hibited in the azeotropes formed seem to be in at least semi-quantitative agreement with the extent of deviation from ideal behavior, as is to be expected.

No conclusions are drawn concerning the reaction observed in the study of the bromine–carbon disulfide system. A survey of the literature revealed no mention of the occurrence of a reaction between these two components below 180°.[7] It is not beyond the realm of possibility that the reaction was promoted by the presence of some impurity in small amount in the carbon disulfide, although this is considered unlikely due to the fact that tests made for the detection of impurities in this solvent[8] were all negative. Furthermore, refractive index and boiling point measurements gave excellent agreement with values recorded in the literature.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation, whose financial assistance made this investigation possible, and to both the General Chemical Division of the Allied Chemical and Dye Corporation and the Hooker Electrochemical Company, who furnished without charge some of the chemicals.

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[7] R. Gerstl, *Ber.*, **3**, 508 (1870).

[8] B. L. Murray, "Standards and Tests for Reagent and C. P. Chemicals," second edition, D. Van Nostrand Company, New York, N. Y., 1927, pp. 192-194.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, CALIFORNIA]

Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide[1]

BY ROBERT L. MILLS AND HAROLD S. JOHNSTON

The rate of the initial reaction between nitrogen pentoxide and nitric oxide is that of the elementary unimolecular decomposition $N_2O_5 \rightarrow NO_2 + NO_3$.

This reaction has been studied over a 10^5-fold range of total pressure, and both the high-pressure first-order limit and the low-pressure second-order limit of the unimolecular reaction have been essentially attained. Foreign gases, notably carbon dioxide, sustain the high value of the first-order constant almost as well as the reactants themselves. Previously proposed mechanisms for this reaction and that for the decomposition of nitrogen pentoxide alone have been confirmed experimentally and extended to account explicitly for the effect of inert gases. Detailed analysis of these two closely similar mechanisms has brought out quantitative relations between the kinetic systems. The anomalies long associated with the low-pressure decomposition of nitrogen pentoxide are explained and removed by this study and these mechanisms.

The gaseous reactants nitrogen pentoxide and nitric oxide were first brought together by Busse and Daniels[2] who described the reaction as being "immeasurably fast." Subsequently the reaction was assumed to be a rapid secondary step in mechanisms proposed for the decomposition of nitrogen pentoxide alone. However, Daniels[3] raised a question regarding the possibility that this supposedly bimolecular reaction might be slow enough at low pressures to limit the rate of decomposition of nitrogen pentoxide. Smith and Daniels[4] studied the kinetics of the reaction at pressures from 0.1 to 20 mm. They found the reaction to be homogeneous, quantitatively given by the relation

$$NO + N_2O_5 = 3NO_2 \qquad (1)$$

and first order with respect to nitrogen pentoxide and essentially zero order with respect to nitric oxide. They proposed the mechanism

$$\begin{aligned} N_2O_5 &\xrightarrow{k_1} NO_2 + NO_3 \text{ (slow)} \\ NO_2 + NO_3 &\xrightarrow{k_2} N_2O_5 \text{ (fast)} \\ NO + NO_3 &\xrightarrow{k_3} 2NO_2 \text{ (fast)} \end{aligned} \qquad (2)$$

From this mechanism the rate expression can be derived

$$R = -\mathrm{d}(N_2O_5)/\mathrm{d}t = k_1(N_2O_5)\,\frac{k_3(NO)}{k_3(NO) + k_2(NO_2)} \qquad (3)$$

where parentheses denote concentration. Thus the initial rate, when the concentration of nitrogen dioxide is about zero, is that for the primary unimolecular dissociation of nitrogen pentoxide. The apparent experimental error reported by Smith and Daniels could be explained in terms of their study having been made in the so-called "falling-off" region of a unimolecular reaction. It was thus of considerable interest to study this reaction over a very large pressure range. The present study reports the rate of this reaction over a 100,000-fold range of total pressure, and the results and mechanism are compared with those for the decomposition of nitrogen pentoxide alone.

Experimental

Materials.—The reactants, nitrogen pentoxide and nitric oxide, were freshly prepared prior to the various kinetic studies. Pure anhydrous nitrogen pentoxide was made by the action of excess ozone on nitrogen dioxide. Nitric oxide was generated by the addition of sulfuric acid to a solution of potassium iodide and sodium nitrite, after which the gas was purified.[5] In addition to the reactants, various other gases were required to complete the studies. These were obtained from commercial tanks and included nitrogen dioxide, which was used for calibrations, and nitrogen, hydrogen, argon, nitrous oxide, carbon dioxide and Freon, which were used at different times to dilute the reactants.

Apparatus.—Smith and Daniels[4] have shown that a visual colorimetric method for following the progress of the nitrogen pentoxide–nitric oxide reaction is ideal for total pressures below about 20 mm. In order to extend kinetic studies of this reaction to higher pressures, it has been necessary to employ the absorptiometric technique for following fast reactions which was developed by Johnston and Yost.[6] The present studies encompass the pressure range 7×10^{-2} to 7×10^{3} mm. To complete the measure-

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[1] Abstracted from a dissertation by Robert L. Mills in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Stanford University, 1950. Shell Fellow 1949.

[2] W. F. Busse and F. Daniels, THIS JOURNAL, **49**, 1257 (1927).

