oxidative sulfitolysis. The similarity of these values indicates that in proteins which are rich in dithio bonds, most of the change in $[\alpha]_D$ is caused by the cleavage of dithio bonds. Our observations give some information on the resistance of various proteins to denaturing agents and on the role of dithio bonds in maintaining the conformation of the native proteins. The stabilizing role of dithio bonds seems to be particularly strong in insulin where it is, most probably, responsible for the abnormal optical rotation of this protein after reduction or sulfitolysis.

Kinetics of the Reaction of Ammonia and Nitric Oxide in the Region of Spontaneous Ignition[1]

BY DONALD R. POOLE AND WENDELL M. GRAVEN

Rates of the NO–NH₃ reaction were measured within the temperature range of 850 to 1050° using a flow technique and were adequately represented by the expression

$$\frac{d(H_2O)}{dt} = \frac{3.2 \times 10^{10} \exp(-58400/RT)(NH_3)^{1/2}(NO)}{1 - k_2(NH_3)^{1/2}(NO)}$$

Hydrogen, but no N₂O, was found in the reactor effluent in addition to the major products, N₂ and H₂O. Spontaneous ignition was observed above 960° and the boundaries of inflammable reactant compositions were used to obtain k_2. The temperature dependence of the ignition limits gave an activation energy of 30.0 kcal. for k_2.

Investigations of high temperature reaction systems involving NO are of importance for interpretation of combustion phenomena. Nitric oxide supported flames, including the NO–NH₃ flame, have received considerable attention recently.[2-4] The spontaneous ignition temperature of stoichiometric mixtures of NO and NH₃ has been reported.[5] Kinetic studies of the NO–NH₃ reaction at lower temperatures have resulted in a number of disparities.[6-8] There is a lack of agreement on the kinetic order of the reaction, the activation energy and even the reaction products.

The present work is an attempt to assist in the elucidation of an apparently complex reaction by procuring kinetic data in the temperature region of spontaneous ignition.

Experimental

Materials.—Anhydrous ammonia from two sources was used. Shell Chemical Co. refrigeration grade NH₃ was condensed by means of liquid air and the non-condensable gas was pumped off. A repetition of this procedure gave a product which, upon chromatographic examination, showed only a trace of N₂. A majority of the rate measurements was made with Matheson Co. anhydrous ammonia, specified as having 99.9% minimum purity. The same purification procedure was employed at first, but later it was established that use of NH₃ taken directly from the cylinder had no effect on the measured rates.

Nitric oxide from Matheson Co., specified as having 99.0% minimum purity, was purified in the same manner as was the NH₃. With this procedure it was not possible to eliminate traces of nitrous oxide, an impurity whose possible presence in the first of the two cylinders used was indicated by infrared analysis. The content of the second cylinder was analyzed by the supplier and was alleged to contain no N₂O, 0.275% N₂ and 0.14% NO₂. Ascarite was used to remove NO₂ from the NO and to dry the helium, H₂ and N₂O which were obtained from commercial sources. Matheson Co. "prepurified" N₂ and helium were used as diluent alternately without detectable differences in the measured reaction rates.

Methods.–A flow technique was employed for measurement of both reaction rates and explosion limits. Use was made of the same quartz reaction vessels, mixing chambers, furnace, temperature controls and measuring devices which have been described in previous reports.[9]

Temperatures at the center of the reaction vessel were controlled to ± 1°. Measurement of the temperature profile along the axis of the furnace demonstrated that the temperature gradient between entrance and exit of the reactor was approximately 1° for the smaller vessel and approximately 3° for the larger vessel. The total pressure of the reactant mixture was approximately 80 cm. for all of the rate measurements. A total flow rate of either 100 or 1000 ml./min. was maintained for various reactant compositions by addition of diluent gas.

An improved design of the capillary tube flowmeters and use of Hoke metering valves facilitated control of the gas flow rates and extended the ranges of the meters to permit measurement of flow rates from 5 to 1000 ml./min. White paraffin oil was the fluid used in the flowmeters, which were calibrated individually for specific gases.

Reaction rates were determined by absorption of water vapor in Ascarite. The presence of NH₃ in the effluent necessitated the selection of Ascarite, rather than the more common desiccants. Gravimetric measurement of the amount of H₂O collected during an appropriate time interval permitted the determination of the steam content of the reactor effluent with a precision of ± 2%.

