camphorsulfonic acid–chloroform amounted to about 10%. Within the over-all experimental error of about 10% the activity in both fractions was the same, and there was no definite evidence for greater recovery of activity in the initially active than in the initially inactive species. We therefore conclude that, using an extraction technique of separation, complete exchange is found between ferroin-5,6 and ferriin-5,6 within 15 seconds at 0°, at concentrations of 2.2 × $10^{-5}f$ in each species.

We are grateful to Dr. R. W. Dodson for his guidance and stimulation.

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The Ammonia Induced Decomposition of Nitric Oxide

BY CHARLES P. FENIMORE[1] AND JOHN R. KELSO

A means of catalyzing the sluggish decomposition of nitric oxide is suggested by reaction (A) which occurs in the thermal decomposition of nitrous oxide.[2]

$$O + N_2O \longrightarrow 2NO + 36.6 \text{ kcal.} \qquad (A)$$

The suggestion we draw from (A) is that its reverse might go if the unfavorable energy change could be overcome. If the oxygen atom could react with a particle, X, to form a labile oxide of dissociation energy, *q*, then the following scheme might permit the desired catalysis.

$$\begin{gathered} 2NO + X \longrightarrow N_2O + XO + (q - 36.6) \text{ kcal.} \\ XO + NO \longrightarrow NO_2 + X + (71 - q) \\ NO + N_2O \longrightarrow NO_2 + N_2 \\ 2NO_2 \longrightarrow 2NO + O_2 \end{gathered}$$

For if *q* lies between 37 and 71 kcal., the first two steps would be exothermal and, perhaps, relatively fast. The last two steps describe the catalytic decomposition of nitrous by nitric oxide and are known to be consistent with that process.[2] Since an N–O single bond possesses an energy in the desired range, we hoped that ammonia or some intermediate derived from ammonia might catalyze the decomposition of nitric oxide.

Experimental

Premixed ammonia and nitric oxide were heated in a spherical quartz vessel of 523-cc. volume. Both gases were distilled and were spectroscopically pure (infrared spectra). In a few runs in which hydrazine was used, the hydrazine was twice distilled from barium oxide.

The reacting gas was sampled by opening the quartz vessel to an evacuated bulb which was fitted with a manometer and a very small freezing appendix. The condensible gases, including oxygen in the presence of excess nitric oxide, were frozen with liquid nitrogen and the permanent gas measured. This was infrared inactive, hydrogen and oxygen free by analysis, and therefore all nitrogen.

A small amount of nitrous oxide was identified in the condensible portion by its infrared spectrum. The nitrous oxide was found only in partially reacted mixtures and disappeared toward the end of the catalytic decomposition.

Results

At temperatures at which pure nitric oxide is decomposed only very slowly, the ammonia induced decomposition of a constant initial pressure of nitric oxide, which is always in excess, is characterized by: (1) The yield of nitrogen, $(N_2)_\infty$, is proportional to the square root of the initial concentration of ammonia, $(NH_3)_0^{1/2}$.

(2) The half-time of the evolution of nitrogen is independent of $(NH_3)_0$.

TABLE I

DECOMPOSITION OF NO, NH_3 MIXTURES AT 700 MM. INITIAL PRESSURE[a]

T, °C.	(NH_3), %	$(N_2)_\infty/(NH_3)_0^{1/2}$, mm.$^{1/2}$	½ time, min.
702	5	44	19
	2.5	41	17
	1.0	42	18
	0.5	43	18
725	2.5	34	9.0
	1.0	35	8.5
	0.5	35	9.0
740	2.5	28	4.4
	1.0	28	4.6
755	2.5	32	3.2
	1.0	30	3.2

[a] All pressures measured at reaction temperature.

These findings are proved by the data in Table I and illustrated by the typical curves in Fig. 1.