[3] F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938.

[4] J. H. Smith and F. Daniels, THIS JOURNAL, **69**, 1735 (1947).

[5] H. L. Johnston and W. F. Giauque, *ibid.*, **51**, 3194 (1929).

[6] H. S. Johnston and D. M. Yost, *J. Chem. Phys.*, **17**, 386 (1949).

ments three different apparatuses were required. These will be described briefly.

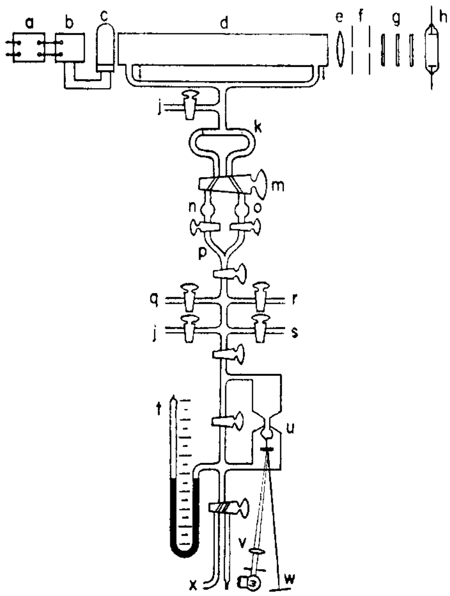

Fig. 1.—The low-pressure apparatus: a, constant voltage transformer; b, electronic voltmeter; c, photoelectric tube; d, quartz reaction cell; e, quartz lens; f, apertures; g, glass filters; h, mercury arc; i, graded quartz–Pyrex seal; j, oil diffusion pump and McLeod gage; k, mixing chamber; m, stopgate; n, N_2O_5 pipet; o, NO pipet; p, y pipet; q, N_2O_5 trap and generator; r, NO trap and generator; s, foreign gases; t, mercury manometer; u, glass-diaphragm gage; v, lens; w, scale; x, pump.

Low-Pressure Range.—The apparatus which was used to study the reaction at total pressures varying from 0.07 to 7 mm. is diagrammed in Fig. 1. The reaction cell was a cylindrical quartz tube 145 cm. in length and 3.3 cm. in diameter with optical quartz windows fused on the two ends. The cell was in a water-bath held at constant temperature. Calibrated pipets could be filled separately with reactants to known pressures measured with a glass-diaphragm gage. When these pipets were emptied into the large evacuated reaction cell by way of the mixing chamber, and when initial pressure equilibrium was established, the resulting low pressures of mixed reactants in the cell could be calculated from a knowledge of the relative volumes and temperatures. The Y pipet was occasionally filled with inert gases which could be emptied with the reactants into the cell.

The optical system consisted of a mercury arc light, glass filters which selected the 436 mμ line of the spectrum, apertures, and a lens properly placed so that the beam through the cell was slightly convergent. The beam having traversed the cell impinged on an RCA 1P28 electron-multiplying photoelectric tube whose output voltage was placed on the terminals of an electronic Model 11C voltmeter. Readings were made visually. The reaction cell and photoelectric circuit were calibrated by placing in the cell quantitative mixtures of air and nitrogen dioxide. The pipets were calibrated by filling them with known pressures of nitrogen dioxide, emptying them into the evacuated reaction cell, and determining absorptiometrically the final pressures of nitrogen dioxide which resulted.

Intermediate-Pressure Range.—Reactions at total pressures ranging from 7 to 700 mm. were followed by means of the apparatus shown in Fig. 2. The reactants were caused to flow from the storage flasks into a vacuum reservoir at a flow rate of 250 cc. per sec. which was maintained by a critical orifice. En route the gases passed through an efficient mixing chamber and a 10.5 cm. reaction cell whose inlet and outlet were valved with a fast-acting double stopcock. The stopcock permitted the mixed reactants to be isolated in the cell whereupon the progress of the reaction could be followed absorptiometrically. This was done by shining a periodically interrupted pencil of monochromatic light through the cell and onto a photoelectric tube. The output of the tube was placed on the Y-deflection plates of a Dumont Model 208 oscilloscope so that the height of the scope beam gave a pulsating measure of the intensity of light having traversed the reacting medium. The pulse rate was set at 20 sec.$^{-1}$. The time consumed in mixing the reactants and isolating the mixture was of the order of a single beam pulse. The pulsating beam was made to give a single sweep of the oscilloscope in the X direction at a speed suitable for separating the pulses and at a time synchronized by an external circuit and switch with the closing of the stopcock. A camera with shutter open recorded the travel of the beam across the oscilloscope face.

It was hoped that pressure equilibrium would be established on the high-pressure side of the critical orifice when the gases flowed. Such, however, proved not to be the case and a slight pressure-drop correction was applied to gage and manometer readings made outside the cell in order to arrive at initial pressures of reactants in the cell.

The temperature control built into the intermediate-pressure apparatus was found to be inadequate. Use of the equilibrium between nitrogen dioxide and nitrogen tetroxide as a thermometer established that room temperature was held in the reaction cell during actual flow. Thus the temperature of the room was adjusted to 27° for all measurements with this apparatus.