A gas chromatograph[10] was used to ascertain qualitatively the purity of the reactants and to identify the reaction products.

Results

In addition to water the presence of N₂ and H₂ in the reactor effluent was established by gas chromatography. It was also demonstrated that in the absence of NO, but under the same reactor conditions, considerable decomposition of NH₃ occurred. No unequivocal evidence of N₂O was

(1) Taken in part from the Ph.D. thesis of D. R. Poole, University of Oregon. Financial support was received from the Research Corporation.

(2) G. K. Adams, W. G. Parker and H. G. Wolfhard, *Discussions Faraday Soc.*, **14**, 97 (1953).

(3) H. G. Wolfhard and W. G. Parker, "Fifth International Symposium on Combustion," Pittsburgh, Pa., Sept., 1954, Reinhold Publishing Co., New York, N. Y., 1955, p. 718.

(4) A. I. Rozlovskiĭ, *Zhur. Fiz. Khim.*, **30**, 912, 1444 (1956).

(5) H. G. Wolfhard and A. Strasser, *J. Chem. Phys.*, **28**, 172 (1958).

(6) C. P. Fenimore and J. R. Kelso, THIS JOURNAL, **74**, 1593 (1952).

(7) H. Wise and M. W. Frech, *J. Chem. Phys.*, **22**, 1463 (1954).

(8) A. Volders and A. van Tiggelen, *Bull. soc. chim. Belges*, **63**, 542 (1954).

(9) W. M. Graven, THIS JOURNAL, **79**, 3697 (1957); *ibid.*, **81**, 6190 (1959).

(10) W. M. Graven, *Anal. Chem.*, **31**, 1197 (1959).

obtained by either gas chromatography or infrared spectrophotometry.

With the appropriate choice of reaction vessel and total flow rate the residence time of the reactant mixture in the reactor was varied approximately 100-fold. The extent of reaction was proportional to the residence time to about 13% conversion. For most of the rate data the extent of reaction was less than 12%. Thus, it was justifiable to use a differential rate law and initial reactant concentrations to obtain the rate constants. In a few cases an integrated rate expression was used.

Preliminary experiments showed that the order of the reaction was approximately 2/3, with respect to NH_3, and slightly greater than unity, with respect to NO. The rate expression

$$R = \frac{d\,(H_2O)}{dt} = \frac{k_1\,(NO)(NH_3)^{1/2}}{1 - k_2\,(NO)(NH_3)^{1/2}} \quad (1)$$

was found to represent the data adequately. Figures 1 and 2 illustrate the manner in which eq. 1 was tested, as well as the means whereby the parameters k_1 and k_2 were evaluated.
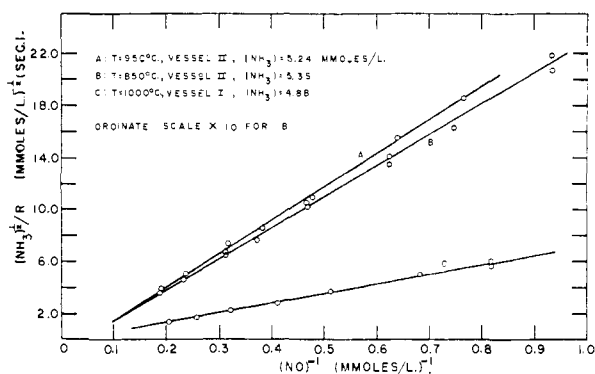

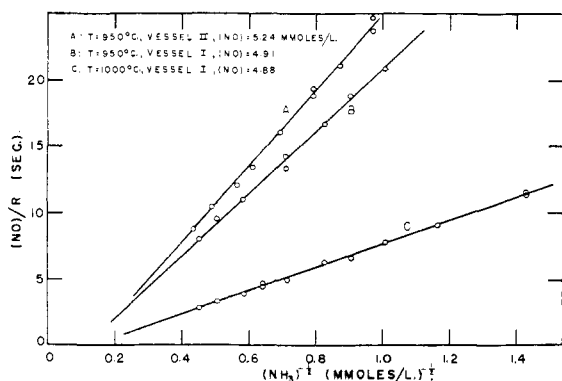Fig. 1.—Effect of NO concentration on reaction rate.

