[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Kinetics of the Decomposition of N_2O at High Temperature[1]

BY WENDELL M. GRAVEN

RECEIVED APRIL 27, 1959

Rates of thermal decomposition of N_2O have been measured within the temperature range of 800 to 1000° with the use of a flow technique and gas chromatography for product analysis. Decomposition to yield NO_2 and N_2 was of secondary importance under the experimental conditions. Although NO accelerated and O_2 retarded the reaction rate a first-order dependence upon N_2O concentration was observed to 25% conversion. Within the limits of the variables which were investigated the rate constant for decomposition to yield N_2 and O_2 was found to be $2.1 \times 10^9 \exp(-52500/RT)$ sec.$^{-1}$.

The thermal decomposition of N_2O, although thoroughly investigated many years ago, has recently received additional attention.[2-4] Although Lindars and Hinshelwood were concerned primarily with the initial activation process, while Kaufman, *et al.*, dealt principally with the secondary steps, both groups observed NO formation in the initial part but little, if any, in the latter part of the reaction.

Nitric oxide formation was observed in the first reported kinetic study of the decomposition of N_2O[5] and later studies showed that it inhibited its own further formation,[6] but not until a recent investigation[3] has a satisfactory explanation of its role been postulated. At temperatures above the range within which rate measurements have been reported[7] considerably higher yields of NO, increasing with temperature, have been found.[8]

This work was undertaken since it appeared to be of interest to extend the investigation of the role of NO in N_2O decomposition to as high temperatures as possible.

In each of the previous investigations the rate of N_2O decomposition has been determined by pressure measurements. Only the rate of NO formation has been obtained by an unambiguous technique. In view of the present availability of suitable analytical devices it was thought desirable to measure directly the rates of formation of at least two of the decomposition products.

Experimental

Measurements of reaction rates were made with a flow technique which permitted rapid heating of pre-mixed reactant and diluent, as well as rapid quenching of effluent mixtures. Use was made of the same reaction vessels which were employed in a previous investigation.[9] Both vessels were constructed from fused silica according to the same pattern, although the dimensions of vessel I were approximately one-half of those for vessel II. The volume of vessel I was 5.60 ml. and its surface/volume ratio was 5.6 cm.$^{-1}$. Vessel II had a volume of 42.6 ml. and a surface/volume ratio of 2.3 cm.$^{-1}$.

Both tangential entry and exit of the gas stream were designed to ensure complete "sweeping" of the free volume. Residence time of the gas in the capillary leads, where a temperature gradient existed, amounted to approximately 1% of the total reaction time. The two thermocouple wells permitted control of the temperature at the center of the vessel, which was situated in a tubular electric furnace, while the temperature profile along the major axis of the vessel was monitored with a N.B.S.-calibrated Pt, Pt-Rh thermocouple. A modified Simplytrol pyrometer-relay maintained the temperature constant to within one degree. With the use of an auxiliary heating coil paralleling the capillary entrance lead it was possible to reduce the temperature gradient between entrance and exit of the vessel to approximately one degree with the vessel at 1000° and a gas flow rate of 1.5 l. min.$^{-1}$.

With the use of He as a diluent to maintain a constant total flow rate of 1.5 l. min.$^{-1}$ it was possible to vary the initial N_2O concentration over a ten-fold range without changing the reaction time or the total pressure in the reaction vessel of 80 (±1) cm. Flow rates were measured and controlled with capillary tube flowmeters which had been calibrated for the individual gases. Mixing of reactant and diluent was accomplished with tangential jet mixing chambers.

Compressed N_2O from a commercial cylinder was passed through a copper tube containing Ascarite at −78° before being frozen at −190° in an evacuated stainless steel cylinder, whereupon the volatile gases were pumped off. Several repetitions of the "thawing–freezing–pumping" procedure left a product which upon chromatographic examination showed no evidence of gaseous impurities. Commercial NO was passed through Ascarite and O_2 and "pre-purified" N_2 were dried prior to their usage. Chromatographic examination of the NO and O_2 showed the presence of N_2 only, whereas with N_2, no gaseous impurities were revealed.

Analysis of the effluent from the reactor for N_2 and O_2 was accomplished with the use of gas adsorption chromatography. The gas chromatograph was constructed especially for this purpose and is described elsewhere.[10] Satisfactory separation of O_2, N_2 and NO was obtained at ambient temperature on a ten-foot column packed with 40/80 mesh type 5A Molecular Sieves. With this instrument it was possible to detect 0.1 mole % of either gas in the effluent. However, satisfactory reproducibility of the measurements required a minimum of about 0.5 mole % of each gas.

