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Synthesis of Hydroxylamine

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The platinum-catalyzed hydrogenation of nitric oxide at atmospheric pressure in 10% hydrochloric acid has given 67–73% yields of hydroxylamine at 73–77% conversions of nitric oxide. Optimum reaction conditions include the use of platinum catalyst, a *p*H less than 2.25, and nitric oxide:hydrogen molar ratios of 1:2 to 1:3.

The catalytic hydrogenation of nitric oxide to hydroxylamine has received relatively little attention since Cooke[1] observed that mixtures of nitric oxide and hydrogen reacted over water in the presence of platinum catalyst to give hydroxylamine, nitrous oxide, ammonia and nitrogen. Jouve[2] reported that the hydrogenation of nitric oxide at 100–120° over platinum catalyst gave hydroxylamine (1–2% yield) and ammonia, and stated that it was necessary to use nitric oxide in excess of the stoichiometrically required amount to prevent destruction of the hydroxylamine formed. Butterworth and Partington[3] reported that hydroxylamine and ammonia were formed in small amounts when a 4:1 molar mixture of nitric oxide: hydrogen was brought into contact with platinized platinum in the presence of dilute hydrochloric acid. A special device was used by these authors in order that the platinum catalyst could be alternately wet by the acid and exposed to the synthesis gas mixture.

In the present work hydroxylamine was obtained in 67–73% yields at 73–77% conversions of nitric oxide by the use of dilute hydrochloric acid medium, 10% platinum-on-carbon catalyst, nitric oxide: hydrogen molar ratios of 1:2 to 1:3 and temperatures of 0–5°. Ammonia in variable amounts (5–10% yield) was also formed and presumably the remainder of the nitric oxide was converted to nitrogen or nitrous oxide. Evaporation of the filtered solution yielded hydroxylamine hydrochloride of purity up to 95%, and analyses indicated ammonium chloride to be essentially the only impurity.

The yield of hydroxylamine realized was demonstrated to be dependent upon *p*H and nitric oxide:hydrogen gas ratios. Under conditions examined, the hydroxylamine yield was not significantly affected by the concentration of hydroxylamine hydrochloride or ammonium chloride formed in the reaction solution, nor by the presence of nitrogen or nitrous oxide in the synthesis gas. Furthermore, the catalyst appeared to suffer little loss in activity over a period of one week (the longest evaluation), and a continuous synthesis can be visualized through simultaneous withdrawal of the resulting hydroxylamine hydrochloride solution and addition of fresh acid.

Although sulfuric and phosphoric acids were not investigated as extensively as hydrochloric acid, they were found to be effective media for hydroxylamine formation, giving yields of 45–53% of the respective acid salts. A moderately acidic medium was necessary in this reaction since the synthesis gas converted hydroxylamine to other products at *p*H values greater than 2.5. At lower *p*H values, hydroxylamine hydrochloride in aqueous solution was not reduced at room temperature in the presence of platinum-on-carbon catalyst, even at 73 atmospheres hydrogen pressure.

In contrast, it was found that nitric oxide slowly converted hydroxylamine in acid solution to other products in the presence of platinum catalyst. This slow reaction of nitric oxide with hydroxylamine salts may account for the necessity of using hydrogen in excess of that stoichiometrically required in order to obtain good yields of hydroxylamine. For example, no hydroxylamine was obtained from an equimolar nitric oxide:hydrogen gas mixture, and only an 11% yield resulted from a 1:1.5 molar nitric oxide:hydrogen mixture. The use of nitric oxide:hydrogen gas mixtures of molar ratios 1:5 to 1:6 did not result in significantly higher conversion of nitric oxide than that obtained from 1:2 to 1:3 mixtures, probably because of inefficient gas contact with the catalyst in the simple laboratory apparatus that was used for this investigation.

The presence of nitrogen and nitrous oxide in the synthesis gas, even in large amounts, had no effect on the production of hydroxylamine except to reduce the conversion of nitric oxide.

While platinum was the most effective catalyst examined for the reduction of nitric oxide to hydroxylamine, palladium gave an 18% yield of hydroxylamine at 53% nitric oxide conversion using 10% hydrochloric acid medium. Under similar conditions, the use of iridium catalyst failed to yield hydroxylamine in detectable amount. DuParc[4] has reported that the hydrogenation of nitric oxide with palladium or iridium catalyst yields nitrogen.