The reaction cell was calibrated with air-diluted mixtures of nitrogen dioxide. Complete series of runs at successively lower pressures were made from single fillings of the storage flasks. It was customary to allow the reactants to flush through the cell for 3 to 5 sec. prior to each rate determination. The reagent nitrogen pentoxide was checked periodically to determine the amount of decomposition which had occurred in the storage flask.

High-Pressure Range.—Figure 3 is a schematic representation of the high-pressure apparatus. The electronic circuits and optical system were similar to those described in the preceding paragraphs. The flow system, however, merits additional discussion.

A mixture of nitric oxide and nitrogen at high pressure was made to flow at a prescribed rate through a reaction cell. At a point just above the cell, a jet fed into the stream a small concentration of nitrogen pentoxide which had been picked up by a nitrogen carrier. When steady state conditions obtained, a fast-acting stopgate isolated the cell and initiated an oscillographic recording of the reaction.

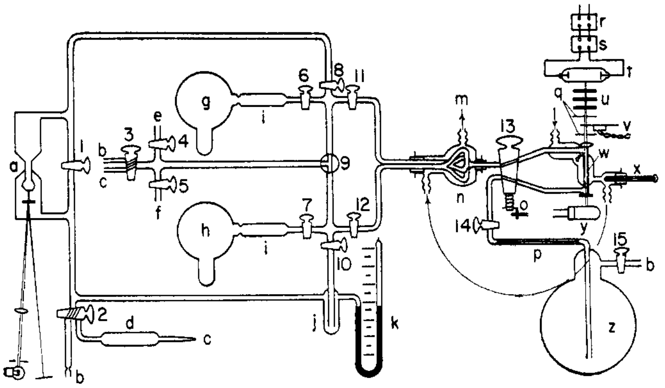

Fig. 2.—The intermediate pressure apparatus: a, glass-diaphragm gage; b, vacuum pumps; c, atmosphere; d, NaOH pellets; e, N_2O_5 and NO_2 source; f, NO and foreign gas source; g, N_2O_5 storage flask; h, NO storage flask; i, P_4O_{10}-coated glass beads; j, Dry ice-acetone trap; k, mercury manometer; m, bath water; n, mixing chamber; o, external synchronization switch; p, critical orifice; q, apertures; r, constant voltage transformer; s, high voltage transformer; t, mercury arc; u, glass filters; v, light chopper; w, reaction cell; x, miniature thermometer; y, photoelectric cell; z, vacuum reservoir.

Two steel nitrogen tanks served as the high-pressure gas reservoirs. One was filled with a mixture of nitric oxide and nitrogen, the other with pure nitrogen. Each tank was fitted with a reducing valve whose low-pressure gage covered the range 0–120 p.s.i. The tanks were linked by a combination of brass compression fittings, brass needle valves and cooper tubing. Adjacent to the reducing valves, the copper tubing was bent into traps which were cooled to Dry Ice–acetone temperature and served to remove moisture and other condensables from the effluent gases. The nitrogen pentoxide trap maintained solid reactant at 0°. This trap, needle valves 5, 6, 7 and 8, the reaction cell, and connecting lines were made of stainless steel. Valves 7 and 8 were joined by a connecting rod so that they operated in tandem and functioned as a stopgate.

The reaction cell was closed at the two ends with $^1/_4$-in. optical Pyrex windows, which were sealed with annular Teflon gaskets. The reaction cell and its inlet were water jacketed.

Exhaust gases from the cell passed through a cold trap where small concentrations of nitrogen dioxide and nitrogen pentoxide were removed. Valve 9 functioned as an adjustable critical orifice. The flow rate through it was indicated by a dibutyl phthalate flowmeter which emptied at atmospheric pressure into a hood.

The gates were used to check constancy of pressure across the reaction cell at various flow rates. For flow rates of 5 liters per min. or less no significant difference in the readings of the gages was detected at the total pressures used.

With the high-pressure apparatus it was necessary to allow each reaction to proceed to completion so that a measure could be made of the final pressure of nitrogen dioxide. Since the initial partial pressure of nitric oxide in the reaction cell was always in excess of the nitrogen pentoxide pressure, it was possible to compute the initial pressure of nitrogen pentoxide from the total nitrogen dioxide formed.

Treatment of Data.—Values of I/I_0, where I is the intensity of the beam which is partially absorbed and I_0 is the intensity of the beam with no absorbing substance present, were determined visually from voltmeter readings and photographically from traces on the oscilloscope. Observed pressures of nitrogen dioxide corresponding to the various values of I/I_0 were taken from appropriate calibration curves. The observed pressures of nitrogen dioxide were first corrected[7] for the partial association of nitrogen dioxide to nitrogen tetroxide (positive correction). Subsequent corrections when of significant magnitude were made in the following order. A correction[8,9] for nitrogen dioxide formed by the reaction of nitric oxide with oxygen (negative correction) was based on pressures of oxygen taken to be one-fourth the pressure of nitrogen dioxide initially present as a decomposition product in the nitrogen pentoxide. A correction[7] was made for all nitrogen dioxide tied up as nitrogen sesquioxide by the equilibrium $NO + NO_2 \rightleftarrows N_2O_3$ (positive correction). Finally a correction was made for the pressure of nitrogen dioxide present initially due to previous decomposition of nitrogen pentoxide. From the initial pressure of nitrogen pentoxide the pressure of nitrogen pentoxide at the various times constituting a run could be calculated from the much-corrected pressures of nitrogen dioxide which increased during the reaction according to the stoichiometric relationship $N_2O_5 + NO = 3NO_2$.

