The deviation of the N–S–O and the O–S–O bond angles from the normal tetrahedral value is significant and probably due to a combined effect of the mutual repulsion of the negatively charged oxygen atoms, and the attractive forces between these and the positively charged ammonia ion. This distortion results in a molecule which is nearly tetrahedral, except that the three oxygen atoms are drawn more closely into the plane of the central sulfur atom.

The hydrogen bonds are so disposed throughout the structure that no well defined cleavage was found in any direction in the crystal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, AND THE M. W. KELLOGG COMPANY]

The Kinetics of the Thermal Decomposition of Nitric Acid Vapor

BY HAROLD S. JOHNSTON, LOUISE FOERING, YU-SHENG TAO AND G. H. MESSERLY

The thermal decomposition of nitric acid vapor was studied in two glass cells of considerably different surface-to-volume ratio from 100 to 465°. The rate was followed colorimetrically as the appearance of nitrogen dioxide. The decomposition is a heterogeneous reaction at low temperatures and predominantly a fast homogeneous first-order reaction above 400°. The heterogeneous reaction is initially first order, but its rate is reduced by water or nitrogen dioxide on the surface. It has a very low energy of activation, about 5 kcal. The homogeneous rate is independent of reaction products; its energy of activation is 40 kcal. or higher. A partial mechanism is proposed whereby nitric acid decomposes to hydroxyl radical and nitrogen dioxide.

The equilibrium constants for the reaction

$$2HNO_3 = 2NO_2 + H_2O + {}^1/_2O_2 \qquad (1)$$

were established by Forsythe and Giauque,[1] but the reaction as written has not been given a kinetic study over a wide range of conditions. Part of the reason for neglect of this reaction is probably that it is very fast in the temperature region of greatest interest. Thus the colorimetric and oscillographic method of following fast reactions[2] at constant temperature and constant volume was used for this investigation.

Experimental

Apparatus.—The flowmeters, saturator for nitric acid, mixing chamber, stop-gate, photoelectric tube, oscilloscope, light chopper and camera were essentially the same as those described by Johnston and Yost.[2] The light source was a mercury arc filtered to give the 436 mμ line. The reaction cells were quite different and will be described in detail. (a) Small glass reaction cell. Flat Pyrex windows were fused to the end of a glass tube 6 mm. i.d. and 10 cm. long. About one mm. from each window side arms led off as entrance and exit tubes. The entrance tube was 50 cm. long and formed into a flat coil. The exit tube led straight out. The coil, reaction cell and exit tube were tightly and heavily wound with copper foil to equalize the temperature. Over the foil was wrapped asbestos paper and then a 1000 watt heating coil of chromel wire. Over the heating elements was molded a three inch thickness of plumbers magnesia insulation. A 500-degree thermometer was inserted into the copper foil, and a calibrated platinum-platinum rhodium thermocouple was inserted down the exit tube so that its junction just entered the reaction cell. The entry hole for the thermocouple was sealed with a cement made of water glass and talc. Thus the gases were mixed at room temperature or slightly higher (leads from the saturator were wrapped with heating wires to keep the temperature at 60°), brought through the stop-gate into the furnace, heated up as they flowed, brought into the reaction cell and out the exit tube through the stop-gate. When the stop-gate was closed, the reactants were isolated at constant volume, and flowrates were chosen such that it was also at constant temperature. The thermometer outside the reaction cell and the thermocouple inside gave the same temperatures to within ±3°. Some reaction occurred as the gases were heated up, but this did not usually offer any complication to interpreting the results. (b) Large glass cell. Flat Pyrex windows were fused to a glass tube 25 mm. i.d. and 10 cm. long. About 3 mm. from each window a side arm led off as in the case of the small cell. The thermocouple was inserted into the reaction tube about 8 mm. The cell was wrapped in copper, asbestos, heating coil and insulation as in the other case.