Fig. 2.—Effect of NH_3 concentration on reaction rate.

For a series of runs in which the NH_3 concentration was fixed a plot of the ratio of the square root of the NH_3 concentration and the reaction rate against the reciprocal of the NO concentration resulted in a straight line, as shown in Fig. 1.

Similarly, for a series of runs in which the NO concentration was maintained constant a plot of the ratio of the NO concentration and the rate against the square root of the reciprocal of the NH_3 concentration yielded a straight line, as demonstrated in Fig. 2.

Aggregate rate data comprised 39 series of runs, each consisting of 10 to 30 individual measurements. Table I summarizes the results of those runs in which N_2O-free NO was used. Each series of runs is characterized by a fixed initial concentration of one reactant and a range of variation of the initial concentration of the other reactant. Because of a rather large extent of conversion in those series of runs at 900°, it was necessary to use the integrated form of eq. 1 to obtain k_1. The parenthetical value of k_2 was estimated from the data with the aid of eq. 1. For the remaining series k_1 was obtained from the slope and k_2/k_1 from the ordinate intercept of the previously described plots by least squares treatment of the data.

It is apparent that k_2 is only slightly temperature-dependent. However, the extrapolation required to obtain k_2 introduces an uncertainty which tends to obscure the effect of temperature. A better estimate of the temperature dependence can be obtained from the ignition data.

TABLE I

RATE DATA FOR NO–NH_3 REACTION

No. of runs	T (°C.)	(NO)i, mmoles/l.	(NH₃)i, mmoles/l.	$k_1 \times 10^3$ (l./mmole)$^{1/2}$ sec.$^{-1}$	$k_2 \times 10^2$ (l./mmole)$^{3/2}$
22[b]	850	5.35	1.07–5.35	4.64	1.02
16[b]	850	1.07–5.35	5.35	4.16	1.63
13[b]	850	1.07–6.42	4.28	4.24	1.28
14[b]	900	1.02–5.12	5.12	13.7	(1.50)
15[b]	900	4.10	1.02–6.15	13.1	(1.50)
12[b]	900	1.02–6.15	4.10	13.6	(1.50)
15[a]	950	4.91	0.49–4.91	42.9	2.17
11[b]	950	5.24	1.05–5.24	35.0	2.50
16[a]	950	3.93	0.98–5.90	44.1	1.96
11[a]	950	0.98–5.90	3.93	48.9	1.13
10[b]	950	1.05–6.30	4.19	35.7	2.76
19[a]	1000	4.88	0.49–4.88	115	2.49
18[a]	1000	0.49–4.88	4.88	128	1.96
15[a]	1000	0.98–5.85	3.90	125	2.09

[a] Vessel I.	[b] Vessel II.

It may be observed from the data at 950° that k_1 is approximately 20% larger in vessel I, which has a surface/volume ratio 2.5 times larger than that of vessel II. This effect was also apparent from the Arrhenius-type temperature dependence of k_1. In spite of unequal rates measured in the two vessels the same activation energy, 58.4 kcal., was computed from data obtained with both vessels. Average values of k_1 obtained with vessel II were combined with the activation energy to obtain

$$k_1 = 3.2 \times 10^{10}\,\exp\,(-58400/RT)\,(l./mole)^{1/2}\,sec.^{-1} \quad (2)$$

The effect of H_2 on the reaction rate was ascertained and it was established that for H_2 concentrations less than a few mole per cent. the effect was negligible. Nitrous oxide had a very pronounced effect on the rate. The addition of 1% N_2O to the reaction mixture at 900° produced a 5-fold increase in the rate of reaction.

Certain mixtures of NO and NH_3 ignited spontaneously at temperatures above 960°. Ignition was observed as pulsating, bright white flashes, which often were propagated several feet into the entering gas stream. Each pulse was audible and

produced a sharp pressure fluctuation in the system.

