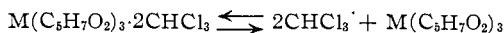


symmetry would be formed. The X-ray powder method used here is not sufficiently powerful to provide the final answer to the question of chloroform attachment, but there is an indication that a lattice expansion has occurred, causing the appearance of weak lines at 10.4–10.6 Å. in at least two of the patterns. Unfortunately, the symmetry of the crystals is too low to allow unequivocal indexing of more than a few lines.

It is not probable that a hydrogen bond is formed between the chlorine of chloroform and the methylene hydrogen of the acetylacetonate since carbon tetrachloride shows no tendency to form similar solvates. If, as seems likely, the positions assumed by the chloroform molecules are those shown in Fig. 2c, the hydrogen would be linked to three oxygen atoms, and the result could be called a "trifurcated hydrogen bond." There are objections⁸ to calling such a conformation a hydrogen bond since the bonds are not linear. Possibly there is a hydrogen bond formed to only one of the three oxygens at random throughout the structure, or perhaps there is a simple electrostatic attraction between the chloroform dipole and the oxygens.

An attempt was made to find a value for the energy of bond formation in these compounds. A plot of the vapor pressure as a function of temperature is shown in Fig. 3. From the slope of the lines and the van't Hoff equation, a value of ΔH^0 of approximately 13 kcal./mole was calculated for the reaction



where M is either iron, aluminum or chromium. This value is equivalent to an energy of approximately 6 kcal. for each chloroform-metal bond. Since the heat of decomposition of the compound (per chloroform-chelate bond) is no greater than the heat of vaporization of chloroform, the bonding must be due largely to van der Waals forces. If a hydrogen bond exists it must be a very weak one.

(8) J. Donohue, *J. Phys. Chem.*, **56**, 502 (1952).

The tetrahedral copper, zinc and cadmium acetylacetonates do not form crystalline solvates with chloroform. This seems to indicate that the spacing of the oxygens is of major significance in the

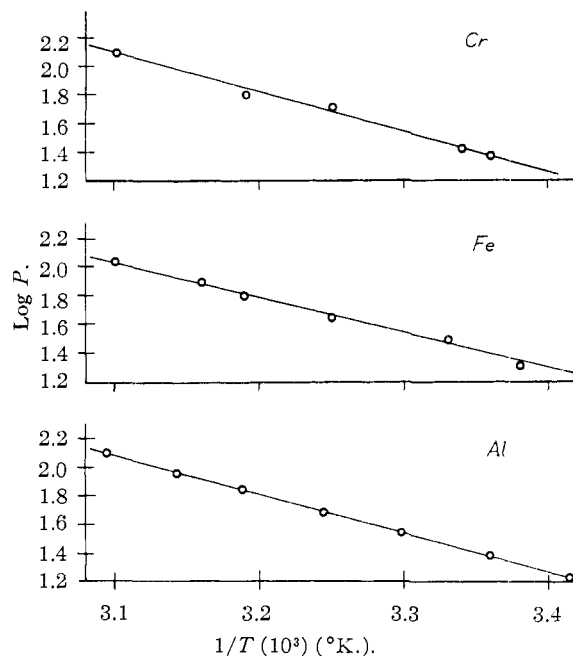


Fig. 3.—Vapor pressure of chloroformates as a function of $(1/T)$.

formation of solvates of this type. It also should be noted that in general the solubility of the trivalent acetylacetonates in chloroform is much higher than that of the divalent acetylacetonates.

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LEXINGTON, KENTUCKY

[CONTRIBUTION NO. 2237 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Shock Waves in Chemical Kinetics: The Decomposition of N_2O_5 at High Temperatures¹

BY GARRY SCHOTT AND NORMAN DAVIDSON

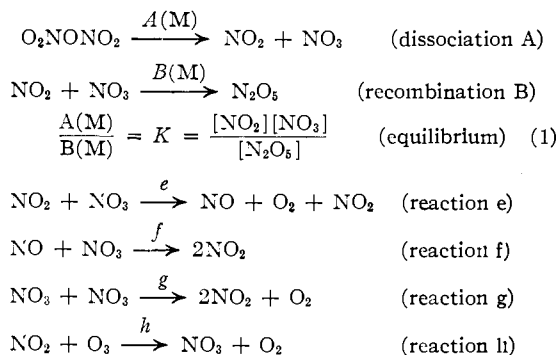
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The shock pyrolysis of N_2O_5 in the presence of excess argon has been studied, thus providing information about the properties and reactions of the nitrate free radical, NO_3 . The important reactions are: $N_2O_5 \rightleftharpoons NO_2 + NO_3$ (A and B), $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$ (e), $NO + NO_3 \rightarrow 2NO_2$ (f), $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$ (g). In the concentration and temperature range studied ($[argon] \sim 0.0076$ mole/l., 450–550°K.), the dissociation reaction is a unimolecular reaction close to its second order low pressure limit, $-d[N_2O_5]/dt = A'[A][N_2O_5]$, with $A' = 10^{13.7} \exp(-16,500 \pm 700/RT)$ (mole/l.)⁻¹ sec.⁻¹. The equilibrium constant of the dissociation reaction is given by $K_e = 10^{4.97} \exp(-20,100 \pm 1100/RT)$ (mole/l.). The rate constants of e and g are given (550–1100°K.) by $e = 2.3 \times 10^8 \exp(-4400 \pm 700/RT)$ (mole/l.)⁻¹ sec.⁻¹ and $g = 2.6 \times 10^9 \exp(-7700 \pm 1000/RT)$ (mole/l.)⁻¹ sec.⁻¹. On the basis of this and other data, the following thermodynamic quantities are calculated: $N_2O_5 = NO_2 + NO_3$, $\Delta H_{300^\circ K.}^0 = 21,600$ cal./mole, $\Delta S_{300^\circ K.}^0 = 33.6$ e.u., $\Delta H_{f,300}^0(NO_3) = 17,100$ (± 1000) cal./mole, $S_{300}^0(NO_3) = 60 \pm 2$ e.u. The kinetics of various reactions involving NO_3 are reviewed and recommended rate constants and activation energies at 300°K. computed. In general, the present investigation, where NO_3 was a major constituent whose concentration was directly measured, confirms the results of previous investigations in which NO_3 was present at low, undetermined concentrations as a reactive intermediate.

(1) Research carried out under contract Nonr-220(01) between the Office of Naval Research and the California Institute of Technology. This paper was presented to the 130th National Meeting, American

Chemical Society, Atlantic City, N. J., September, 1956. A more detailed account is contained in the Ph.D. thesis of Garry L. Schott, California Institute of Technology, 1956.