Materials.—Commercial sources of compressed gases were: nitrogen and oxygen, Linde; carbon dioxide, Pure Carbonic; nitrogen dioxide, Matheson. These gases were dried by passing through traps at Dry Ice temperature, and not otherwise purified except for nitrogen dioxide which was vacuum fractionated. Anhydrous nitric acid was prepared by vacuum distillation from concentrated sulfuric acid and sodium nitrate at room temperature to −30°. The nitric acid was condensed directly into an all-glass saturator and was completely colorless. All stopcocks were greased with chloro-trifluorocarbon stopcock grease. This grease is poor for continual vacuum work, but it is inert to nitric acid and very useful for flowmeter work and short periods of vacuum.

Taking of Data.—The flow-rate of dry nitrogen was given by manometer readings and calibration curve for the flowmeters. Concentration of nitric acid was found by freezing out nitric acid from the carrier nitrogen stream with liquid nitrogen. The acid was slowly thawed, dissolved and titrated with standard base. The apparent vapor pressure was always less than the true vapor pressure,[1] and so analyses had to be made as a part of every series of runs. The reaction cells were calibrated for nitrogen dioxide by passing streams of known concentration through them. The light intensity before (I_0) and with nitrogen dioxide (I) gave the optical density log I_0/I which is proportional to concentration of nitrogen dioxide. The calibration curve was found to be constant from room temperature to 450° provided that concentration of nitrogen dioxide and not its pressure is considered. For a run the following light intensity readings were taken: I_0 with only nitrogen flowing, I at zero time with nitrogen and nitric acid flowing, and after the stop-gate closed a series of readings I at regular time intervals as the reaction progressed. At the end of each run the cell was swept out, and another value of I_0 taken. At low temperatures the readings were made visually at clocked intervals, and at high temperatures they were recorded photographically as the beam of the oscilloscope swept once across the screen. From values of I_0/I the concentration of nitrogen dioxide was found as a function of time.

Results

1. Rate.—The equilibrium of the reaction given by Equation (1) lies well to the right under all conditions reported here. The quantity measured is the concentration of nitrogen dioxide. The initial concentration of nitric acid is known

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[1] W. R. Forsythe and W. H. Giauque, THIS JOURNAL, **64**, 48 (1942).

[2] Harold S. Johnston and Don M. Yost, *J. Chem. Phys.*, **17**, 386 (1949).