Results and Discussion

No NO was observed by gas chromatographic examination of the effluent from the reactor during any of the kinetic runs. In certain of the runs, however, NO_2 was identified. Indirect evidence for its presence was to be found in the observation that, with few exceptions, the O_2/N_2 ratio in the effluent was always slightly less than one-half. It should be noted that the results do not distinguish between the production of NO_2 within the reactor, or its subsequent formation by combination of NO with O_2 in the gas stream at ambient temperature.

The equations which represent the two modes of decomposition of N_2O may be expressed in terms of the observed products

---

(1) This work was supported by grants from the Research Corporation and the Graduate School of University of Oregon, for which grateful appreciation is acknowledged.

(2) F. J. Lindars and C. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A231**, 162, 178 (1955).

(3) F. Kaufman, N. J. Gerri and R. E. Bowman, *J. Chem. Phys.*, **25**, 106 (1956).

(4) T. N. Bell, P. L. Robinson and A. B. Trenwith, *J. Chem. Soc.*, 1474 (1957).

(5) M. A. Hunter, *Z. physik. Chem.*, **53**, 441 (1905).

(6) F. F. Musgrave and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A135**, 23 (1932).

(7) C. N. Hinshelwood and R. E. Burk, *ibid.*, **A106**, 284 (1924).

(8) E. Briner, C. Meiner and A. Rothen, *Helv. Chim. Acta*, **9**, 409 (1926); *J. chim. phys.*, **23**, 609 (1926).

(9) W. M. Graven, THIS JOURNAL, **79**, 3697 (1957).

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

$$2N_2O = 2N_2 + O_2 \qquad (1)$$

$$4N_2O = 2NO_2 + 3N_2 \qquad (2)$$

With knowledge of percentages of N_2 and O_2 in the reactor effluent, obtained from the chromatographic analysis, it was possible to separate the total rate of decomposition of N_2O into the two components represented by equations 1 and 2.

In Fig. 1 it may be seen that the per cent. reaction by each of these paths, at three temperatures over a ten-fold range of initial N_2O concentration, is independent of reactant concentration. In addition to the first-order behavior of the rates of each of these reactions it may be observed that approximately six times as much N_2O decomposes by path 1 as by path 2 in vessel II while in vessel I the ratio is approximately 3:1, essentially independent of temperature.

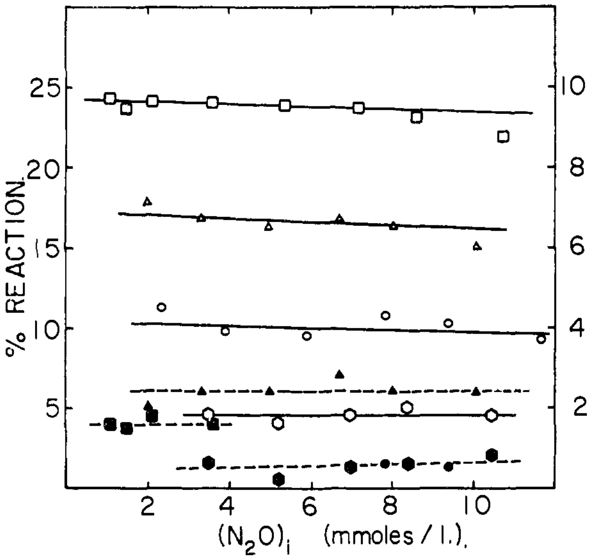

Fig. 1.—Effect of initial N_2O concentration on extent of reaction; open figures and solid lines indicate decomposition which produces O_2; closed figures and broken lines indicate decomposition which produces NO_2: (□, ■) left ordinate axis, vessel II, T = 926°, t = 0.41 sec.; (△, ▲) right ordinate axis, vessel I, T = 971°, t = 0.053 sec.; (○, ●) right ordinate axis, vessel II, T = 826°, t = 0.46 sec.; (◇, ◆) right ordinate axis, vessel I, T = 926°, t = 0.056 sec.