The effect of pressure on the platinum-catalyzed reaction was investigated briefly. At total pressures of 3.5 atmospheres gas mixtures containing 20–28 mole % nitric oxide gave hydroxylamine in 60–79% yields. In agreement with atmospheric pressure experiments, no hydroxylamine was obtained when gas mixtures containing more than 50 mole % nitric oxide were used.

Experimental

Hydrogenation of Nitric Oxide[5] (Procedure A).—A four-necked, 500-ml., creased flask was equipped with a sealed stirrer, a sintered-glass gas dispersing tube, a thermometer and a gas exit tube which was attached to a wet test meter

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(1) S. Cooke, *Proc. Phil Soc. Glasgow*, **18**, 291 (1887).

(2) A. Jouve, *Compt rend.*, **128**, 435 (1899).

(3) A. J. Butterworth and J. R. Partington, *Trans. Faraday Soc.*, **26**, 144 (1930).

(4) L. DuParc, *et al.*, *Helv. Chim. Acta*, **11**, 337 (1928); *C. A.*, **22**, 1890 (1928).

(5) R. E. Benson, U. S. Patent 2,628,889 (February 18, 1953).

TABLE I

PLATINUM-CATALYZED HYDROGENATION OF NITRIC OXIDE AT ATMOSPHERIC PRESSURE

Expt.	Procedure	Approximate NO/H_2 ratio	Medium	Rate, ml./min. NO	Rate, ml./min. H_2	NH_2OH, % yield	NO % conversion
1	A	1/2.0	10% HCl	37–39.5	77–81	67.5 (5.1% NH_3)	77
2	A	1/2.6	10% HCl	32.5–33	85–89	73.6 (10% NH_3)	73
3	C	1/2.3	10% HCl	26.5–28	150 then 59.5–63.5	61.8	77
4	B	1/7.1	10% HCl	28–29	197–205	64.5	60
5	B	1/7.4	10% HCl plus 1% NH_4Cl	25–28	190–200	68.6	69
6	B	1/7.0	10% HCl plus $NH_2OH \cdot HCl$[a]	24.5–27	160–200	71	43
7	A	1/0.88	10% HCl	31–33.5	27–28.5	0	8
8	A	1/1.5	10% HCl	32–34	48–50	11.4	29[c]
9	B	1/5.5	10% H_3PO_4	23–35	150–170	52.8	86
10	B	1/6.7	10% H_3PO_4	26–28	175–185	49.3	68
11	B	1/10	10% H_2SO_4	32–35	295–350	45	37
12	B	1/6.4	10% CH_3COOH	26–27	164–167	16	82
13	B	1/6.6	10% HNO_3	25–27.5	170–175	[b]	89
14	A	1/3.5	H_2O	39.5–41	137–141	0	37
15	A	1/5.1	8% NaOH	26–28.5	135–140	0	52

[a] Initial concentration of NH_2OH was 15.9%; final concentration, 16.9% NH_2OH. On cooling, $NH_2OH \cdot HCl$ separated from solution. [b] Yield not determined, but qualitative test for hydroxylamine was strongly positive. [c] Conversion fell from 83 to 8% in 6 hours.

joined to a large drying tower containing calcium chloride. A manometer was connected to the system in front of the gas dispersing tube to indicate the positive pressure on the system. The aqueous medium (usually 300 ml.) was placed in the flask, 1.0 g. of 10% platinum-on-carbon catalyst was added, vigorous stirring was begun and the gas dispersing tube was adjusted so as to extend as far as possible below the surface of the liquid. After the system had been flushed with nitrogen, hydrogen was metered into the vessel at approximately 100 ml./minute. The contents of the flask were warmed to 35–50° for 20 minutes and then cooled to 0–5°, and the hydrogen flow was adjusted to the desired rate. The wet test meter for nitric oxide was flushed with that gas, the rate was adjusted and nitric oxide was introduced into the hydrogen stream. After one-half hour, the hydrogen, nitric oxide and exit gas rates were determined (10 minute reading), and a gas bottle was attached to the exit line connected to the drying tower. After one-half hour the gas bottle was removed and the nitric oxide concentration determined by photometric analysis. This procedure was repeated each hour.