Many of the reactions of nitrogen pentoxide depend upon the dissociation of N_2O_5 into the molecular radicals NO_2 and NO_3 and the subsequent reactions that result in the reduction of NO_3 .²⁻⁵ The mechanisms of several reactions involving N_2O_5 and lower oxides of nitrogen near room temperature have been formulated in terms of the reactions³



The reactions above are written as elementary processes characterized by the rate constants indicated. The dependence of the dissociation and recombination rate constants on the nature and concentration of inert gas molecules, M, is implied. The notation is that used in reference 3.

The path of the NO , N_2O_5 reaction consists of steps A and f, the former being rate determining.⁶ The concentration and temperature dependences of the unimolecular dissociation process A have been extensively studied.⁷ Recent experiments in the presence of excess NO_2 have demonstrated inhibition by the recombination step, B, and have yielded values of the product fK .⁸ The well known first-order decomposition of N_2O_5 consists of reactions A, B and e²; the over-all rate constant is $2eK$, with activation energy, 24.7 kcal.⁹ The N_2O_5 catalyzed decomposition of O_3 involves reactions A, B, g and h.¹⁰ In this system, the steady-state concentration of NO_3 is large enough so that its absorption spectrum can be recorded.¹¹ Enough relationships and data are available that the activation energy of reaction g and the dissociation energy of N_2O_5 can be deduced.³ However, near room temperature, K is very small and it has not been possible to devise experiments in which the value of K (or of the NO_3 concentration) can be separated from the rates of reactions e and g.

The research described here is an investigation of the decomposition of N_2O_5 between 450 and 1200°K. The rate of dissociation of N_2O_5 and the dissociation equilibrium have been observed directly between 450 and 550°K., and the decom-

position of NO_3 has been studied between 600 and 1200°K. under conditions where N_2O_5 is completely dissociated. The measurements have been made by the shock wave-spectrophotometric method developed recently in this Laboratory for the direct examination of rapid gaseous reactions.¹²⁻¹⁴ Particular use has been made of the absorption spectra of the blue intermediate NO_3 and the brown product NO_2 .

The results that have been obtained agree very well with the predictions made by extrapolation of the room temperature results. They add to the information derivable from room temperature experiments by providing directly measured values of $A(M)$, K (and hence $B(M)$), e and g and independent determinations of the temperature coefficients of these quantities. Perhaps the most significant contribution of this investigation is the preparation and direct study of known concentrations of the intermediate NO_3 whose importance in several reactions has been deduced kinetically but whose concentration and absolute reaction rates have not previously been measurable.

Experimental Method

The equipment and procedures used in previous applications of the shock wave method have been described elsewhere.^{12,13} The adaptation of the method to the study of N_2O_5 decomposition is considered here.

Shock waves in homogeneous mixtures of N_2O_5 and argon produced the reaction temperatures. The shock wave behavior was essentially determined by the carrier gas, argon, whose properties are simple and well known. Computation of the temperature and density of the reaction mixture from the measured velocity of the shock wave allows for the presence of the reacting components.¹³ The changes in temperature and density with reaction are kept small by the buffering action of the carrier gas, so that the treatment of rate data is simplified. The dissociation of N_2O_5 is kinetically similar to the dissociation of N_2O_4 . The important differences, aside from the difference in the energy and the temperature range of dissociation, are: (1), two differently colored dissociation products are formed; and (2), one of these, NO_3 , is unstable and decomposes further. Two spectrophotometric records in each experiment were used to determine NO_2 and NO_3 simultaneously. N_2O_5 pressures near 10^{-3} atm. in the unshocked gas provided concentrations of NO_2 and NO_3 that were convenient for spectrophotometric measurement. The argon pressures were typically 10^{-1} atm. Under these concentration conditions, the bimolecular decomposition of NO_3 by reactions e and g was effectively separated in time from the dissociation of N_2O_5 .

Instrumentation.—The shock wave experiments were carried out with the 6 in. diameter tube¹³ and the optical slit system¹⁴ described in the iodine work. Triggering of the oscilloscopes and the intervalometer employed schlieren optics, since the initial mixture of N_2O_5 and argon was colorless.

An Osram HBO-200 high pressure d.c. mercury arc provided an intense monochromatic source of light for one of the spectrophotometric records in each experiment. The light output of this lamp was satisfactorily free of 120-cycle ripple when it was operated from a 150 volt generator stabilized by a choke input filter with $L = 1$ henry and $C = 1.5 \times 10^3 \mu f$. The prominent lines in the mercury spectrum were isolated with the appropriate Bausch and Lomb interference filter and a Corning sharp cut filter as follows: 366 $m\mu$, no. 5562; 405 $m\mu$ and 436 $m\mu$, no. 3060; 546 $m\mu$, no. 3384. RCA 931-A photomultipliers were used to detect this radiation.

- (2) R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 337 (1947); **18**, 572 (1950).
- (3) H. S. Johnston, *THIS JOURNAL*, **73**, 4542 (1951).
- (4) H. S. Johnston and F. Leighton, *ibid.*, **75**, 3612 (1953).
- (5) J. C. D. Brand, *ibid.*, **77**, 2703 (1955).
- (6) J. H. Smith and F. Daniels, *ibid.*, **69**, 1735 (1947).
- (7) (a) D. J. Wilson and H. S. Johnston, *ibid.*, **75**, 5763 (1953), is paper IV of a series. The earlier papers are: (b) H. S. Johnston, *ibid.*, **75**, 1567 (1953); (c) H. S. Johnston and R. L. Perrine, *ibid.*, **73**, 4782 (1951); (d) R. L. Mills and H. S. Johnston, *ibid.*, **73**, 938 (1951).
- (8) I. C. Hisatsune, B. Crawford and R. A. Ogg, *ibid.*, **79**, 4648 (1957).
- (9) F. Daniels and E. H. Johnston, *ibid.*, **43**, 53 (1921).
- (10) G. Sprenger, *Z. Elektrochem.*, **37**, 674 (1931).
- (11) E. J. Jones and O. R. Wulf, *J. Chem. Phys.*, **5**, 873 (1937).

- (12) T. Carrington and N. Davidson, *J. Phys. Chem.*, **57**, 418 (1953).
- (13) D. Britton, N. Davidson and G. Schott, *Disc. Faraday Soc.*, **17**, 58 (1954).
- (14) D. Britton, N. Davidson, W. Gehman and G. Schott, *J. Chem. Phys.*, **25**, 810 (1956).

