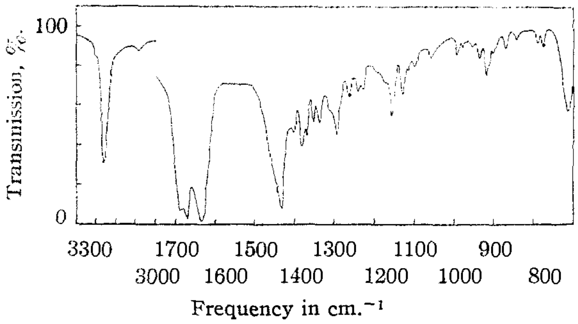

Fig. 1.

reacted with ninhydrin to give the deep purple color characteristic of α-amino acids. Paper strip chromatograms[6] showed the hydrolysis mixtures to contain leucine and proline. These data indicated the unknown to be one of the leucylproline anhydrides, and a search of the literature revealed it to be identical with the L,L-isomer described by Fischer and Reif.[2] Hydrolysis of this material with 33% aqueous sulfuric acid has been found to yield L-leucine and L-proline of good optical purity. Fischer and Reif reported hydrolysis with 20% aqueous hydrochloric acid to cause appreciable racemization of the amino acids.

Experimental

Isolation of L-Leucyl-L-proline Anhydride from the Culture Filtrates.—The culture fluid from a 100-gallon fermenter of the *Streptomyces* sp. (180 l.) was clarified by filtration. The filtrate was extracted with six 3.5-liter portions of chloroform, and the chloroform extract was concentrated *in vacuo* to about 750 ml. On standing overnight at 5°, a brown crystalline precipitate formed. It was collected by filtration and recrystallized from amyl acetate. The yield was 3.61 g. of white hexagonal plates. The sample for analysis was recrystallized from methanol; m.p. 158–161° after softening at about 145°; $[\alpha]^{21}D$ −142.4 ± 0.5° (*c*, 3.33 in ethanol). Fischer and Reif[2] reported $[\alpha]^{20}D$ −143.4°.

Anal. Calcd. for $C_{11}H_{18}O_2N_2$: C, 62.82; H, 8.62; N, 13.33; mol. wt., 210. Found: C, 62.91; H, 8.36; N, 13.48; mol. wt. (Rast), 235.

Acid Hydrolysis and Isolation of the Amino Acids.—A suspension of 3 g. of the fermentation metabolite in a mixture of 16 ml. of concd. sulfuric acid and 32 ml. of water was heated overnight on a steam-bath, then under reflux in an oil-bath for five hours. The reaction mixture was diluted to 250 ml., and solid barium hydroxide octahydrate was added to the hot solution until it was only weakly acidic. The precipitated barium sulfate was removed by filtration, and the filtrate was evaporated to dryness yielding 3.82 g. of a white crystalline residue. The residue was extracted with four 25-ml. portions of hot absolute alcohol.

L-Proline.—The alcohol extract was concentrated *in vacuo* to 10 ml. and 60 ml. of ether was added to precipitate the L-proline. The precipitate was collected by filtration, and the precipitation from absolute alcohol was twice repeated. The yield of L-proline was 1.11 g., or 70% of the theoretical amount; $[\alpha]^{22}D$ −77.7 ± 0.5° (*c*, 4.36 in water). Fischer and Zemplén[7] reported $[\alpha]^{20}D$ −79.8°.

Anal. Calcd. for $C_5H_9NO_2$: C, 52.16; H, 7.88. Found: C, 51.97; H, 7.74.

L-Leucine.—The alcohol-insoluble residue was recrystallized three times from water yielding 1.47 g. of L-leucine, 78% of the theoretical amount; $[\alpha]^{22}D$ +16.83 ± 0.4° (*c*, 5.02 in 20% HCl). Fischer[8] reported $[\alpha]^{20}D$ +17.5°.

Anal. Calcd. for $C_6H_{13}NO_2$: C, 54.94; H, 9.99. Found: C, 54.98; H, 9.80.

(6) Run according to the procedure of R. J. Williams and H. Kirby, *Science*, **107**, 481 (1948).

(7) E. Fischer and G. Zemplén, *Ber.*, **42**, 2989 (1909).

(8) E. Fischer, *ibid.*, **34**, 433 (1901).

Acknowledgments.—The authors wish to express their appreciation to Mr. George B. Whitfield for technical assistance, and to Mr. W. A. Struck and his associates for the microanalytical data.

RESEARCH DIVISION
THE UPJOHN COMPANY
KALAMAZOO, MICH.
RECEIVED FEBRUARY 9, 1951

Oxidation of Nitric Oxide at High Pressures of Reactants

BY HAROLD S. JOHNSTON AND LOREN W. SLENTZ

The reaction between nitric oxide and oxygen was studied in considerable detail at pressures of reactants up to one-half atmosphere at the one temperature, 25°. The method and apparatus are identical with the intermediate pressure equipment of Mills and Johnston.[1] Three series of runs were made: (1) with equal pressures of reactants, (2) with nitric oxide in tenfold excess and oxygen diluted with 9 parts of nitrogen, and (3) with oxygen in tenfold excess and nitric oxide diluted with 9 parts of nitrogen. At high pressures of reactants the rate was followed on the oscilloscope since half-times were of the order of magnitude of one-tenth second. At lower pressures of reactants, the rate was followed visually on an electronic voltmeter. The third-order rate law was observed throughout this range of conditions, and no trend in the values of the rate constants was observed in going from high to low pressures. The results are summarized in Table I.

TABLE I

THIRD ORDER RATE CONSTANTS FOR THE REACTION BETWEEN NITRIC OXIDE AND OXYGEN AT 25°

Ratio (NO)/(O_2)	Range of initial pressures of NO, mm.	Number of runs	Average rate constant, sec.$^{-1}$ mm.$^{-2}$ × 10^5	Standard error of mean, sec.$^{-1}$ mm.$^{-2}$ × 10^5
10	10.6 to 340	28	1.98	0.06
1	18.4 to 130	15	2.11	.05
0.1	8.1 to 43.0	20	2.02	.05
	Average of all	63	2.02	.03

The average rate constant is 7.10×10^9 cc.^{2} mole^{-2} sec.$^{-1}$, and the standard error of the mean is 0.12×10^9. This value agrees exactly with Bodenstein's[2] 7.06×10^9 cc.^{2} mole^{-2} sec.$^{-1}$ at 30°, and it is slightly, though perhaps not significantly, higher than Smith's[3] 6.00×10^9 cc.^{2} mole^{-2} sec.$^{-1}$ at 25°.

(1) Robert L. Mills and Harold S. Johnston, THIS JOURNAL, **73**, 938 (1951).

(2) M. Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918); *Z. physik. Chem.*, **100**, 87 (1922).

(3) J. H. Smith, THIS JOURNAL, **65**, 74 (1943).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIF.
RECEIVED DECEMBER 4, 1950

Thermal Decomposition of Nitrogen Pentoxide at High Temperature

BY HAROLD S. JOHNSTON AND YU-SHENG TAO

The thermal decomposition of nitrogen pentoxide is a very extensively investigated reaction. The