After six hours, the nitric oxide valve was closed, the wet test meter for nitric oxide was read and the system was flushed with hydrogen for 15 minutes, and finally with nitrogen. The reaction solution was filtered and the filtrate was analyzed for hydroxylamine and, in some instances, ammonia. The results of Experiment I, Table I, are detailed below. The aqueous medium was 300 ml. of 10% hydrochloric acid, and 13.61 l. of nitric oxide was introduced at a positive pressure of 60 mm. on the system at a barometric pressure of 758 mm.

EXPERIMENT 1

Interval, hr.	Gas rates, ml./min.			Nitric oxide analysis					Hourly % NO conversion
	NO	H_2	Exit	Sample, mm.	% Transmission[6]	Mm. NO	% NO	Av. % NO	
1	38	78	95	145	11	27	18.6	18.5	56.8
				127	14	23.5	18.5		
2	39.5	78	80	155	9	30	19.3	19.1	64.0
				135	12	25.5	18.9		
3	37	81	39	141	14	23.5	16.7	16.8	83.4
				151	12	25.5	16.9		
4	..	..	..	128	27	14.5	11.3	11.1	(85 est.)
				141.5	25	15.5	10.9		
5	38.5	77	45	129	27	14.5	11.2	11.3	87.7
				144	23	16.5	11.5		
6	37.5	80	52	130	25	15.5	11.9	11.9	84.5
				151.5	21	18	11.9		

The hourly conversion values were calculated in the following manner

$$\text{ml. NO (introduced)/min.} = \text{rate} \times \frac{\text{pressure} + \text{barometer reading}}{760}$$

$$\text{ml. NO (in exit gas)/min.} = \text{rate} \times \frac{\text{barometer reading}}{760} \times \%\ \text{NO}$$

The difference in the corrected rates is the ml. NO/min. converted, and this value divided by the corrected introduction rate gives the % NO conversion. For the first hour

$$\text{NO (introduced)} = 38 \times \frac{60 + 758}{760} = 40.8 \text{ ml. NO/min.}$$

$$\text{NO (vented)} = 95 \times \frac{758}{760} \times 0.185 = 17.6 \text{ ml. NO/min.}$$

$$\text{Conversion} = \frac{23.2 \text{ ml. NO/min.}}{40.8 \text{ ml. NO/min.}} \times 100 = 56.8\%$$

An over-all conversion value of 77.0% was obtained by averaging the hourly conversion figures.

$$\text{mole NO converted} = 13.61 \times \frac{60 + 758}{760} \times \frac{273}{298} \times \frac{1}{22.4} \times 0.77 = 0.462 \text{ mole}$$

Analysis of the reaction solution (310 g.) indicated 0.0332 g. of NH_2OH/g. solution. Thus, 10.3 g. of hydroxylamine was formed (67.5% yield). Analysis of the reaction solution indicated 0.0013 g. of NH_3/g. solution, corresponding to 5.14% yield of ammonia.[7]

Procedure B.—The equipment and procedure described in A were the same, except that the reaction was begun at room temperature without preactivating the catalyst with hydrogen. After 30 minutes, the temperature of the reaction medium had risen several degrees, and the mixture was cooled to 0–5° for the remainder of the run.

Procedure C.—The procedure described in B was modified slightly, in that after the temperature rise was noted, the hydrogen flow was adjusted to a lower rate before cooling the flask contents to 0–5°.

Effect of *p*H on Synthesis of Hydroxylamine.—Procedure B was used, and the reaction flask was equipped with a Y-

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(6) See photometric analysis of nitric oxide.

(7) The authors are indebted to Dr. W. H. Taylor and Mr. F. J. Friel of the Physical and Analytical Division for the ammonia analyses.

tube to provide for a sintered glass filter stick extending below the surface of the liquid. The medium was 13 ml. of concentrated hydrochloric acid diluted to 350 ml. Samples (15–20 ml.) were removed through the filter stick by vacuum filtration without interrupting the reaction. In calculating the apparent hydroxylamine yields no correction was applied for the samples removed. The results are summarized in Table II.