For the spectrophotometric measurements with red light, a 500 watt tungsten projection bulb, operated at 120 volts d.c., served as source. An RCA 6217 photomultiplier was the detector. This photomultiplier tube has the S-10 spectral response, with maximum sensitivity at 540 $m\mu$ and 34% of that sensitivity at 650 $m\mu$. In most of the experiments, a wave length band of triangular profile and 3.6 $m\mu$ half width centered at 652 $m\mu$ was isolated by means of a two prism glass spectrograph¹⁵ with an exit slit mounted in the focal plane. The dispersion and the position of the spectrum in the focal plane were determined from a plate of the mercury arc emission. The entrance slit was adjusted to subtend the same angle on the prism as the exit slit, thus giving the optical band its triangular profile.¹⁶ This monochromator was about three times as fast as a Bausch and Lomb 500 mm. reflection grating instrument in this application.

Calibration of the photoelectric records is not a trivial matter for anyone executing such experiments; our method is described in detail elsewhere.¹

Reagents.— $\text{NO}_2\text{-N}_2\text{O}_4$ was condensed from a cylinder (Matheson) into a trap at -10° . Oxygen (Linde), purified by passage through a U-tube at -80° packed with glass wool, was bubbled through the liquid N_2O_4 . The effluent oxygen stream, saturated at -10° with nitrogen dioxide vapor, was directed through a 35-ml. column of P_2O_5 coated glass beads and through a storage trap on the vacuum line. After the liquid N_2O_4 had become pale yellow, solid N_2O_4 was condensed from the stream by application of Dry Ice to the storage trap. When the liquid was exhausted to the point that its composition was formally 95% N_2O_4 and 5% HNO_3 , as indicated by the appearance of a denser nitric acid rich phase,¹⁷ the flow was stopped and the oxygen was pumped from the solid preparation. In one instance the product was surrounded by an ice-salt bath in a Dewar flask at about -15° and allowed to stand 5 hr. On examination, the N_2O_4 was partially melted and the temperature of the bath was -11° . The melting point is reported as -11.20° .¹⁸

N_2O_5 was prepared from N_2O_4 by oxidation with ozone in a flowing system in the glassware described above. The oxygen stream was divided after passage through the Dry Ice-glass wool trap and the major portion was passed through a P_2O_5 column into an ozonizer. The effluent stream, which was about 5% ozone, was fed into the $\text{NO}_2\text{-N}_2\text{O}_4$ stream immediately after the latter had passed its P_2O_5 chamber. The flow rates were adjusted so that the stream was colorless after the junction. (The glass was warm to the touch for a few cm. after the junction.) The $\text{O}_3\text{-N}_2\text{O}_5\text{-O}_2$ mixture flowed through about a foot of tubing, which could be examined lengthwise for color, before it reached the collecting trap at -80° . After each preparation, the nitronium nitrate crystals were warmed to 0° and the vapor was examined for color.

Two points of caution should be made about this preparation. First, in using the batch process described by Nightingale, *et al.*,¹⁹ one should NOT concentrate the ozone and then admit it to a bulb containing N_2O_4 or N_2O_5 for, in the absence of diluent gas, the mixture may ignite and destroy the preparation and perhaps the apparatus. The behavior of these decomposition flames is known.²⁰ Spontaneous ignition is probably caused by the exothermic oxidation of N_2O_4 , and the flame propagates through the already oxidized mixture of N_2O_5 and O_3 . Second, if the flow method described above is used to prepare large quantities of N_2O_5 in a small vessel, care should be taken to avoid condensing too thick a layer of N_2O_5 on the inside of the trap. Solid N_2O_5 has a significantly higher coefficient of thermal expansion than Pyrex and is a hard ionic solid even at room temperature, so that it is not possible to warm the preparation without cracking the container.

Argon (Linde, 99.92% pure, principal impurity N_2) was passed through a Dry Ice-glass wool trap and admitted to the vacuum line through a P_2O_5 column.

$\text{N}_2\text{O}_5\text{-argon}$ mixtures were prepared individually for each shock wave experiment because of the instability of N_2O_5 vapor. The mixtures were made up in a five-liter flask immersed in an ice-water-bath. The flask was evacuated to a pressure of 10^{-4} mm. of Hg or less. The N_2O_5 storage trap was warmed to 0° and a charge of vapor was withdrawn. The pressure of N_2O_5 in the mixing bulb was measured with a dibutyl phthalate manometer. The balance of the mixture was made up with argon, and the total pressure, which was usually near one atmosphere, was measured on a mercury manometer. A cold finger in the mixing bulb was then filled with an ice and salt mixture at about -15° to promote convective stirring. The reagents were allowed 2 hr. to mix in this fashion. The $1/e$ time for the first-order decomposition of N_2O_5 at 0° is 350 hr.,²¹ so that the decomposition during the mixing period was always less than 1%. The shock tube was routinely evacuated to 2×10^{-3} mm. of Hg or less. In the later experiments it was purged of water by a five minute exposure to a few millimeters pressure of N_2O_5 vapor and re-evacuated before the experimental mixture was admitted. In order to avoid a pressure measurement after the charge was admitted to the warm shock tube, the expansion ratio involved in admitting gas from the mixing bulb into the shock tube and connecting manifold was determined accurately in separate experiments. When the stopcock was opened admitting the charge to the shock tube, one minute was allowed for the attainment of thermal equilibrium, and then the shock tube was isolated and the experiment was initiated as soon thereafter as possible. Thus the N_2O_5 was at room temperature for no more than two minutes before the gas was shocked. Eighty-five seconds at 25° is equivalent to an hour at 0° , from the standpoint of N_2O_5 decomposition.²¹ Thus the total decomposition in the handling of a charge of N_2O_5 was not more than 1%.

$\text{NO}_2\text{-N}_2\text{O}_4\text{-N}_2\text{O}_5\text{-Argon}$ Mixtures.—In those experiments in which extra NO_2 was included in the charge of N_2O_5 , the latter was admitted to the mixing bulb at 0° first. $\text{NO}_2\text{-N}_2\text{O}_4$ was admitted second, the total pressure was again measured on the dibutyl phthalate manometer and finally argon was added. Calculation of the formal mole fraction of NO_2 in these mixtures was carried out using the value $K = p^2_{\text{NO}_2} p^{-1}_{\text{N}_2\text{O}_4} = 0.016$ atm. at 0° . This value is an average of extrapolated data of Verhoek and Daniels and Bodensteln and Boës and measurements at 0° by Wourtsel.²²

Results

Extinction Coefficients of NO_2 .—Analysis of the final decomposition products of N_2O_5 and the kinetic interpretation both depend on knowledge of the extinction coefficients of NO_2 for selected wave lengths over the entire temperature range of the experiments. Therefore a number of shock wave experiments have been done in which mixtures of NO_2 and argon were compressed and heated to temperatures between 500 and 1000°K . The extinction coefficients of NO_2 at the shock wave temperatures have been calculated from the initial conditions and the measurements of light transmission after the passage of the shock wave.

