodstra, *8th Int. Cong. Chem.*, **22**, 25 (1912); Colani, *Bull. soc. chim.*, [4] **10**, 405 (1916); see also Rivett and O'Conner, *J. Chem. Soc.*, **115**, 1346 (1919).

(4) McBride, THIS JOURNAL, **34**, 393 (1912).

of any solid phase other than the monohydrate; cooling curves also gave no indication of a change of phase down to the eutectic temperature, −0.75°.

By the method of least squares, the parabolic curve for the solubility was calculated with the following constants: wt. per cent. solubility $= 2.314 + 0.06272t + 0.001714t^2$. The solubilities at round temperatures calculated by this equation are given in Table II. When compared with the figures of Table I, the solubilities calculated from the equation show an average deviation of ±0.073% with respect to the total solution, or ±0.84% with respect to the ammonium oxalate concentration; when comparison is made with the average curve given in "International Critical Tables,"[2] it is indicated that that curve is approximately 5% too low at 0° and 3.9% too low at 50°.

TABLE II

SOLUBILITY OF AMMONIUM OXALATE IN WATER

Calculated by equation:

Soly. $= 2.314 + 0.06272t + 0.001714t^2$

T, °C.	Wt. per cent. $(NH_4)_2C_2O_4$	T, °C.	Wt. per cent. $(NH_4)_2C_2O_4$
0	2.314	50	9.735
10	3.112	60	12.25
20	4.254	70	15.10
25	4.953	80	18.30
30	5.738	90	21.84
40	7.565	100	25.73

Summary

The solubility of ammonium oxalate in water has been determined from 0 to 100°; the solid phase is the monohydrate throughout the entire range; the average figures in "International Critical Tables" are distinctly too low at 0 and at 50°.

NEW YORK CITY RECEIVED JULY 19, 1935

[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Catalytic Hydrogenation of Aldonic Acid Delta and Gamma Lactones and of the Aldoses

BY J. W. E. GLATTFELD AND G. WEBER SCHIMPFF[1]

These laboratories have been occupied for some time in the development of a practical method for the reduction of the C_4-saccharinic (dihydroxybutyric and dihydroxyisobutyric) acids to the corresponding aldehydes and also in the reduction of *dl*-erythronic lactone to *dl*-erythrose. The work reported in this paper was carried out chiefly in connection with the second of these problems. Since difficulties were encountered when the reduction of *dl*-erythronic lactone was attempted, a study was made of the reduction of similar but less expensive lactones. As a result of this work the conditions for the reduction of *dl*-erythronic butyl ester to crystalline erythritol in good yield have been established,[2] but, as yet, *dl*-erythrose has not been obtained. Efforts in this direction are being continued.

A preliminary study of the method of catalytic hydrogenation in the presence of platinic oxide as applied to the aldonic acids was made by Glattfeld and Shaver.[3] They found it possible to reduce *d*-gluconic acid, freshly liberated from its calcium salt by means of sulfuric acid, to *d*-glucose in 14–28% yield (measured as osazone).

In the present study the procedure used by Glattfeld and Shaver was modified and applied to the reduction of the delta and gamma lactones of certain of the aldonic acids, and it was further extended to the reduction of several of the aldoses. Efforts were made to determine the conditions for the production, in the first case, of a maximum yield of the corresponding sugar with a minimum of the corresponding alcohol (hereinafter called alcohol), and in the second, of a high yield of alcohol.

The work was begun with a study of the hydrogenation of the pure delta lactone of *d*-gluconic acid. This substance should upon reduction give the sugar with the 1,5-ring, which should be less easily reduced to the alcohol than the sugar with the 1,4-ring that would be expected to result from the reduction of the gamma lactone of the acid. Glacial acetic acid was the solvent first used, because it was thought that in this solvent the conversion of the delta lactone to gamma lac-

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[1] This article is from the dissertation presented by G. Weber Schimpff in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] Results to be communicated in a forthcoming article.

[3] Glattfeld and Shaver, THIS JOURNAL, 49, 2305 (1927).