TABLE II

EFFECT OF *p*H ON SYNTHESIS OF HYDROXYLAMINE

Sample	Time, min.	Mole NO converted	*p*H	g. NH_2OH/g. sample	g. HCl/g. sample	Apparent yield, % NH_2OH
0	0	0	0.80			
1	120	.0643	0.90	0.00205		34
2	165	.122	1.12	.00490		40
3	195	.144	1.30	.00700	0.0049	46
4	240	.199	2.25	.0102	.0007	46.5
5	260	.219	5.55	.00814		32
6	305		9.20	.000		0

Catalyst Life.—Procedure B was used and the reaction flask was equipped with a Y-tube to provide for a sintered glass filter stick extending below the surface of the liquid. The main portion of the reaction solution was removed daily by filtration through the filter stick, and fresh acid was added without interrupting the reaction. The hydroxylamine yields averaged about 50% over a six-day period. The nitric oxide conversion value for the seventh day was not determined, but the conversion to hydroxylamine was 35%. Since the nitric oxide conversions averaged about 60% for the first six days of this experiment, it is evident that there was no serious loss in catalyst activity.

Effect of Added Gases on Hydrogenation of Nitric Oxide.—The various gases were introduced into the hydrogen stream by means of a Y-tube. Procedure B was followed in each case. The results are summarized in Table III.

TABLE III

EFFECT OF ADDED GASES ON HYDROGENATION OF NITRIC OXIDE

Expt.	Added gas	Approx. NO/H_2/gas ratio	Rates, ml./min. NO	Rates, ml./min. H_2	Rates, ml./min. Gas	NH_2-OH, % yield	NO % conversion
1	N_2	1/6.2/5.6	20–30	150–160	135–145	74	31
2	N_2	1/12/10	6–17	135–145	110–117	55.6	55
3	N_2O[a]	1/7/0.75	27–37	220–230	20–28	56.5[a]	54
4	N_2O	1/6.1/0.94	31	185–195	24–34	56	49

[a] Conducted reaction for 3 hours before introducing nitrous oxide. The yield of hydroxylamine at the end of this time was 49.3%.

Hydrogenation of Nitric Oxide Under Pressure.—The effect of pressure on the catalytic hydrogenation of nitric oxide was investigated briefly using a Parr catalytic shaker.[8] The gas reservoir was removed and mounted on a mechanical shaker so that nitric oxide/hydrogen gas mixtures could be agitated in the presence of water to assure mixing of the gases. The equipment was located behind a barricade since the gas mixtures were within the explosive range.

The reservoir containing 500 ml. of distilled water was evacuated to 45 mm. and nitric oxide was added to a desired pressure followed by hydrogen to a total pressure of 50 lb./sq. in. The catalyst and acid medium were placed in the reaction bottle, hydrogen was added, and the mixture was heated briefly to activate the catalyst. During this time the reservoir was agitated to mix the gases. After 15 minutes, the hydrogen in the bottle was released, the bottle was evacuated, and a gas sample was removed from the reservoir and analyzed for nitric oxide. The reservoir was opened to the reaction bottle and shaking begun. At the end of the reaction time a sample of the reservoir gas was analyzed again for nitric oxide. There appeared to be no significant differences between experiments conducted at these modest pressures and at atmospheric pressure. The results are summarized in Table IV.

TABLE IV

HYDROGENATION OF NITRIC OXIDE UNDER PRESSURE[a]

Expt.	Approximate NO/H_2 ratio	% NO in synthesis gas	Pressure drop, lb./sq. in.	NH_2OH, % yield	Time, hr.
1	1/4	20[b]	6	79	5
2	1/2.6	28,[b] 28[c]	20	64	18
3	1/2.2	31[b]	38	48	18
4	1/1.3	43,[b] 46[c]	12	0	6
5	1.4/1	58,[b] 58[c]	0.5	0	6

[a] Parr catalytic shaker,[7] total pressure of 50 lb./sq. in. Medium was 100 ml. of 10% hydrochloric acid containing 0.5 g. of 10% platinum-on-carbon catalyst. [b] Analysis of synthesis gas at beginning of reaction. [c] Analysis of synthesis gas at conclusion of reaction.