Let i_0 represent the intensity of the incident light beam, i_t the light that is transmitted to the photomultiplier through the NO_2 sample before it is shocked and i_1 the light transmitted after the shock wave passes the observation station. In the unshocked gas, the concentration of NO_2 is $C_0\phi$, where C_0 is the total concentration of gas and ϕ is the mole fraction of NO_2 . The concentration of NO_2 in the shocked gas is given by $C_0\phi\Delta$, where Δ is the density

(21) F. Daniels and R. A. Alberty, "Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 342.

(22) F. H. Verhoek and F. Daniels, THIS JOURNAL, **53**, 1250 (1931); M. Bodensteln and F. Boës, Z. physik. Chem., **A100**, 75 (1922); E. Wourtsel, Compt. rend., **169**, 1397 (1919).

(15) R. G. Dickinson and R. T. Dillon, Proc. Natl. Acad. Sci. U. S., **15**, 695 (1929). Professor R. M. Badger has generously loaned this instrument for this work.

(16) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 64.

(17) G. W. Elverum and D. M. Mason, J. Phys. Chem., **60**, 104 (1956).

(18) W. F. Giauque and J. D. Kemp, J. Chem. Phys., **6**, 40 (1938).

(19) R. E. Nightingale, A. R. Downie, D. L. Rotenberg, B. L. Crawford, Jr., and R. A. Ogg, Jr., J. Phys. Chem., **58**, 1047 (1954).

(20) T. M. Lowry and R. V. Seddon, J. Chem. Soc., 1461 (1937).

compression ratio across the shock front. The optical densities $D_1 = \log(i_0/i_1)$, $D_r = \log(i_0/i_r)$ and $D' = \log(i_r/i_1)$ are defined.

$$\epsilon(\lambda, T_2) C_0 \phi \Delta L = D_1 = D_r + D' = \epsilon(\lambda, 300^\circ\text{K}) C_0 \phi L + D' \quad (2)$$

The length of the light path is L . The unshocked optical density D_r is calculated from the measured concentration and room temperature extinction coefficient quoted from other measurements.²³

D' is the increment in optical density observed in the experiment. The value of the high temperature extinction coefficient, $\epsilon(\lambda, T_2)$, is calculated from these data and the particular T_2 and Δ of the shock wave. Correction of D_r for the small amount of transparent N_2O_4 is straightforward.

Figure 1 contains the results of these experiments at 366, 546 and 650 $m\mu$. The results at 436 $m\mu$ are substantially the same as those at 366 $m\mu$, and the temperature dependence at 405 $m\mu$ is similar, but the values of ϵ are generally higher. Tables of the data are presented in the thesis.¹

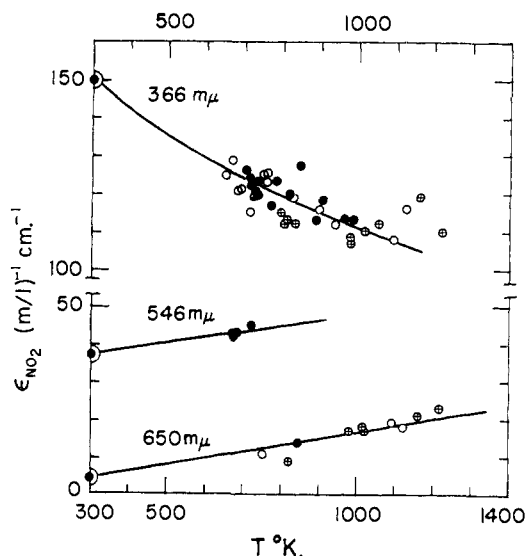


Fig. 1.—Extinction coefficients of NO_2 : (●) in NO_2 -argon mixtures; (⊕) in final decomposition products of N_2O_5 ; (○) in mixtures containing NO_2 and N_2O_5 , after decomposition.

Figure 1 also contains the results of measurements based entirely or in part on the observed absorption by the NO_2 formed in the decomposition of N_2O_5 . The agreement among the NO_2 extinction coefficients calculated from the different experiments is evidence that the conversion of N_2O_5 to NO_2 and O_2 is quantitative.

The significant qualitative conclusion that can be drawn from these measurements is that near the maximum in the NO_2 absorption spectrum, the absorption coefficient decreases with temperature, while in the green and red regions the weaker absorption has a positive temperature coefficient. This spreading of the absorption spectrum is typical of molecular electronic spectra and is due to the population of higher vibrational states of the ground electronic state as the temperature is raised.

(23) J. K. Dixon, *J. Chem. Phys.*, **8**, 157 (1940); T. C. Hall, Jr., and F. E. Blacet, *ibid.*, **20**, 1745 (1952); H. H. Holmes and F. Daniels, *THIS JOURNAL*, **56**, 630 (1934).

Absorption by NO_3 .—Figure 2 shows a flash spectrogram of a decomposing N_2O_5 sample in a shock wave experiment. The flash, which lasted for about 50 $\mu\text{sec.}$, was triggered 12 $\mu\text{sec.}$ after the shock wave passed the segment of the shock tube between the lamp and the spectrograph slit. The timing of this exposure was arranged so that the dissociation of N_2O_5 was virtually complete when the flash was started, but the decomposition of NO_3 was less than half over when the flash ended. The strong absorption bands at 624 and 662 $m\mu$ and the weaker structure in the green and yellow clearly identify NO_3 in the reaction mixture.^{10,11}

Figures 3a–3d are typical of the oscillographic transmission *versus* time records obtained at selected wave lengths in the decomposition of N_2O_5 between 600 and 1100°K. Immediately after the passage of the shock wave, the transmission falls sharply as N_2O_5 dissociates completely into NO_2 and NO_3 . The subsequent changes in transmission which accompany the decomposition of NO_3 occur more slowly. The time required for dissociation of N_2O_5 is of the order of 5 $\mu\text{sec.}$ near 600°K. and shorter than that at higher temperatures. These times are in agreement with the rates of dissociation computed by extrapolation of the dissociation rate data from room temperature experiments and from the experiments near 500°K. reported in this work. That the dissociation of N_2O_5 is in fact complete is indicated by the optical densities observed in the initial burst of absorption after the shock wave. These optical densities, which represent the combined absorptions of NO_2 and NO_3 , are found in every case to be proportional to the formal N_2O_5 concentration and to be relatively insensitive to temperature between 600 and 1100°K. The authors know of no other acceptable interpretation of these observations.