Results

It was found that when the logarithm of the pressure of nitrogen pentoxide was plotted against time, essentially straight lines resulted in all cases, at least for the first one-third or so of reaction which could be followed. Empirical first-order rate constants were obtained by multiplying the slopes of such linear curves by 2.303. A complete listing of empirical rate constants at 27° for all reactions in which only reactants were initially present, and these in about one-to-one proportion, is given in Table I.[10]

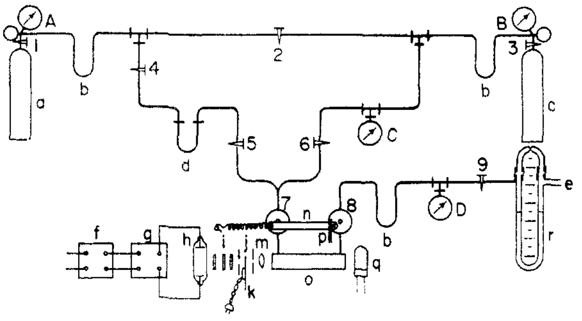

Fig. 3.—The high pressure apparatus: a, high pressure N_2; b, Dry Ice–acetone-trap; c, high pressure N_2 plus NO; d, solid N_2O_5 reservoir; e, hood at atmospheric pressure; f, constant voltage transformer; g, high voltage transformer; h, mercury arc; i, glass filters; j, apertures; k, light chopper; m, lens; n, stopgate; o, reaction cell; p, external synchronization switch; q, photoelectric tube; r, dibutyl phthalate flowmeter.

The rate constants of Table I are in fair agreement with those reported by Smith and Daniels[4] for comparable total pressures at 27°. While for individual reactions the rate appears to be first order with respect to nitrogen pentoxide concentration there is an obvious trend of first-order rate constant with total pressure. In order to extend rate studies to higher pressures and still maintain the one-to-one ratio of reactants, it was necessary to dilute the reactants with inert gases. Rather complete studies were made with carbon dioxide, nitrogen and nitrous oxide as diluent gases. In addition scattered measurements were made at low pressures with hydrogen, argon and Freon. Empirical rate constants computed graphically are presented in Table II.[10]

Here again the rate constants exhibit a noticeable dependence on total pressure. It is significant that the empirical rate constant of a reaction in which only pure reactants were initially present agrees fairly well at some given moderate total pressure with the rate constant of a reaction in which reactants were present at low partial pressures, carbon dioxide accounting for most of the total pressure. Analysis and extrapolation of the data in Table II show that at pressures above one atmosphere carbon dioxide, nitrous oxide and nitrogen are about equally effective in maintaining the rate of reaction. At intermediate and low pressures it appears that carbon dioxide is more efficient in maintaining the rate of reaction than are nitrous oxide and nitrogen whose efficiencies decrease in that order. Experimental error is too great to rank the relative efficiency of the other gases tested, though all of them increased the rate of reaction by their presence.

In order to gain more definite information concerning the dependence of the rate on the concentration of reactants, a series of studies was made in which the ratio of nitric oxide concentration to nitrogen pentoxide concentration was 17, 1.5 and 0.1. Carbon dioxide served as the diluent gas. It was found as before that plots of $\log(N_2O_5)$ against time yielded straight lines. Empirical

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(7) F. H. Verhoek and F. Daniels, THIS JOURNAL, **53**, 1250 (1931).

(8) M. Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918).

(9) E. Breiner, W. Pfeiffer and G. Malet, *J. chim. phys.*, **21**, 25 (1924).

(10) For detailed tables supplementary to this article order Document 2928 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C. remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.60 for photocopies (6 × 8 inches) readable without optical aid.

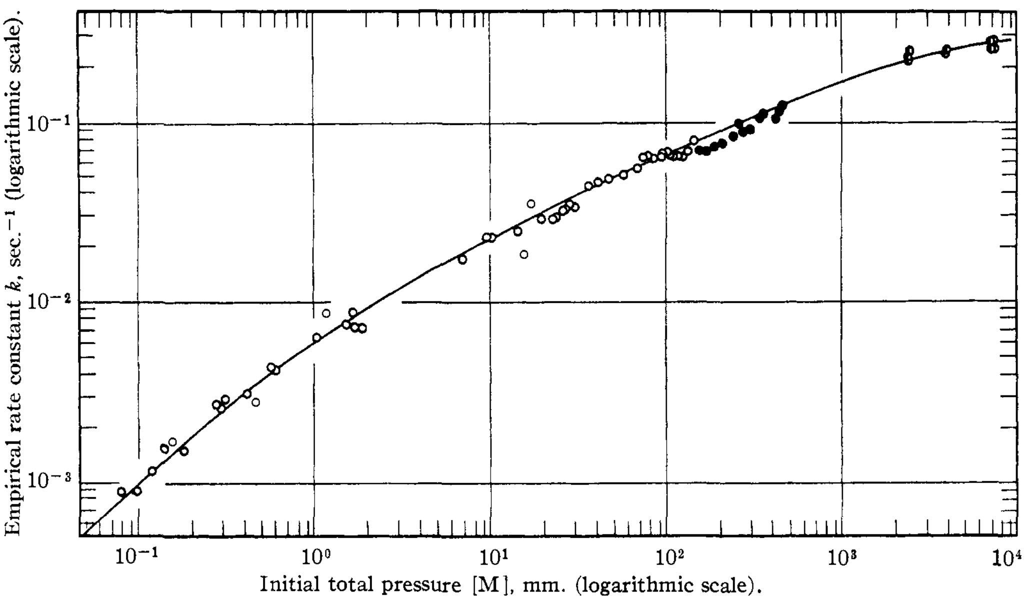

Fig. 4.—Dependence of empirical rate constant on total pressure, 27°: ○, undiluted reactants; ●, CO_2-diluted reactants; ◐, N_2-diluted reactants.