Evaluation of Palladium[9] and Iridium Catalyst.—Palladium was investigated as a catalyst for the hydrogenation of nitric oxide to hydroxylamine in a manner similar to that outlined for platinum. An acid medium and gas mixtures containing more than 50 mole % hydrogen were found necessary for formation of hydroxylamine. The results are summarized in Table V. Nitrous oxide was found to be present in the exit gases from the hydrogenation reaction, and further investigation showed that this gas was a product of the reaction of nitric oxide with hydroxylamine in acid solution.

TABLE V

PALLADIUM-CATALYZED HYDROGENATION OF NITRIC OXIDE AT ATMOSPHERIC PRESSURE[a]

Expt.	Approximate NO/H_2 ratio	Rate, ml./min. NO	Rate, ml./min. H_2	NH_2OH, % yield	NO % conversion
1[a]	1/4	37–40	153–160	17.9[b]	53
2[a]	1/2	49–53	102–115	6.7[c]	18
3[a]	1/4	40–42	166–169	(13.7)[d]	. .

[a] 10% hydrochloric acid medium. [b] Reaction temperature was 31–33° for first three hours, and 2-3° for last three hours. [c] Reaction temperature was 12-30°. [d] Conversion of NO to NH_2OH, yield not determined. Reaction temperature was 31–79°.

No hydroxylamine was formed when a nitric oxide: hydrogen (1:7) gas mixture was passed through 10% hydrochloric acid containing 10% iridium-on-"Nuchar" catalyst. The nitric oxide conversion appeared to be less than 1%.

Identification and Determination of Hydroxylamine.—Hydroxylamine was identified by means of the salicylaldehyde/copper acetate reagent of Feigl[10] and by conversion to cyclohexanone oxime. Yields of hydroxylamine were determined by the analytical procedure of Raschig[11] modified by the addition of the Zimmermann–Reinhardt reagent to prevent interference by chloride ion when hydrochloric acid was used as the hydrogenation medium.

Determination of Ammonia.—The acidic reaction solution was treated with excess permanganate to destroy the hydroxylamine present. Excess base was added and the ammonia was removed by distillation and determined by adsorption in standard acid and back-titration with standard base.[7]

Isolation of Hydroxylamine Hydrochloride.—A portion of the reaction solution from expt. 1, Table I, was evaporated to dryness at reduced pressure to yield a white, crystalline product. Analyses of the solid indicated it to be a mixture of hydroxylamine hydrochloride (95.8%) and ammonium chloride (4.2%). Similarly, the product obtained from expt. 2, Table I, contained 88.2% hydroxylamine hydrochloride and 11.7% ammonium chloride.

Action of Hydrogen on Hydroxylamine Hydrochloride.—A hydrochloric acid solution of hydroxylamine (0.0118 g./g.

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(8) Available from Parr Instrument Co., Moline, Illinois.

(9) R. E. Benson, U. S. Patent 2,628,888 (February 18, 1953).

(10) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., New York, N. Y., 1946, p. 187.

(11) N. H. Forman, "Scott's Standard Methods of Chemical Analysis," 5th Ed., D. Van Nostrand Co., New York, N. Y., 1939, Vol. I, p. 617.

solution) containing 1.0 g. platinum-on-carbon catalyst was placed in a glass liner of a rocker tube. The tube was closed and the aqueous mixture agitated under 73 atm. of hydrogen for 3 hours. Analysis of the filtered solution indicated no loss of hydroxylamine (0.0118 g. NH_2OH/g. sample). A similar result was obtained upon repeating the experiment. However, when the glass liner was not used approximately 50% of the hydroxylamine present was converted to other products, and the resulting solution contained considerable amounts of metallic ions, formed by the action of the acid solution on the metal vessel.

No loss of hydroxylamine was noted when hydrogen was passed through a dilute acid solution of hydroxylamine at atmospheric pressure and room temperature for three hours in the presence of platinum-on-carbon catalyst.

Action of Nitric Oxide on Hydroxylamine Hydrochloride.—An acid solution of hydroxylamine (0.0194 g./g. solution) was vigorously stirred while nitric oxide was passed through at 30 ml./min. for one hour at 25° and for an additional two hours at 0–3° in the presence of platinum-on-carbon catalyst. Analysis indicated a hydroxylamine content of 0.0182 g./g. solution, representing an approximate 6% loss of hydroxylamine.