TABLE I
ABSORPTION COEFFICIENTS OF NO_3

λ , $m\mu$	T , °K.	ϵ (decadic) (moles/l.) ⁻¹ cm. ⁻¹	Estimated uncertainty
652	1050	305	25
652	825	282	15
652	650	260	15
652	300 (extrap.)	220	30
546	650	530	50
436	650	130	20
405	650	90	20
366	825	40	15
366	600	25	15

At 652 and 546 $m\mu$ (Figs. 3a and 3c), the absorption coefficient of NO_3 is much larger than that of NO_2 , and the absorption decreases as NO_3 decomposes. At 366 $m\mu$ (Fig. 3b), NO_2 is the stronger absorber, and the absorption increases to the final constant value, which corresponds to complete conversion of N_2O_5 to NO_2 . The increase in optical density is substantially less than the initial rise, showing that absorption by NO_3 is not negligible. At 436 $m\mu$ (Fig. 3d), NO_2 and NO_3 have substantially the same absorption coefficient at high temperatures, so that no change in transmission occurs as NO_3 decomposes into NO_2 and oxygen. At 405 $m\mu$, the records are similar to Fig. 3b, since

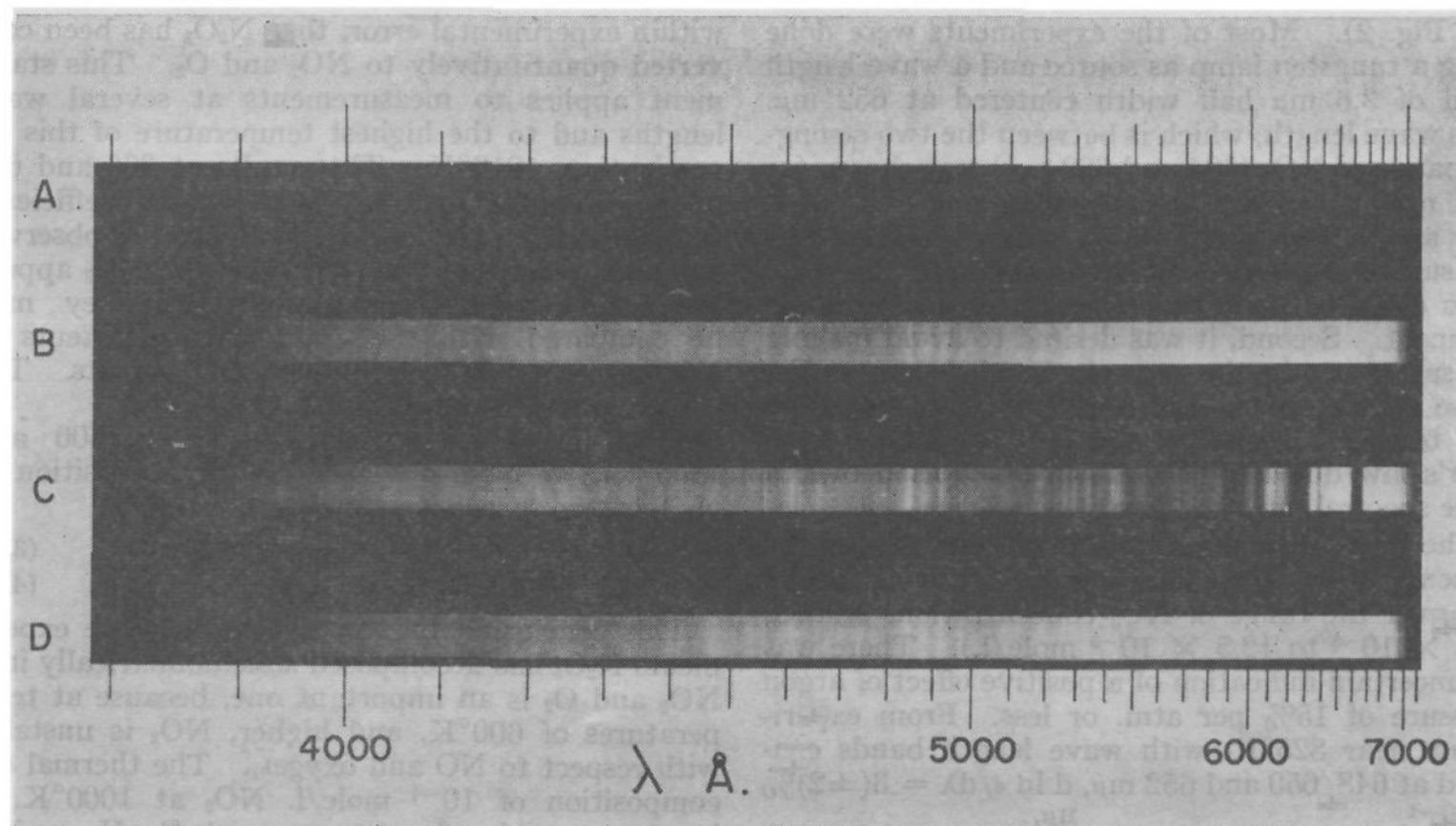


Fig. 2.—Flash absorption spectrogram of NO_3 . The characteristic bands of NO_3 , together with absorption by NO_2 , are shown in exposure c. The source, a xenon flash lamp, is shown through the empty 15 cm. shock tube in b and through the unshocked mixture of N_2O_5 and argon in d. The difference between b and d is the slight irreproducibility of the source. Exposure a is a blank, a two minute exposure to the other lights that were used in the experiment. On the original plate, the 5461 and 4358 Å. lines of mercury and some continuous exposure in the red are faintly visible. The plate is an Eastman Kodak Co. type 103-F. The formal N_2O_5 concentration was 23×10^{-5} mole/l., the shock temperature was about 530°K . and dissociation was at least 90% complete before the fifty microsecond flash started. A G.E. FT-126 was operated with a 1 μf . capacitor at 12 kv.