rate constants computed from the slopes are presented in Table III.[10]

Values of the rate constants at given total pressures compare favorably with the values presented in Tables I and II. The essentially zero-order dependence of the rate on nitric oxide concentration is strikingly shown by the last three entries of Table III. For a 150-fold variation in the ratio of nitric oxide concentration to nitrogen pentoxide concentration, no significant change in the empirical rate constant at a total pressure of about 32 mm. was noted.

A definite correlation between empirical rate constant and total pressure has been observed. This is probably best seen by a plot of log k against log (M), where k is the first-order rate constant and (M) denotes total pressure. Experimental data taken from Tables I, II and III are plotted in Fig. 4. At high pressures the curve approaches a limiting value of k and a limiting slope of zero. This behavior is a strong indication that the reaction at high pressure becomes first order with respect to nitrogen pentoxide and zero order with respect to the variable (M). Below a total pressure of about 8 mm. the slope of the curve approaches a limiting value of unity. At low pressures, therefore, the first-order rate constant k assumes first-order dependence on the total pressure.

The high-pressure limit of k is not too well defined by the points of Fig. 4. In order to determine more precisely this limit an additional plot of $1/k$ against $1/(M)$ was made for the nitrogen-diluted reactions of Table II. The plot is shown in Fig. 5. In the region of the high-pressure limit the experimental points of Fig. 5 show a fair degree of linearity. A straight line, fitted to the points by the method of least squares, when extrapolated to infinite pressure yields the value 0.29 sec.$^{-1}$ for k_∞, the high-pressure limit of k, at 27°.

The limiting value of $k/(M)$ at low pressures was obtained from a plot of k against (M). The slope of the straight line through the origin gave 2.3×10^5 cc. mole^{-1} sec.$^{-1}$ as the low-pressure limit at 27°.

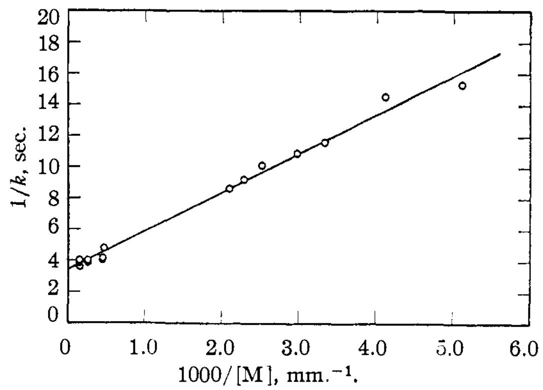

Fig. 5.—Determination of k_∞ from rate studies with N_2-diluted reactants, 27°: least squares fit, intercept = 3.45 sec., k_∞ = 0.290 sec.$^{-1}$.

The rate measurements which were taken at other than 27° include those made in the region of 40° with the low-pressure apparatus and those made in the vicinity of 0° at high pressures. The results are summarized in Table IV.[10]

Following the procedures already outlined the low-pressure limit of $k/(M)$ was found to be 6.4 $\times$ 10^5 cc. mole^{-1} sec.$^{-1}$ at 40°, and the high-pressure limit of k was evaluated as 0.0088 sec.$^{-1}$ at 0°. Substituting these values and those given above for 27° into the Arrhenius equation, the energy of activation at infinite pressure E_∞ was found to be 21 ± 2 kcal. per mole, and the energy of activation at limiting low pressure E_0 was 14.5 ± 2 kcal. per mole. At a total pressure of about 6 mm. values of k were determined at 4°, 27° and 40°. When these data are plotted log k against $1/2.3RT$, the slope of the straight line gives as the energy of activation 16.0 kcal. per mole, which is in good agreement with the value

15.7 kcal. per mole reported by Smith and Daniels[4] for a similar total pressure.

Smith and Daniels reported moisture to have an erratic catalytic effect on this reaction. In spite of extreme care taken to exclude moisture, the first two sets of runs made in the intermediate-pressure apparatus were anomalously high and were rejected. More stringent precautions to exclude water from the system and the "aging" of reaction cell and connecting glassware by flushing with small amounts of nitrogen pentoxide prior to each run resulted in measurements which were reproducible to ±10%.