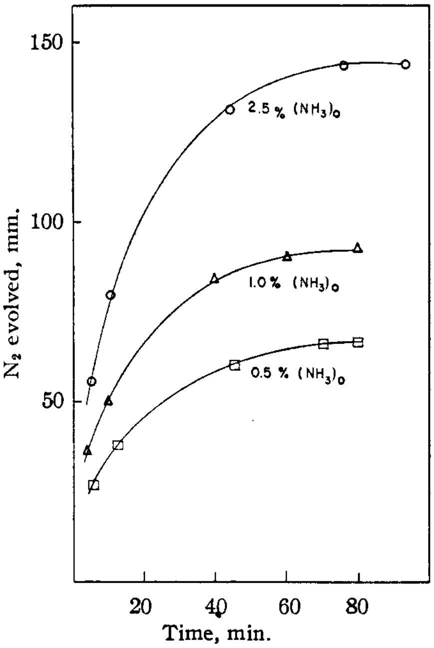

Fig. 1.—Evolution of N_2 from 700 mm. NO + NH_3 at 725°. Initial % of NH_3 is marked on each curve.

With varying initial pressures of nitric oxide, we find the data given in Table II, typical curves in Fig. 2.

(3) At 700 and 900 mm. pressure, the half-time of the evolution of nitrogen varies roughly inversely with the square of initial nitric oxide. On the initial reaction, rate varies roughly directly with this quantity.

(4) The yield of nitrogen at a fixed pressure is approximately independent of the initial nitric oxide concentration as long as this is in excess. This conclusion is not obvious from Fig. 2, but note in Table II that the low yield of nitrogen obtained

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[1] General Electric Research Laboratory, The Knolls, Schenectady, New York.

[2] F. F. Musgrave and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **135A**, 23 (1932).

TABLE II

DECOMPOSITION OF NO, NH_3 MIXTURES AT VARYING NO CONCENTRATIONS[a]

T, °C.	Reactants, mm. NH_3	Reactants, mm. NO	$(N_2)_\infty$, mm.	½ Reaction time, min. obsd.	½ Reaction time, min. calcd.	$k_a = 10_8$
702	17.5	882	182	9.0	9.5	19
		682	172	17.0	17.0	
		482[b]	140	24.0	36.0	
		482	174			
725	3.5	896	82	5.5	5.5	36
		696	67	9.0	9.0	
740	7.0	893	84	2.5	2.6	74
		693	76	4.6	4.5	
755	17.5	882	158	1.8	1.9	104
		682	132	3.2	3.2	
		682[b]	152	3.4	3.2	

[a] All pressures measured at reaction temperatures. Half-reaction time calculated from

$$t_{1/2}(\text{calcd.}) = \frac{2}{k_a[(NO) - 2(N_2)_\infty]}\left[\frac{1}{[2(N_2)_\infty - (NO)_0]}\ln\left\{\frac{(NO)}{2[(NO)_0 - (N_2)_\infty]}\right\} - \frac{(N_2)}{(NO)_0[(NO)_0 - (N_2)_\infty]}\right]$$

[b] The reactants for the last runs at 702 and 755° contained added N_2 to give an initial pressure of 900 mm.

from 482 mm. nitric oxide at 702° can be raised almost to the yield from 882 mm. nitric oxide by the addition of inert gas to give the same initial pressure. The effect is observed at 755° also.