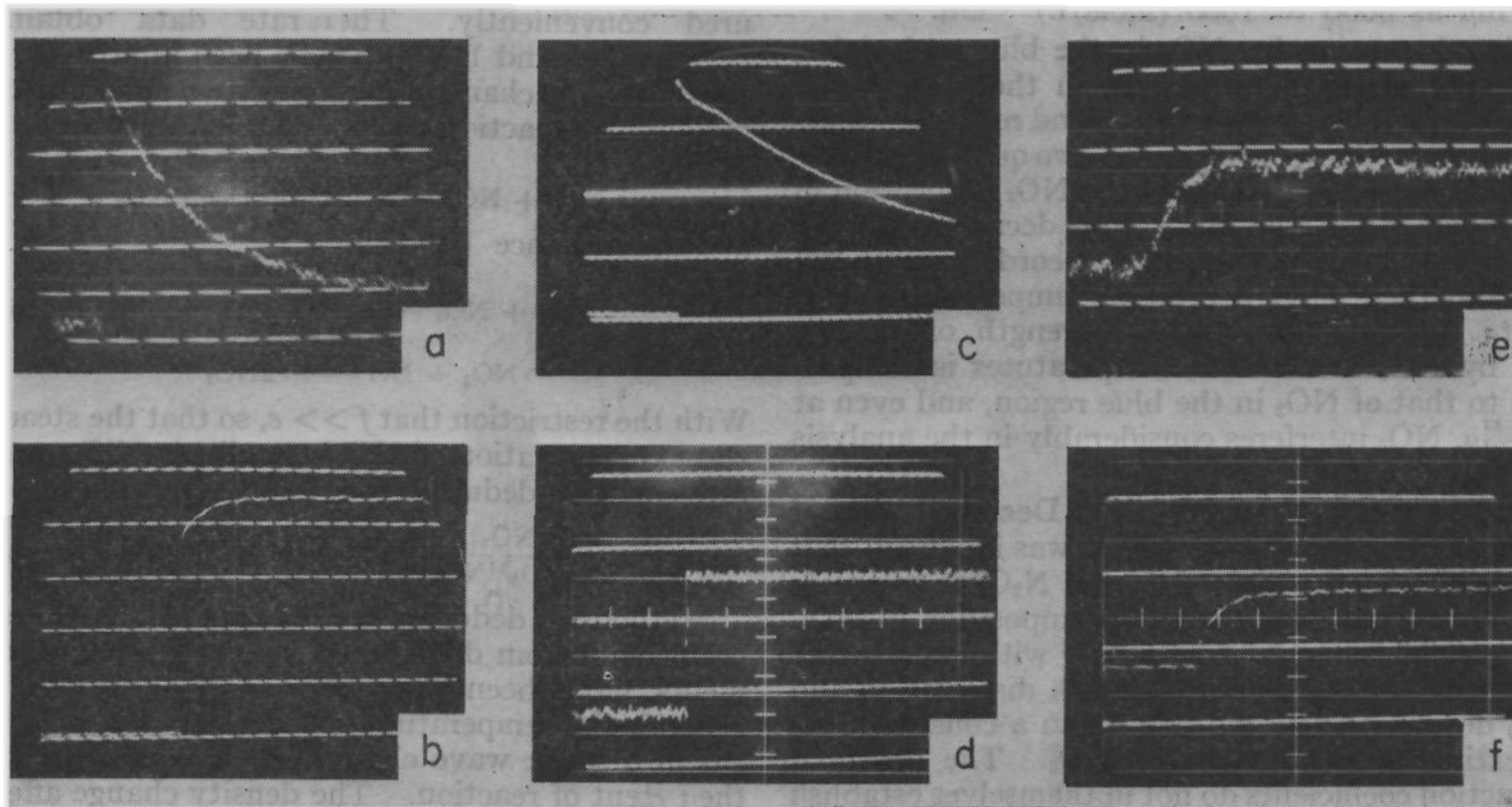


Fig. 3.—Oscillographic records of light transmission *vs.* time in the decomposition of N_2O_5 . In a ($652 \text{ m}\mu$) and b ($366 \text{ m}\mu$), at 801°K ., and in c ($546 \text{ m}\mu$) and d ($436 \text{ m}\mu$), at 627°K ., the dissociation of N_2O_5 is immediate and the rate of decomposition of NO_3 is shown. In e ($652 \text{ m}\mu$) and f ($366 \text{ m}\mu$), at 480°K ., the rate of dissociation of N_2O_5 , which reaches 79% at equilibrium, is shown, followed by much slower changes as NO_3 decomposes. The timing blanks in the traces are at 30 μsec . intervals.

the NO_3 absorption coefficient is larger than at $366 \text{ m}\mu$ but smaller than at $436 \text{ m}\mu$. At $487 \text{ m}\mu$, one exploratory experiment showed that NO_3 absorption is dominant.

The absorption coefficients of NO_3 were deduced from the optical densities just after dissociation of

N_2O_5 by subtracting the independently determined components of the optical density due to NO_2 . The results are shown in Table I.

In the green and red, where the NO_2 absorption is relatively unimportant, NO_3 has several very strong bands overlying an absorption continuum

(see Fig. 2). Most of the experiments were done using a tungsten lamp as source and a wave length band of 3.6 $m\mu$ half width centered at 652 $m\mu$. This wave length, which is between the two strongest bands of NO_3 (624 and 662 $m\mu$) was chosen for two reasons. First the absorption coefficient is only about twice that of NO_2 in the violet, so that measurements in two different regions of the spectrum could be made conveniently in the same experiment. Second, it was desired to avoid making measurements in the strongly banded regions because of the difficulties that arise from pressure and temperature broadening and departure from Beer's law due to non-uniform absorption over a finite spectral interval.

The light absorption at 652 $m\mu$ by NO_3 in the presence of *ca.* 10^{-2} mole/l. of argon obeyed Beer's law over the range of NO_3 concentrations studied (2.5×10^{-5} to 12.5×10^{-5} mole/l.). There was an uncertain indication of a positive effect of argon pressure of 15% per atm. or less. From experiments near 825°K. with wave length bands centered at 648, 650 and 652 $m\mu$, $d \ln \epsilon/d\lambda = 3(\pm 2)\%$ ($m\mu$)⁻¹.

A few experiments with 546 $m\mu$ light (from a high pressure mercury arc) indicated that ϵ at this wave length, which is close to one of the strong absorption bands, is pressure dependent.

From these measured extinction coefficients and visual examination of the flash spectrograms like Fig. 2, one can estimate the maximum absorption coefficients of NO_3 in the strong bands at 662 and 624 $m\mu$ as 3000 ± 1000 (mole/l.)⁻¹ cm.⁻¹.

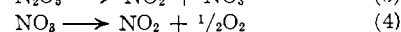
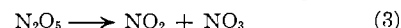
The absorption by NO_3 in the blue and violet, while not nearly so strong as in the case of the characteristic bands in the green and red, is considerable. From the present results, two qualitative conclusions can be drawn about the NO_3 absorption in the blue. First, the absorption decreases toward the violet. The lowest values recorded are at 366 $m\mu$, and these have a positive temperature coefficient. Second, the absolute strength of absorption by NO_3 at elevated temperatures is comparable to that of NO_2 in the blue region, and even at 366 $m\mu$, NO_3 interferes considerably in the analysis of NO_2 .

Stoichiometric Formation and Decomposition of NO_3 .—In the previous section it was indicated that above 600°K. the dissociation of N_2O_5 is complete and rapid compared to the decomposition of NO_3 . This conclusion is consistent with our other knowledge of the kinetics of N_2O_5 dissociation and NO_3 decomposition and has led to a consistent set of extinction coefficients of NO_3 . The observed extinction coefficients do not in themselves establish the stoichiometric formation of NO_3 , for such reasoning is circuitous. However, the observed optical densities which lead to a consistent set of extinction coefficients over the entire range of concentrations and temperatures are not kinetically reconcilable with any other stoichiometry.