Discussion

Decomposition of Nitrogen Pentoxide in Presence of Nitric Oxide.—This study substantiated the mechanism proposed by Smith and Daniels[4] which is written in the following enlarged form taking explicit recognition of the effect of inert gas M and the fact that the rate of decomposition of a given molecule depends on its degree of excitation.

$$\begin{aligned}
&N_2O_5 + M \xrightarrow{a_i} N_2O_5{}^*{}_i + M\\
&N_2O_5{}^*{}_i + M \xrightarrow{b_i} N_2O_5 + M\\
&N_2O_5{}^*{}_i \xrightarrow{c_i} NO_2 + NO_3 \qquad\qquad (4)\\
&NO_2 + NO_3 \xrightarrow{d_i} N_2O_5{}^*{}_i\\
&NO + NO_3 \xrightarrow{f} 2NO_2
\end{aligned}$$

Here i represents the energy levels of the nitrogen pentoxide molecule above the critical energy and the asterisk indicates excitation. Using the steady state assumption that over short intervals of time excited molecules in the state i disappear in some way at the same rate that they are formed, and also that nitrogen trioxide NO_3 is a transient intermediate, there are obtained

$$\mathrm{d}(N_2O_5{}^*{}_i)/\mathrm{d}t = a_i(N_2O_5)(M) - b_i(N_2O_5{}^*{}_i)(M) - c_i(N_2O_5{}^*{}_i) + d_i(NO_2)(NO_3) = 0 \quad (5)$$

$$\mathrm{d}(NO_3)/\mathrm{d}t = \sum_i c_i(N_2O_5{}^*{}_i) - \sum_i d_i(NO_2)(NO_3) - f(NO)(NO_3) = 0 \quad (6)$$

Solving these relations for the steady-state values of (NO_3) and $(N_2O_5{}^*{}_i)$, the macroscopic rate of reaction is

$$R = -\mathrm{d}(N_2O_5)/\mathrm{d}t = \frac{(M)(N_2O_5)\sum\limits_i \dfrac{c_ia_i}{(b_i(M) + c_i)}}{1 + \dfrac{(M)(NO_2)}{f(NO)}\sum\limits_i \dfrac{d_ib_i}{(b_i(M) + c_i)}} \quad (7)$$

For the initial reaction when $(NO_2) \cong 0$ the rate becomes simply that of an elementary unimolecular reaction

$$R = (M)(N_2O_5)\sum_i \frac{c_ia_i}{(b_i(M) + c_i)} \quad (8)$$

Both in this study and in that of Smith and Daniels the initial rate was found to be first order with respect to the nitrogen pentoxide concentration and independent of the nitric oxide concentration except insofar as nitric oxide contributed to the concentration of M.

The low-pressure limit for a unimolecular reaction is that for which $b_i(M) \ll c_i$ for all i. In this case the rate expression becomes

$$R_0 = \frac{(M)(N_2O_5)\sum\limits_i a_i}{1 + [(M)(NO_2)/f(NO)]\sum\limits_i d_ib_i/c_i} \quad (9)$$

$$= (M)(N_2O_5)\sum_i a_i \text{ for the initial rate}$$

The low-pressure limit of the initial reaction is the second-order rate of activation, and the rate constant is the sum of the rate constants for the individual excited states of the molecule. The low-pressure limit indicated by this mechanism can be seen as the 45° slope of Fig. 4, and as explained above it was evaluated at two temperatures. Thus in terms of the mechanism $\sum_i a_i$ has the value 2.3×10^5 cc. mole^{-1} sec.$^{-1}$ at 27° and 6.4×10^5 cc. mole.$^{-1}$ sec.$^{-1}$ at 40°.

The high-pressure limit where $b_i(M) \gg c_i$ for all i is

$$R_\infty = \frac{(N_2O_5)\sum\limits_i c_ia_i/b_i}{1 + [(NO_2)/f(NO)]\sum\limits_i d_i} \quad (10)$$

$$= (N_2O_5)\sum_i c_ia_i/b_i \text{ for the initial rate} \quad (11)$$

The high-pressure limit indicated by this mechanism was closely approached in this study as can be seen by the flat right-hand side of the curve through the points in Fig. 4, and its evaluation by extrapolation is given in Fig. 5. In terms of the mechanism, $\sum_i c_ia_i/b_i$ has the value 0.29 sec.$^{-1}$ at 27° and 0.0088 sec.$^{-1}$ at 0°. Furthermore, an upper limit can be placed on $\sum_i d_i/f$. In experiments where the concentration of nitrogen dioxide was as great as that of nitric oxide, the rate was found to be independent of both which implies that $\sum_i d_i/f \ll 1$.

As can be seen from Fig. 4, most of the experimental points of this study were taken in the region between the low-pressure second-order limit and the high-pressure first-order limit. Even for the initial rate the mechanism is complicated in this region, and to fit the curve in Fig. 4 one must know the detailed values of a_i, b_i and c_i for all energy states i. It can be argued,[11] however, that b is essentially constant. In this case the pressure range between high-pressure and low-pressure limits gives some measure of the range of values of c_i over the energy states which significantly contribute to the rate of reaction. At the high-pressure limit $b(M) \gg c_{\max.}$ and at the low-pressure limit $b(M) \ll c_{\min}$. For definiteness assume that in Fig. 4 $b(M)$ at the high-pressure side is one order of magnitude larger than the maximum c, and one order of magnitude smaller than the minimum c on the low-pressure side. Since (M) itself had to be varied over a factor of 10^5 to yield these two limits, the maximum value of c must be at least 10^3 times as big as the minimum value of c.

[11] L. S. Kassel "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Company, N. Y., 1932, p. 99.