The boundary between reactant compositions which ignited and those which did not ignite was determined with an uncertainty of less than 5% at each of 4 temperatures, as shown in Fig. 3. Reactant compositions obtained from the smooth curves which defined the ignition boundaries were used, together with eq. 1, to calculate k_2 at each temperature on the assumption that under ignition conditions the denominator of eq. 1 becomes zero. Reasonably constant values of k_2 resulted. At 1000° an average value of 0.130 (l./mmole)$^{1/2}$, with a standard deviation of 3%, was obtained. This may be compared with the average value of k_2 of 0.022 (l./mmole)$^{1/2}$ obtained from rate measurements at the same temperature. Better agreement of the values obtained by the two methods would be observed at lower temperatures.

The temperature dependence of k_2, obtained from the ignition data, was fitted to an Arrhenius-type expression, from which an activation energy of 30.0 kcal. was calculated.

Nitrous oxide had an appreciable effect on the ignition properties of NO–NH$_3$ mixtures. The addition of approximately 0.3% N$_2$O to a NO–NH$_3$ mixture in vessel II at 950° produced ignition, whereas no ignition occurred under the same conditions in the absence of N$_2$O. For mixtures in vessel II at 900° about 2.5% N$_2$O caused ignition. In vessel I, with a larger surface/volume ratio, at the same temperature approximately 10% N$_2$O was added before ignition occurred. It was also observed that, in the absence of N$_2$O, ignition was obtained with greater difficulty in vessel I at temperatures and compositions which produced ignition readily in vessel II.

Discussion

From the temperature dependence of k_2 it is possible to predict that at 700° for NO–NH$_3$ mixtures at atmospheric pressure, the denominator of eq. 1 will differ from unity by less than 5%. Therefore, the reaction rate should show a half order dependence on NH$_3$ and a first order dependence on NO concentration. This is in approximate agreement with the 0.5-order dependence on NH$_3$ and the 1.3-order dependence on NO observed by Volders and van Tiggelen[8] for reaction mixtures containing more than 14% NO but is not consistent with other reported rate expressions.[6,7] Similarly, the activation energy of k_1 in the present work is in reasonable agreement with previously reported values of 50[8] and 54.7 kcal.[7] but is somewhat lower than the third reported value of 70 kcal.[6]

It should be noted that the experimental technique of Fenimore and Kelso has been criticized,[11] and the method of measuring reaction rates by observing changes in pressure within the reaction system[7] may be open to question.

Attempts to fit the empirical rate expression with a mechanistic sequence did not meet with complete success. Unfortunately, the experimental observations were insufficient to distinguish between the possibilities of thermal or branching chain ignition. The observed effects on the ignition limits of in-

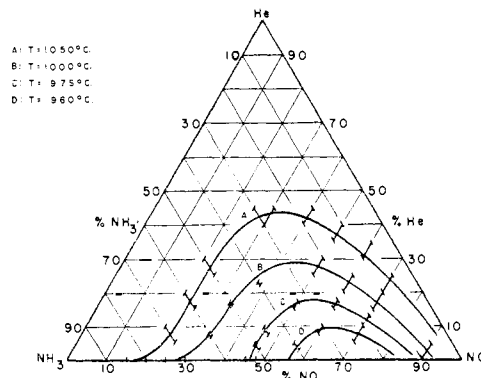(11) F. Kaufman and J. R. Kelso, This Journal, **74**, 2694 (1952).

Fig. 3.—Dependence of ignition limits on composition and temperature.

creased surface/volume, S/V, and changes in composition would be expected for either process. It was not feasible to examine the pressure dependence of the ignition limits with the flow system in use.

The relation derived by Semenov,[12] which prescribes the conditions for thermal explosions, could be applied if one had knowledge of the heat transfer coefficient, K, that is applicable in a continuous-flow reactor. If the questionable approximation of substituting the thermal conductivity of the reactant mixture for K is made, then

$$\frac{(\Delta H)Ee}{RT^2} > \frac{K[S/V]}{\left[\frac{d\,(H_2O)}{dt}\right]_i} \text{ by an order of magnitude, thus}$$

predicting the possibility of a thermal explosion.[12] Although the reaction possesses a large heat of reaction ($\Delta H = -72.2$ kcal.) and a high energy of activation ($E = 58.4$ kcal.), both requisite for thermal explosions at high temperature, the evidence for thermal ignition in the present case is inconclusive.