When the decomposition of NO_3 is complete, as indicated by the final constant optical densities in Figs. 3a–3d, determination of the NO_2 present is straightforward. The results of all the experiments in which the final state was observed show,

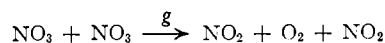
within experimental error, that N_2O_5 has been converted quantitatively to NO_2 and O_2 . This statement applies to measurements at several wave lengths and to the highest temperature of this investigation, 1216°K. The results at 366 and 652 $m\mu$ are presented in Fig. 1 as extinction coefficients calculated from the final optical densities observed and the assumption that two moles of NO_2 appear in place of every one of N_2O_5 . They may be compared with the extinction coefficients of NO_2 measured in independent experiments. The complete results are recorded in the thesis.

Thus, in the experiments between 600 and 1100°K., we have observed the decomposition of N_2O_5 in two successive stoichiometric steps

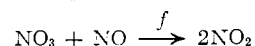
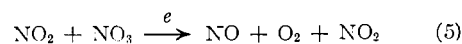


This conclusion that in the shock wave experiments N_2O_5 has decomposed stoichiometrically into NO_2 and O_2 is an important one, because at temperatures of 600°K. and higher, NO_2 is unstable with respect to NO and oxygen. The thermal decomposition of 10^{-4} mole/l. NO_2 at 1000°K. is known to require about two seconds.²⁴ Hence it is too slow to be significant in the present experiments, which are of much shorter duration. However, the present result also excludes the possibility that significant amounts of NO are formed in the mechanism of decomposition of NO_3 .

Kinetics of Decomposition of NO_3 .—From photographs like Figs. 3a, b, c, the rate of decomposition of NO_3 according to equation 4 can be measured conveniently. The rate data obtained between 600 and 1100°K. have been interpreted in terms of a mechanism involving two simultaneous bimolecular reaction paths



and the sequence



With the restriction that $f \gg e$, so that the steady-state concentration of NO is small, the differential rate equation deduced from this mechanism is

$$\frac{-(\partial[\text{NO}_3]/\partial t)_v}{2[\text{NO}_2][\text{NO}_3]} = e + g[\text{NO}_3]/[\text{NO}_2] \quad (6)$$

Methods of deducing conventional isochoric rate coefficients from data taken in shock wave experiments have been considered previously.^{12,13} In general, the temperature and density of a reacting gas in a shock wave change in a known way with the extent of reaction. The density change affects the concentrations of the reactants, and the temperature change affects the rate coefficients and the extinction coefficients of the absorbing constituents. Further, the time scale in which a stationary observer sees the reaction is different from that experienced by an element of the reacting gas. The specific method of considering these factors in using equation 6 is discussed in the thesis.¹ It is based on evaluation of the fractional extent of decomposition of NO_3 at a sequence of times over the

(24) W. A. Rosser, Jr., and H. Wise, *J. Chem. Phys.*, **24**, 493 (1956).

course of the reaction and approximate evaluation of the differential rate of reaction over successive intervals. It should be emphasized that because the experiments were done in a large excess of inert gas, the effects of the temperature and density changes introduced only small adjustments of the raw data.

To determine e and g , the function representing the left side of equation 6 was plotted against $[\text{NO}_3]/[\text{NO}_2]$. In the absence of added NO_2 , this plot covers the interval between zero and unity. The mechanism predicts that the plot is linear with positive slope equal to g and positive left intercept equal to e . In practice, the points are scattered, but in all but one case the most plausible curve is a straight line with positive slope and intercept. This exception is a very fast reaction at 1127°K ., and a negative slope is indicated.

The intercept of these plots at $[\text{NO}_3]/[\text{NO}_2] = 1$ (the right intercept) is the apparent bimolecular rate constant at the beginning of the reaction, which is the sum ($e + g$). This is the quantity that is most accurately deduced from the experiments by this plotting procedure. The data measured early in the reaction are inherently more reliable, and the later data are included as a guide in extrapolating to the beginning of the reaction. The values of ($e + g$) thus obtained are satisfactorily independent of the formal N_2O_5 concentration over a fivefold range and of the argon concentration over a fourfold range. They are plotted on logarithmic scale against reciprocal temperature in Fig. 4. The nearly linear form of this plot indicates that e and g have not very different temperature coefficients. It gives the average activation energy as 6.42 ± 0.3 kcal./mole. The equation of the line (least squares) is

$$\log(e + g) = -(1403 \pm 60)/T + 9.340 \quad (7)$$

The two rate constants, e and g , have been separated in two ways. The most reliable of these uses the initial rate data in a series of experiments in which NO_2 was added to the initial mixture so that at the beginning of the decomposition, $[\text{NO}_3]/[\text{NO}_2]$ was between 0.3 and 0.1. These values of ($e + g[\text{NO}_3]/[\text{NO}_2]$) were combined with the values of ($e + g$) from equation 7. The values of e obtained in this way are plotted in the lower part of Fig. 4. The equation of the line through them is

$$\log(e) = -(965 \pm 150)/T + 8.41 \quad (8)$$

and the activation energy is 4.42 ± 0.7 kcal./mole.

The other set of values of e are obtained as the left intercepts of the plots of equation 6. These values of e are summarized by the equation

$$\log(e) = -(1981 \pm 60)/T + 9.590 \quad (9)$$

and the activation energy is indicated as 9.1 ± 0.3 kcal./mole. The strong disagreement between the values of the activation energy of reaction e calculated by the two procedures arises largely from the data at the low end of the temperature range. Here the reaction is not followed past about 50% decomposition, and the extrapolation to $[\text{NO}_3]/[\text{NO}_2] = 0$ is long and uncertain. The plots always yielded positive intercepts, but the values of e indicated were substantially lower than those

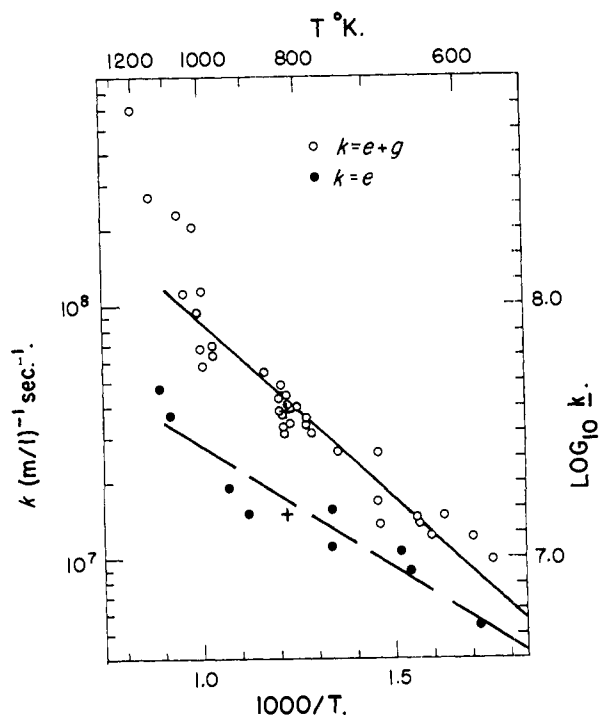


Fig. 4.—Bimolecular rate constants from the initial rate of decomposition of NO_3 : (O) $k = (e + g)$; solid line, equation 7; (●) $k = e$; broken line, equation 8; (+) equation 10.

measured by the method of adding NO_2 to the original mixture.