The energy of activation of the low-pressure limit was 14.5 ± 2 kcal. per mole, and that of the high-pressure limit was 21 ± 2 kcal. per mole. The fact that the energy of activation at high pressures exceeds the energy of activation at low pressures indicates that the specific rate constants c_i increase with the energy of the molecule.

Decomposition of N_2O_5 Alone.—The mechanism for the decomposition of pure nitrogen pentoxide appears to be given very well by Ogg,[12] whose mechanism is reproduced below with, however, explicit recognition being given to the effect of foreign gases and to specific rate constants for the individual excited states of the molecule.

$$\begin{aligned}
&N_2O_5 + M \xrightarrow{a_i} N_2O_5{}^*{}_i + M \\
&N_2O_5{}^*{}_i + M \xrightarrow{b_i} N_2O_5 + M \\
&N_2O_5{}^*{}_i \xrightarrow{c_i} NO_2 + NO_3 \qquad (12) \\
&NO_2 + NO_3 \xrightarrow{d_i} N_2O_5{}^*{}_i \\
&NO_2 + NO_3 \xrightarrow{e} NO + O_2 + NO_2 \\
&NO + NO_3 \xrightarrow{f} 2NO_2
\end{aligned}$$

It is seen that this mechanism is identical with that for the decomposition of nitrogen pentoxide in the presence of nitric oxide except that here the steady-state concentration of nitric oxide is so low that another reaction e must be considered also.

Using the steady-state conditions to evaluate (NO), (NO_3) and ($N_2O_5{}^*{}_i$), there is found the general expression for the rate of reaction

$$R = -(^1/_2)\mathrm{d}(N_2O_5)/\mathrm{d}t = \frac{(^1/_2)(M)(N_2O_5)\sum\limits_i \dfrac{c_ia_i}{(b_i(M)+c_i)}}{1 + [(M)/2e]\sum\limits_i \dfrac{d_ib_i}{(b_i(M)+c_i)}} \qquad (13)$$

This expression is similar to that for nitric oxide plus nitrogen pentoxide, Equation 7, with two important differences: (1) the concentration of nitrogen dioxide has cancelled out completely so that the initial rate is no simpler than any other condition; and (2) the summation in the denominator is divided by f in the first case and by $2e$ for this condition, and later it is seen that f is bigger than $2e$ by a factor of 10^5 or more.

The low-pressure limit of a unimolecular reaction occurs when $b_i(M) \ll c_i$ for all i. Equation 13 then gives

$$R_0 = \frac{(^1/_2)(M)(N_2O_5)\sum\limits_i a_i}{1 + [(M)/2e]\sum\limits_i d_ib_i/c_i} \qquad (14)$$

To get the second-order limit there must be added the additional condition that the second term in the denominator is small compared to one. Since $\sum\limits_i d_ib_i/2c_ie$ is a large number, this restriction on the smallness of (M) is much more severe than the one $b_i(M) \ll c_i$ for all i. For this extremely low pressure

$$R_0 = (^1/_2)(M)(N_2O_5)\sum_i a_i \qquad (15)$$

which is identical to the low-pressure limit for the reaction of nitric oxide with nitrogen pentoxide when the stoichiometry of the two reactions is considered. From the data of Hodges and Linhorst[13] on the extremely low-pressure decomposition of nitrogen pentoxide there is found for $k/(M)$ at pressures below 0.004 mm. the average value of 3.2×10^5 cc. mole^{-1} sec.$^{-1}$ at 27° which is in satisfactory agreement with the value 2.3×10^5 cc. mole^{-1} sec.$^{-1}$ reported here. The observed agreement of these two limiting rates is evidence in favor of the mechanisms.

Consider the pressure range from 0.1 to 10 mm. where $b_i(M) \ll c_i$ for all i but $(M)\sum\limits_i d_ib_i/2ec_i \gg 1$. The rate is

$$R = \frac{(N_2O_5)e\sum\limits_i a_i}{\sum\limits_i d_ib_i/c_i} \qquad (16)$$

The rate is first order and independent of foreign gas even though conditions are below the low-pressure limit of the primary unimolecular reaction. The rapid decrease in first-order rate constant finally observed is an effect of the complex mechanism and completely outside the domain of unimolecular reaction-rate theory.

At the high-pressure limit where $b_i(M) \gg c_i$ for all i the rate is

$$R_\infty = \frac{(^1/_2)(N_2O_5)\sum\limits_i c_ia_i/b_i}{1 + (^1/_{2e})\sum\limits_i d_i} \qquad (17)$$

If the high-pressure limit of the initial rate of reaction between nitric oxide and nitrogen pentoxide (see Equation 11) is divided by the high-pressure limit for the decomposition of nitrogen pentoxide alone, the ratio is $2 + \sum\limits_i d_i/e$. Using the original data of Daniels and Johnston[14] for nitrogen pentoxide alone at 27°, this ratio has the numerical value 6500. Thus the additive 2 may be dropped. When d is written in place of $\sum\limits_i d_i$ the relations may be expressed as $f \gg d = 6500e$.