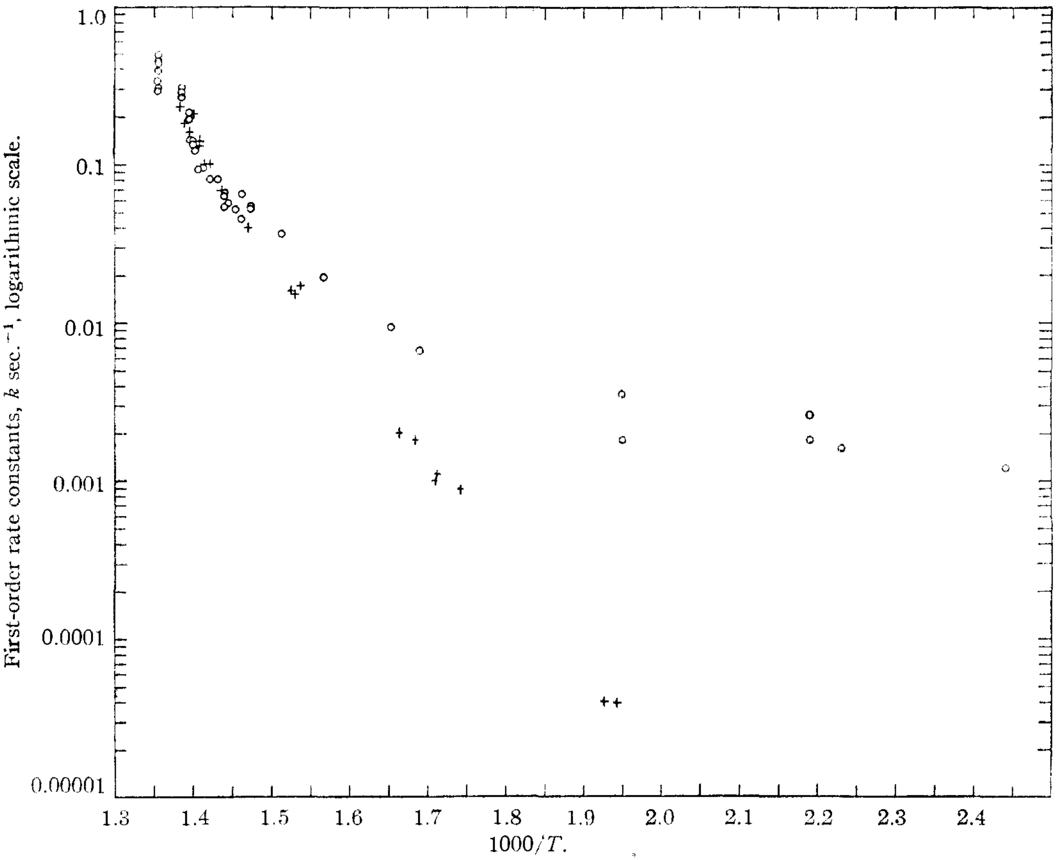

Fig. 1.—Thermal decomposition of nitric acid vapor: O, 6 mm. cell; +, 25 mm. cell.

from flowmeter readings and chemical analyses, and its concentration at any time is considered to be this initial value minus the amount of nitrogen dioxide present at any time—except under conditions where nitrogen dioxide has decomposed into nitric oxide, Section 7 below. The rates discussed here are the rates of disappearance of nitric acid computed in this manner.

2. **Order.**—If the decomposition of nitric acid is a first-order reaction, a plot of the logarithm of concentration of nitric acid against time should be a straight line whose slope is $-k/2.303$ where k is defined by

$$-d(HNO_3)/dt = k(HNO_3) \qquad (2)$$

It has been found that for all studies made above 400° the decomposition is first order. Below 300° the first one-quarter or so of the reaction is first order, but this is followed by a rate slower than first order. By drawing a straight line through the initial points it is possible to get a first-order constant for the reaction at any temperature, although below 300° this number describes only a small fraction of the reaction. In this way 84 successful runs were carried out for a variety of conditions, and these detailed data are available on microfilm.[3] All rate constants with nitric acid vapor plus inert carrier gas at temperatures above 300° for both the small cell and the large cell are shown in Fig. 1, and also shown are all rate constants below 300° for which the initial pressure of reactant was about 10 mm. At low temperature, points for high pressure of reactant were omitted; if included they increase the scatter.

3. **Effect of Foreign Gases.**—All studies reported here were made at a total pressure of one atmosphere. Nitric acid itself was at pressures from about 5 to 25 mm. The rest of the pressure was usually due to nitrogen, although some experiments were done with oxygen and some with carbon dioxide. The rate was the same in the presence of any one of these three gases. At lower total pressures a strong inert-gas effect might be noted.

4. **Energy of Activation.**—The plot of log k against reciprocal temperature (Fig. 1) is by no means a straight line. For the small cell above 400° there is a rapid change of rate constant with temperature, and below 300° the rate constant is extremely insensitive to temperature. The resulting plot can be considered as the sum of two straight lines intersecting near $1000/T = 1.54$ and $k = 0.01$ sec^{-1}. One line has an energy of activation of at least 40 kcal. and the other about 5 kcal.; these estimates are to be considered as only very approximate. This analysis for the small cell alone clearly indicates two modes of decomposition.

5. **Homogeneity or Heterogeneity.**—The comparison (Fig. 1) of results from the large cell with those from the small cell shows agreement above 400° and great divergence below 300°. These

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[3] For tables supplementary to this article order Document 3129 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

results show the reaction to be primarily homogeneous above 400°, essentially heterogeneous below 300°, and some of each between 300 and 400°.