The form of eq. 1 is typical of rate expressions which result from branching chain mechanisms. The correlation of rate measurements and ignition data, as well as the Arrhenius-type behavior of the parameter k_2 obtained from the temperature dependence of the ignition limits, tends to support a branching chain hypothesis.

If a branching chain mechanism is assumed, the observations that increased S/V caused only a slight acceleration of the reaction rate and a more pronounced inhibition of ignition point to surface initiation and termination of chains and gas-phase branching.

Chain initiation might occur on the vessel walls by either of the processes[2]

$$NH_3 \longrightarrow NH + H_2 \qquad (3)$$
$$NH_3 \longrightarrow NH_2 + H \qquad (4)$$
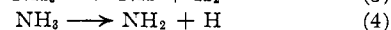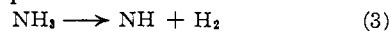
although the latter might be considered more probable in view of the report[3] that in NO–NH$_3$ flames NH bands are very weak and only visible in fuel-rich flames, whereas NH$_2$ and OH bands are readily observed.

Chain propagation could result from the sequence

$$NH_2 + NO \longrightarrow N_2 + OH + H \qquad (5)$$
$$OH + NH_3 \longrightarrow NH_2 + H_2O \qquad (6)$$
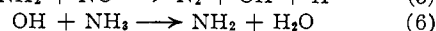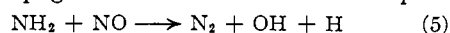
(12) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. II, Princeton University Press, Princeton, N. J., 1959, p. 87.

Reaction 5 has been suggested[2] as a branching step in NO–NH₃ flames. Whether eq. 5 results in chain branching will probably depend on whether H atoms subsequently react with NH₃ or with NO.

$$H + NH_3 \longrightarrow H_2 + NH_2 \qquad (7)$$

$$H + NO \longrightarrow HNO \qquad (8)$$
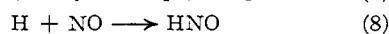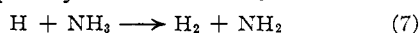
Since NO is known to "catalyze" the recombination of H atoms,[13] probably via reactions 8 and 9, it is

$$H + HNO \longrightarrow H_2 + NO \qquad (9)$$
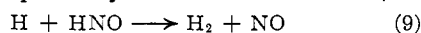
conceivable that only the H atoms which undergo reaction 7 will function as chain carriers.

(13) H. M. Smallwood, THIS JOURNAL, **51**, 1985 (1929).

If the activation energy of k_2 is associated with the chain branching step, the observed value of 30 kcal. is too large to be attributed to reaction 7. Alternatively, the decomposition of HNO

$$HNO \longrightarrow H + NO \qquad (10)$$
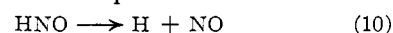
might require such an energy of activation and reaction 10, followed by reaction 7, would result in branching.

Although this admittedly speculative mechanism predicts temperature and composition dependent explosion limits the complex form of the resulting rate expression makes comparison with eq. 1 rather futile.

# The Oxidation of Thiocyanate Ion by Hydrogen Peroxide. II. The Acid-catalyzed Reaction

BY I. R. WILSON AND G. M. HARRIS

The stoichiometry and kinetics of the acid-catalyzed reaction have been studied in the range 0.05 to 1.3 M perchloric acid. The main products are sulfate and hydrogen cyanide, but sulfur dicyanide, $S(CN)_2$, is also formed. The reaction, as determined by iodometry, follows a rate law of the form
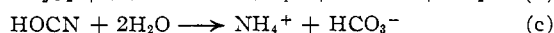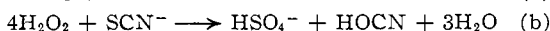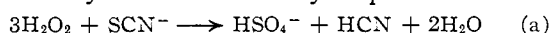
$$R = k_2(H^+)(SCN^-)(H_2O_2)^2/[(H_2O_2) + \alpha(HCN)]$$

in which α is a constant. A mechanism of reaction is deduced, making use of carbon-14 and oxygen-18 tracer experiments as well as conventional rate data, and α is identified as a ratio of rate constants of secondary reactions. The rate constant of the third order primary reaction

$$H_3O^+ + SCN^- + H_2O_2 \longrightarrow HOSCN + 2H_2O$$
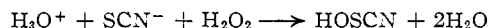
is fitted by the expression $k_2 = 1.75 \times 10^8 \exp(-11000/RT)$ l.² mole⁻² min.⁻¹ in the range 20 to 50°.