The effects upon the rate of N_2O decomposition of the initial presence in the reaction mixture of O_2, N_2 and NO are shown in Fig. 2. Nitrogen apparently does not influence the decomposition rate. The accelerating influence of NO has been observed by previous investigators and has been attributed to the direct interaction of NO with N_2O.[11] A retarding effect of O_2 has not been reported previously for the homogeneous reaction although it has been observed for the heterogeneous decomposition.[12] However, the data of Volmer and Froehlich[13] show that at 670° the N_2O decomposition rate in the presence of O_2 is only one-half as great

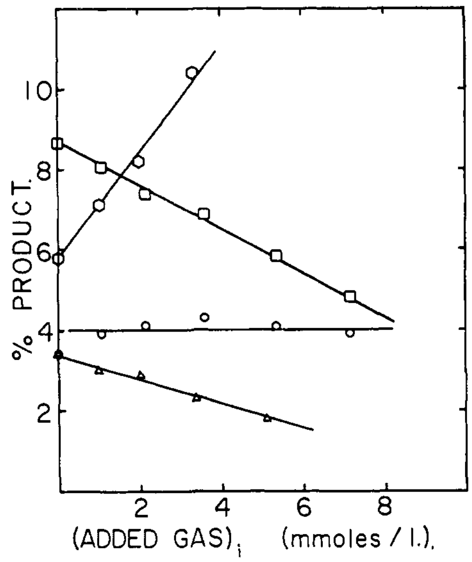

Fig. 2.—Effect of initial presence of reaction products on extent of reaction. Ordinate represents % O_2 in effluent for addition of N_2 and % N_2 for additions of O_2 and NO. (□) O_2 addition, vessel II, $[N_2O]_i$ = 3.57 mmoles/l., T = 926°, t = 0.42 sec.; (◇) NO addition, vessel I, $[N_2O]_i$ = 3.29 mmoles/l., T = 1007°, t = 0.052 sec.; (○) N_2 addition, vessel II, $[N_2O]_i$ = 3.57 mmoles/l., T = 926°, t = 0.42 sec.; (△) O_2 addition, vessel I, $[N_2O]_i$ = 3.36 mmoles/l., T = 971°, t = 0.053 sec.

as in the presence of an equal amount of He, in agreement with the present observations.

Figure 3 shows the variation in extent of reaction with increasing reaction time. In computing reaction times from the total flow rates corrections have been made for the volume changes during the reaction. Although the rates of reaction 1 in both

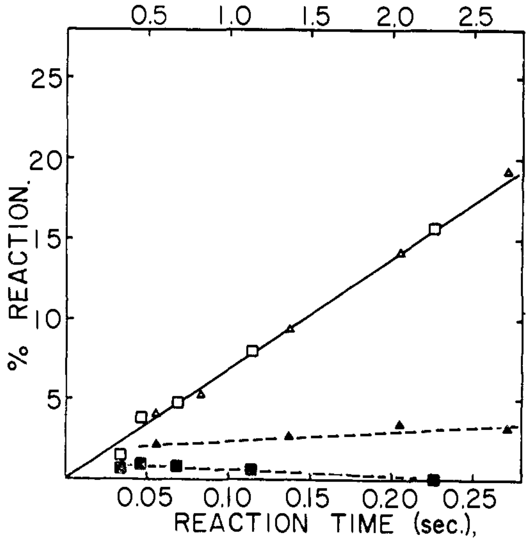

Fig. 3.—Effect of reaction time on extent of reaction; open figures and solid lines indicate decomposition which produces O_2; closed figures and broken lines indicate decomposition which produces NO_2: (□, ■) upper time scale, vessel II, $[N_2O]_i$ = 5.6 mmoles/l., T = 826°; (△, ▲) lower time scale, vessel I, $[N_2O]_i$ = 5.1 mmoles/l., T = 926°.

---

[11] F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, **23**, 602 (1955).

[12] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 327 (1925).

[13] M. Volmer and H. Froehlich, *Z. physik. Chem.*, **B19**, 85, 89 (1932).

vessels appear to be constant within the time interval which was examined, the rate of reaction 2 apparently reaches a maximum within a shorter period of time than that corresponding to the initial measurement and then falls rapidly to a negligible value. A somewhat similar behavior of the reaction at lower temperatures has been observed previously.[2,3]

It may be noted that here, as in Fig. 1, the fraction of the total decomposition which occurs *via* path 2 is larger for vessel I than for vessel II. The data of Fig. 1, which show an invariance of this fraction with temperature in either vessel, renders unsatisfactory any explanation that is based upon the dissimilarity of temperatures. Invariance of the extent of reaction 2 with reaction time makes it unlikely that the larger surface/volume ratio of vessel I can account for the greater relative importance of reaction 2. A more plausible explanation is that the NO_2 formation is self-inhibitory and the greater relative importance of reaction 2 in vessel I is the result of the shorter reaction time permitted by its smaller size. The coincidence of the two curves representing reaction 1 in the two vessels has no significance since it is the result of fortuitous choices of reaction temperatures and graphical time scales.