Photometric Analysis of Nitric Oxide.—The apparatus for the photometric analysis of nitric oxide was designed by Mr. W. H. Aughey of this Laboratory. This analytical method is based on the oxidation of nitric oxide to nitrogen dioxide and the variation of optical density of nitrogen dioxide with concentration. The apparatus was arranged so that light from an AH4 lamp passed through an aperture and through a gas absorption cell to a filter for light of wave length 4047 Å. Light of this wave length passed through the filter to activate a RCA Phototube 929, which was connected to a RCA Ultrasensitive Microammeter No. WV84A. The microammeter recorded the per cent. transmission. Two gas absorption cells with quartz windows and of equal transmission were used in order to facilitate calibration. The distance from the light source to the cell was adjusted before each determination so that a 100% transmission reading was obtained with air in the cell, and 0% transmission when the light beam was blocked.

A manifold vacuum apparatus was used for placing known amounts of gas (nitric oxide or nitric oxide–hydrogen mixtures) in the absorption cell, and dry air was admitted to atmospheric pressure. Constant transmission readings were usually obtained after allowing the cell to stand for about five minutes to complete essentially the oxidation of nitric oxide to nitrogen dioxide. Data relating per cent. transmission to partial pressures of 100% NO_2 were plotted from values obtained with nitric oxide of known purity, and the resulting curve was used for calculation of nitric oxide content in gas mixtures. Because of this, and since all of the readings were made at essentially the same temperature, the usual complications due to nitrogen dioxide–dinitrogen tetroxide equilibrium did not interfere seriously with the accuracy of the measurement. Beer's law was obeyed in the concentration range used for this investigation and good analytical agreement was obtained between the photometric and Orsat methods. The photometric method provided adequate accuracy for these experiments, with the average analysis requiring about 10 minutes compared to 90 minutes required by the Orsat method.

Results and Discussion

The preferred process for the synthesis of hydroxylamine involved preactivation of the catalyst with hydrogen in dilute hydrochloric acid medium at 35–50° for 15 minutes before cooling to 0–5° and admitting nitric oxide (procedure A). Alternatively, good yields of hydroxylamine resulted by conducting the hydrogenation at room temperature until a temperature rise was noted and then cooling the reaction medium (procedure B). With these procedures, nitric oxide:hydrogen mixtures of molar ratios of 1:2 to 1:7 gave 62–73% yields of hydroxylamine at 60–77% conversions of nitric oxide. The use of a 1:1.5 nitric oxide:hydrogen gas mixture gave an 11% yield of hydroxylamine at 29% conversion of nitric oxide, while no hydroxylamine was formed from a 1:0.88 nitric oxide:hydrogen mixture.

The importance of *p*H in the synthesis of hydroxylamine is demonstrated in Table II. As hydroxylamine (and ammonia) was formed in the dilute hydrochloric acid medium, the acid was consumed through salt formation and the *p*H increased. In this particular experiment, the hydroxylamine concentration steadily increased until a *p*H of about 2.25 was reached. Above this value to a *p*H of 5.55 the hydroxylamine concentration actually decreased about 20%. Continuation of the reaction to a *p*H of 9.2 resulted in complete destruction of the hydroxylamine initially formed. Although Cooke[1] has reported the preparation of hydroxylamine under neutral conditions, our attempts to synthesize the compound in detectable amount in neutral water or 8% sodium hydroxide solution were unsuccessful, using either procedure A or B.

The variances of our results with those of Cooke[1] and of Butterworth and Partington[3] may be attributed to the fact that in our experiments the synthesis gas was passed through the solution containing hydroxylamine and platinum catalyst. It was shown in a separate experiment that nitric oxide slowly destroyed hydroxylamine in acid solution. This can account for our failure to obtain hydroxylamine from gas mixtures containing more than 50 mole % nitric oxide. Similarly, hydroxylamine in neutral or basic solutions was readily reduced by hydrogen and/or converted to other products by nitric oxide; this explains our failure to obtain hydroxylamine when the synthesis gas mixture was passed through a neutral or basic medium.

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