The high-pressure limit for the decomposition of nitrogen pentoxide

$$R_\infty = (N_2O_5)(e\sum_i c_ia_i/b_i)/\sum_i d_i \qquad (18)$$

Although this true high-pressure limit looks similar to the spurious limit shown by Equation 16, mathematically they are quite different. The fact that no trend with high pressure has been noticed for the first-order rate constant for nitrogen pentoxide decomposition indicates that for this molecule

$$\frac{\sum\limits_i a_i}{\sum\limits_i b_id_i/c_i} \approx \frac{\sum\limits_i a_ic_i/b_i}{\sum\limits_i d_i} \qquad (19)$$

Writing k as the first-order rate constant, and substituting the approximate relation above into Equation 14, the rate constant for the decomposition

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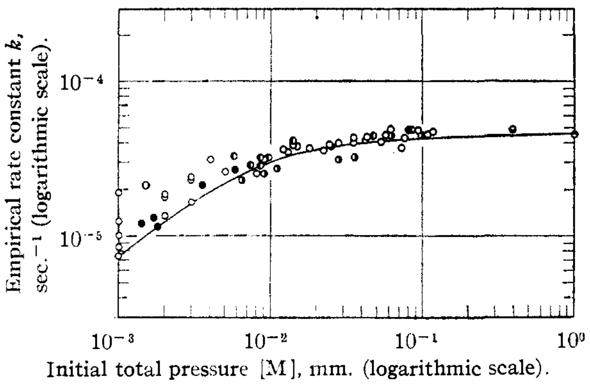

Fig. 6.—Comparison of experimental with computed rate constants; decomposition of pure N_2O_5, 27°, curve given by Equation 21: ○, Hodges and Linhorst; ●, Linhorst and Hodges; ◐, Ramsperger and Tolman; ◑, Schumaker and Sprenger; ◓, Daniels and Johnston; ◒, Mills and Johnston.

of nitrogen pentoxide at any concentration of gases can be written

$$k = \frac{(M)\sum\limits_i a_i}{2 + (M)\left[\sum\limits_i d_i/e\right]\left[\sum\limits_i a_i/\left(\sum\limits_i c_i a_i/b_i\right)\right]} \qquad (20)$$

As has been previously shown in the text, $\sum\limits_i a_i = 2.3 \times 10^5$, $\sum\limits_i d_i/e = 6.5 \times 10^3$ and $\sum\limits_i c_i a_i/b_i = 0.29$ sec.$^{-1}$ When (M) is expressed in units of moles per cc., Equation 20 becomes

$$k = \frac{(M)\ 2.3 \times 10^5}{2 + (M)\ 5.2 \times 10^9}\ \text{sec.}^{-1}\ \text{at}\ 27° \qquad (21)$$

The experimental points from all investigators who used large reaction vessels at low pressures are plotted in Fig. 6. The curve is that given by Equation 21. The experimental points show great scatter, and it has been shown by various authors[15] that heterogeneous reactions are important at very low pressures. The indicated curve was derived only from data for the reaction of nitric oxide with nitrogen pentoxide and from high-pressure data for the nitrogen pentoxide decomposition, yet it fits the low-pressure behavior of nitrogen pentoxide as well as could be desired. All of the individual rate constants that went into the complex expression, Equation 20, are of normal magnitudes. The low-pressure decomposition of nitrogen pentoxide is no longer an anomaly of chemical kinetics.

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Studies of the Fischer–Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis

By Robert B. Anderson, L. J. E. Hofer, Ernst M. Cohn and Bernard Seligman

Phase changes in a reduced fused-iron catalyst have been studied during the Fischer–Tropsch synthesis with $1H_2$-to-1CO gas at 7.8 atmospheres. In the first few days of the synthesis, α-iron was converted to Hägg carbide (Fe_2C). The iron as Hägg carbide increased to a maximum of 29% at 200 hours of synthesis, and then decreased slowly throughout the remainder of the test. Magnetite was formed at a slower rate than Hägg carbide, apparently chiefly at the expense of the α-iron phase. The magnetite phase increased through the experiment.

The study of phase changes in iron catalysts during the Fischer–Tropsch synthesis is difficult because there are no satisfactory chemical methods for differentiating between carbon as carbide, free carbon or other carbonaceous material. In addition to cementite, Fe_3C, the existence of two low-temperature carbides of iron, h.c.p. and Hägg, with composition approximating Fe_2C, has recently been established by X-ray diffraction[1,2,3] and thermomagnetic studies.[3,4] The presence of one or both of these Fe_2C carbides in used iron Fischer–Tropsch catalysts has been reported.[2,4,5] Recently, Hofer and Cohn[6] described a method of quantitative analysis of mixtures of Hägg carbide, α-iron and magnetite by a combination of thermomagnetic, X-ray diffraction and gravimetric analyses. The present paper gives the results of such analyses of samples of a fused-iron catalyst removed at convenient intervals during a 100-day period of testing. Changes in catalyst composition are compared with observed changes in activity.

Experimental

The apparatus and procedure for reducing and testing the catalyst have been described previously[7,8,9]; 155 cc. of 6- to 8-mesh fused catalyst D3001[9] was used in this study. The catalyst composition was: Total iron, 67.4%; MgO, 4.61%; K_2O_3, 0.57%; SiO_2, 0.71%; and Cr_2O_3, 0.65%. The catalyst was reduced (97.7%) in dry hydrogen at a space velocity[10] of 2,500 at 450° for 40 hours and tested in the Fischer–Tropsch synthesis with $1H_2$ to 1CO gas at 7.8 atmospheres. Testing was continuous, except for brief interruptions when the products were removed or when the catalyst was sampled.

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