The dependence upon temperature of the rate of decomposition was investigated from 800 to 925° in vessel II and from 925 to 1007° in vessel I using a constant flow rate of N_2O. In view of the anomalous behavior of the rate of reaction 2, which was indicated by the data of Fig. 3, only the first-order rate constants k for reaction 1 were computed from the rate measurements at each of the temperatures. An Arrhenius-type plot of the data from both vessels yields a straight line, from the slope of which an activation energy of 52.5 kcal. has been calculated for reaction 1.

The rate constants obtained with the use of vessel I agree with those obtained with the use of vessel II within the limits of uncertainty of the experimental measurements. The mean values of k at 926° obtained from 19 measurements using vessel I and 28 measurements using vessel II were 0.52 (±0.20) sec.$^{-1}$ and 0.63 (±0.04) sec.$^{-1}$, respectively. These mean values of k, as well as the average of 28 measurements at 826° using vessel II, 0.071 (±0.014) sec.$^{-1}$, and the average of 13 measurements at 971° using vessel I, 1.39 (±0.13) sec.$^{-1}$, were combined with the observed activation energy E to obtain the A factor for the rate constant of reaction 1.

$$k = 2.1 \times 10^9 \exp(-52500/RT) \text{ sec.}^{-1}$$

Agreement of k with the rate constants computed by previous investigators for the composite decomposition of N_2O is satisfactory. From rate measurements between 560 and 665° within a pressure range of 8 to 800 cm.[14] values of A of 4.0×10^9 sec.$^{-1}$ and E of 53 kcal. have been calculated.[15] However, E has been found to increase with pressure from 53 kcal. at 0.1 atm. to 65 kcal. at 40 atm.[16]

Although previous investigators[3] have proposed a mechanism which satisfactorily accounts for the observed variation with time of the rate of NO formation during N_2O decomposition, their mechanism does not predict the retardation of the decomposition rate by O_2 which has been observed at each temperature in both reaction vessels during the present investigation. In order to account for all of the observations an alternative mechanism will be postulated.

$$N_2O = N_2 + O \qquad (3)$$

$$N_2O + O = N_2 + O_2 \qquad (4)$$

$$N_2O + O = 2NO \qquad (5)$$

$$N_2O + NO = NO_2 + N_2 \qquad (6)$$

$$NO_2 + O = NO + O_2 \qquad (7)$$

$$2NO + O_2 = 2NO_2 \qquad (8)$$

$$2NO = N_2 + O_2 \qquad (9)$$

Initially, decomposition proceeds by way of reactions 3 to 5 only. There is some evidence from product analysis in the early stages of the decomposition that reactions 4 and 5 are about equally probable.[3] As the concentration of NO increases reaction 6 rapidly becomes important.[11] Before the decomposition has proceeded beyond several per cent. reactions 4 and 5 are superseded by reaction 7. The interaction of NO with O, a process which requires a three-body collision, probably does not compete with reactions 6 and 7 within the temperature range which was investigated. This sequence of reactions accounts for the early discontinuation of NO formation during N_2O decomposition, Fig. 3.

Reaction 8 occurs only after large accumulation of products, or if O_2 has been added initially. The gradual replacement of reaction 6 by reaction 8 can explain the observed effect of added O_2 upon the decomposition rate, Fig. 2, as well as the slight decrease in the rate of reaction 1 under conditions of high N_2O concentration and large percentage conversions, Fig. 1. Reaction 9 is offered to explain the slight decrease with time of the per cent. decomposition by path 2 in vessel II, Fig. 3.

The observed activation energy is satisfactorily larger than the endothermicity of the rate-determining initial step, (3), of 39.7 kcal. at 25°.[17]

EUGENE, OREGON

---

[14] N. Nagasako and M. Volmer, *Z. physik chem.*, **B10**, 414 (1930).

[15] H. C. Ramsperger and G. Waddington, *Proc. Natl. Acad. Sci.*, **17**, 103 (1931).

[16] E. Hunter, *Proc. Roy. Soc. (London)*, **A144**, 386 (1934).

[17] Natl. Bureau Standards, Circular 500, "Selected Values of Chemical Thermodynamic Properties," Series I, 1952.