In Part I of the present series,[1] it was pointed out that the reaction between hydrogen peroxide and thiocyanate takes place according to different mechanisms, depending on the acidity of the solution. The main acid-catalyzed process is stated to have the stoichiometry[2] of equation a, while the non-catalyzed reaction[1] obeys equations b and c

$$3H_2O_2 + SCN^- \longrightarrow HSO_4^- + HCN + 2H_2O \qquad (a)$$

$$4H_2O_2 + SCN^- \longrightarrow HSO_4^- + HOCN + 3H_2O \qquad (b)$$

$$HOCN + 2H_2O \longrightarrow NH_4^+ + HCO_3^- \qquad (c)$$

A re-investigation of the acid-catalyzed reaction is reported herewith, in which alternative rate-measuring methods and isotopic tracer technique have provided conclusive evidence concerning its mechanism.

Experimental

All reagents used were as specified in the earlier publication.[1] *Stoichiometric and/or rate measurements* were made by several different procedures, including:

(A) Iodometry of H₂O₂ consumed, as detailed previously.[1] It was found that sulfur dicyanide also liberates I₂ from iodide, so that this determination gives in fact total of (H₂O₂) and (S(CN)₂) in presence of the latter.

(B) Volumetric determination of sulfate formed, using a modification of the EDTA method of Belcher, et al.[3] Aliquots of reaction solution were pipetted into 15 ml. centrifuge tubes containing 5 ml. of 0.02M BaCl₂ and 1 ml. of acetate buffer (the latter raises the pH sufficiently to

"freeze" the reaction). After thorough mixing, centrifuging and washing, the BaSO₄ precipitate was taken up in a mixture of 5 ml. of 0.02 M EDTA and 0.5 ml. of concentrated ammonia, while kept at 50–60° on a water-bath. The resulting solution, buffered to pH 10 with ammonia/ammonium perchlorate, was titrated with 0.005 M Mg(NO₃)₂ solution, using as indicator eriochrome black T screened with methyl yellow.

(C) Acidimetric measurement of bisulfate formed, which was possible when the initial concentration of HClO₄ did not exceed 0.1 M and the initial thiocyanate concentration was at least 0.01 M. Mixed brom cresol green/methyl red indicator was used.

(D) Colorimetric determination of H₂O₂ consumed using the specific Ti(IV) technique devised by Rynasiewicz.[4] Sulfur dicyanide does not interfere in this determination, as it does in Method A.

(E) Titration of HCN formed during reaction with NiSO₄ using dimethyl glyoxime as indicator,[5] or, in the case of complete reaction, by means of Archer's modification[6] of the Liebig method.

(F) Polarographic determination of thiocyanate consumption.[7]

The *identification of sulfur dicyanide*, S(CN)₂, in the reaction products was accomplished by ether extraction followed by evaporation of the ether at reduced pressure and two sublimations of the residue at 30°. White crystals were obtained; m.p. 62.0–62.6°. A comparison sample of S(CN)₂ prepared by the reaction of AgSCN and ICN[8] and purified in the same way as the reaction residue gave m.p. 62.0–62.8° and mixed m.p. 61.9–62.8°. The identity of the two products was also confirmed by infrared spectra in CS₂ solution.

(1) I. R. Wilson and G. M. Harris, THIS JOURNAL, **82**, 4515 (1960).

(2) J. H. Kastle and C. R. Smith, *Amer. Chem. J.*, **32**, 376 (1904).

(3) R. Belcher, R. L. Bhasin, R. A. Shah and T. S. West, *J. Chem. Soc.*, 4054 (1958).

(4) J. Rynasiewicz, *Anal. Chem.*, **26**, 355 (1954).

(5) L. G. Urusovskaya and P. I. Zhilina, *C. A.*, **44**, 481 (1950).

(6) E. E. Archer, *Analyst*, **83**, 571 (1958).

(7) R. A. Plowman and I. R. Wilson, *Analyst*, **35**, 222 (1960).

(8) *Beilstein*, III, 180.