6. **Effect of Reaction Products.**—The products of reaction, nitrogen dioxide, water and oxygen, were separately tested for effect on both the homogeneous and the heterogeneous mode of decomposition. Detailed data are available on microfilm.[3] Oxygen when present at about one atmosphere appears to be without effect in either case. By its presence or by its previous contact with the surface, either water or nitrogen dioxide reduces the rate of the heterogeneous reaction. With ratios of nitrogen dioxide to nitric acid up to one-third, the rate of the homogeneous reaction is unaffected; higher initial concentrations of nitrogen dioxide were not tried. Water at partial pressure equal to that of nitric acid showed no effect on the homogeneous reaction rate.

7. **Subsequent Reaction of Nitrogen Dioxide.**—Above 400° the decomposition of nitrogen dioxide to colorless nitric oxide and oxygen becomes important, and the equilibrium is in favor of the products. This reaction might have spoiled the colorimetric method of analysis for nitrogen dioxide. However, the rate of decomposition of nitric acid was much faster than the rate of decomposition of nitrogen dioxide, and thus runs could be followed to about 90% completion before corrections for nitric oxide became important. A further problem with nitric oxide is the fact that it reacts with nitric acid at a rate unknown at these temperatures.[4] To avoid these difficulties the only data used to compute rate constants were the initial rates.

Discussion

Mechanism.—From section 7 above it is seen that nitrogen dioxide appears as a decomposition fragment not by way of nitric oxide. In section 6 it is shown that for the homogeneous reaction, the final products do not enter into the rate determining step. Since the rate was found to be first order with respect to nitric acid, it is reasonable to postulate as the rate determining step the unimolecular decomposition of nitric acid, for which there are only three possibilities which break a single bond

$$HNO_3 = HO + NO_2 \quad -47 \text{ kcal.} \qquad (3)$$

$$HNO_3 = H + NO_3 \quad -100\ (?) \text{ kcal.} \qquad (4)$$

$$HNO_3 = HNO_2 + O \quad -80\ (?) \text{ kcal.} \qquad (5)$$

Since the observed energy of activation is 40 kcal. or somewhat more, steps (4) and (5) are much less probable than (3) on the basis of thermochemistry.[5] Due to the difficulty in separating out the heterogeneous reaction and due to the large experimental error around 450°, the minimum energy of activation as given by step (3) of 47 kcal. lies well within the range of the observed energy of activation, 40 kcal. or more. The further steps are effectively as follows although this study gives no detailed information about the actual processes

$$4HO = 2H_2O + O_2, \text{ perhaps on the walls} \qquad (6)$$

In the decomposition of hydrogen peroxide,[6] a reaction which has many parallel features with the decomposition of nitric acid, four hydroxyl radicals are destroyed to give two water molecules and one oxygen molecule at temperatures around 500°. Any further progress in analyzing the mechanism of the peroxide decomposition would be applicable toward clarifying the later steps of this reaction. On the other hand, further reaction between hydroxyl radical and molecular nitric acid is possible.

Very little can be said about the mechanism of the heterogeneous reaction. Its initial rate is first order, and so it might go by the same mechanism as the homogeneous reaction, or it might be quite different. The inhibiting effect of water and nitrogen dioxide on the heterogeneous reaction could be due entirely to their occupation of the surface, thus displacing nitric acid.

Indicated Further Studies.—By mixing nitric acid vapor with a great excess of preheated nitrogen, the delay due to heating could be reduced greatly. In this way the study could be pushed to higher temperatures, and a more precise determination of the energy of activation could be made. The effect of inert gases should be studied at reduced total pressures, and for this work one should use a very large bulb to reduce the surface reaction.

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JERSEY CITY, N. J.
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[4] J. H. Smith, THIS JOURNAL, **69**, 1741 (1947).

[5] NO_2, O, H and NO_3 (?): F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936; HNO_3: F. R. Forsythe and W. F. Giauque, THIS JOURNAL, **64**, 48 (1942); HNO_2(?): G. von Elbe and B. Lewis. *ibid.*, **59**, 2022 (1937); HO: Rudulph Edse, *J. Chem. Phys.*. **18**, 244 (1950).

[6] C. K. McLane, *J. Chem. Phys.*, **17**, 379 (1949).