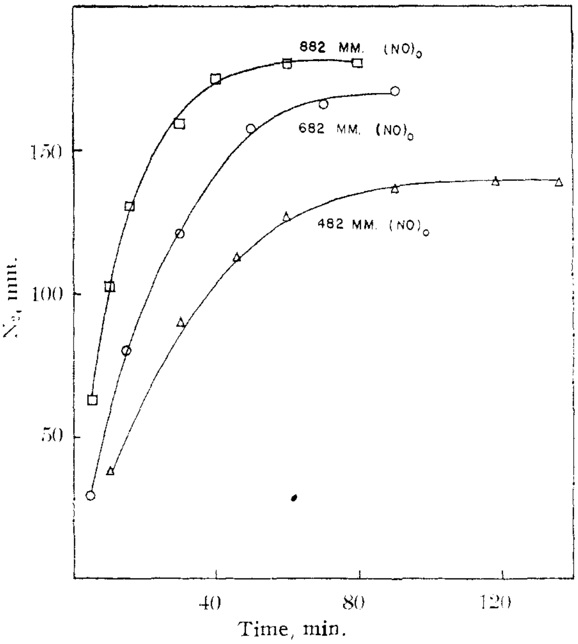

Fig. 2.—Evolution of N_2 from NO, NH_3 mixtures at 702° containing 17.5 mm. NH_3 initially. Initial NO pressure is marked on each curve.

The rate equations

$$-\frac{d(NH_3)}{dt} = k_a(NH_3)(NO)^2$$

$$\text{and } \frac{d(N_2)}{dt} = k_b(NH_3)^{1/2}(NO)^2$$

are consistent with our observations. Because then $(N_2)_\infty = (2k_b/k_a)(NH_3)_0^{1/2}$, characteristics (1) and (4), and $t_{1/2}$ = approximately $2\ln 2/k_a \cdot (NO)_0^2$, characteristics (2) and (3) (more exactly, $t_{1/2}$ is given in the footnote to Table II). But other choices of exponents in the rate equations will not give these relations.

An obvious interpretation of the one-half order ammonia dependence of the rate of formation of nitrogen is that ammonia itself is not the catalytic agent, but that two catalytic particles arise from each ammonia molecule consumed in a rate determining reaction. An inert gas effect in increasing the yield of nitrogen is then explicable because of the possibility of diffusion of the catalytic particles to the vessel wall and their destruction there.

The catalytic particles might be NH_2 radicals, and since the thermal decomposition of hydrazine to NH_2 is first order and homogeneous, in part, above 650–700°,[3] we looked into the possibility of inducing the decomposition of nitric oxide by hydrazine at 800°. The higher temperature was chosen to increase the fraction of hydrazine decomposing unimolecularly in the gas phase. This reaction is not clean: nitrogen (but less than the moles of hydrazine taken) is formed at room temperature when hydrazine is mixed with nitric oxide, and the slow decomposition of nitric oxide is appreciable in our apparatus at 800°. It is scarcely worthwhile to tabulate the yields. Nitric oxide is decomposed by 0.2–1.0% hydrazine at 800° and gives nitrogen in yields comparable to those obtained with the same amount of ammonia at 700–750° although the reaction with hydrazine is less reproducible. We conclude from the runs with hydrazine, rather as we began, that the catalytic framents might be, but need not necessarily be, NH_2 radicals.

The foregoing data are insufficient to illuminate the mechanism. If one identifies X with NH_2 in the four equations set down in the introduction to this paper, assumes that NH_2 radicals are generated two for every ammonia molecule consumed in a reaction 1st order in ammonia and 2nd order in nitric oxide, and supposes that the radicals are destroyed two at a time in the gas phase, then one can arrive at rate equations agreeing with those deduced above. But the values of k_a in Table II give a temperature dependence of the consumption of ammonia corresponding to an activation energy of 70 ± 5 kcal./mole. This large activation energy suggests that the formation of NH_2 radicals cannot be both termolecular and relatively fast and so the question of mechanism must be left open.

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(3) M. Szwarc, *Proc. Roy. Soc.* (*London*), **198A**, 267 (1949).

BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MD. RECEIVED JULY 13, 1951

The Reaction of Some Aryllithium Compounds with Epichlorohydrin

BY HENRY GILMAN, BURT HOFFERTH AND JULIAN B. HONEYCUTT

In connection with the synthesis of some alkamine ethers,[1] it was of interest to prepare a series of aromatic secondary alcohols by the action of

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(1) B. Hofferth, Doctoral Dissertation, Iowa State College, 1950.