Near 820°K ., the center of the temperature range, the two methods of separating e and g agree with each other. Data from twenty-one experiments between 750 and 934°K . have been adjusted to 820°K . using the temperature coefficient of equation 7. These include data from experiments with the initial N_2O_5 concentrations differing by a factor of five and from experiments with NO_2 added to the mixture. The plot of these data according to equation 6 is shown in Fig. 5. The general validity of the kinetic interpretation is supported. The best values of the individual rate constants afforded by this investigation are derived from this plot. The parameters determined from this treatment by the least squares method are

$$e = (1.50 \pm 0.09) \times 10^7 \text{ (mole/l.)}^{-1} \text{ sec.}^{-1} \text{ at } 820^\circ\text{K.}$$

$$g = (2.34 \pm 0.17) \times 10^7 \text{ (mole/l.)}^{-1} \text{ sec.}^{-1} \text{ at } 820^\circ\text{K.} \quad (10)$$

The activation energy, $-R \, d \ln(e + g)/d(1/T)$, is the weighted average of the individual activation energies

$$E_{e+g} = \frac{eE_e + gE_g}{(e + g)} \quad (11)$$

Substituting $E_{e+g} = 6.4$ kcal./mole and the preferred value of E_e , 4.4 kcal./mole, together with the values of e and g at 820°K ., gives the result: $E_g = 7.7$ kcal./mole.

The mechanism of NO_3 decomposition considered so far was deduced from steps identified in various room temperature investigations. An examination of possible breakdown of this mechanism at very high temperatures is in order. It was pointed out in the development of equation 6 that use of the

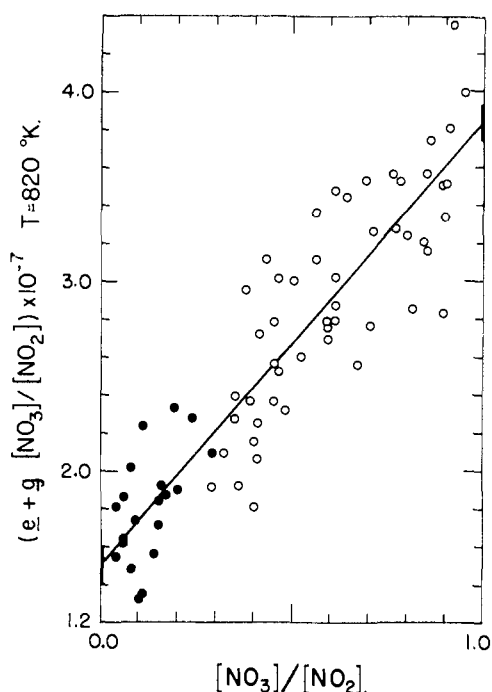


Fig. 5.—Evaluation of e and g at 820°K . using data from 21 experiments between 750 and 934°K . See equations 10. (O) experiments with pure N_2O_5 ; (●) experiments with NO_2 added. The probable errors in the intercepts are shown by the heavy lines.

strong inequality $f \gg e$ is justified by the observation that, within experimental error, no NO is formed in the decomposition of NO_3 . Consideration of the uncertainty in the analysis for NO_2 , which may be as large as 10%, and of the significant participation of reaction g in the NO_3 decomposition mechanism, leads to the safe conclusion that $f \geq 5e$. Actually, this conclusion is a rather weak one, since other information to be developed indicates that f is two or three orders of magnitude greater than e at temperatures near 1000°K .

The most serious complication in the kinetics of NO_3 decomposition above 1000°K . apparently comes from unimolecular dissociation of NO_3 . The present experiments between 1000 and 1200°K . indicate that some reaction with a high activation energy is competing with reactions e and g . In Fig. 4 the computed values of $(e + g)$ break sharply upward from the linear plot at the high temperature limit of the investigation. In the two experiments above 1100°K ., the deviation is unmistakable. Near 1000°K ., the dependence of the initial decomposition rate on the formal N_2O_5 concentration shows slight deviations from the bimolecular rate law. The experiments with the largest NO_2 and NO_3 concentrations give lower values of $(e + g)$ than the experiments with one fifth as much N_2O_5 in the initial reaction mixture. The differences in the apparent rate constants are much smaller than the fivefold variation in concentrations, but they are in the direction of less than second power dependence on the formal N_2O_5 concentration. Among the data at lower N_2O_5 concentrations the highest apparent rate constants are measured in the experiments with the highest argon concentrations. This

dependence on total gas concentration is characteristic of a unimolecular decomposition reaction of a simple molecule at low total pressures.

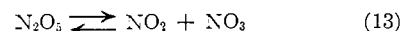
In the experiment at 1216°K ., the initial rate of decomposition is four times that expected from the value of $(e + g)$ given by equation 7. Subtracting the bimolecular contribution gives an estimated unimolecular decomposition rate of

$$-d[\text{NO}_3]/dt = 2.3 \times 10^4 [\text{NO}_3] = 2.5 \times 10^6 [\text{NO}_3][\text{argon}] (\text{mole/l.}) \text{ sec.}^{-1} \quad (12)$$

The rate is consistent with a unimolecular dissociation of NO_3 into NO_2 and O with a dissociation energy of 50 kcal. Other processes such as dissociation to give NO and O_2 via isomerization to the peroxy compound O-O-N-O^{25} are possible. In any case the final products are still NO_2 and O_2 .

Kinetics and Equilibrium in the Dissociation of N_2O_5 .—At temperatures between 450 and 550°K ., shock wave experiments in 1% mixtures of N_2O_5 and argon give photoelectric records like those in Fig. 3e and 3f. These differ from the experiments at higher temperatures in two respects. The increase in absorption after the passage of the shock wave is slow enough that its rate can be measured. Second, the magnitude of the initial rise, which determines the maximum in the NO_3 absorption record at $650 \text{ m}\mu$ (Fig. 3e), is less than that calculated for complete dissociation of the N_2O_5 . The decrease after the maximum and the corresponding slow increase in absorption at $366 \text{ m}\mu$ are generally too slow for accurate measurement. They are also so slow that they do not interfere seriously with measurement and interpretation of the initial increases.

From the initial rates of appearance of NO_2 and NO_3 after the passage of the shock wave, the rate constants for the dissociation of N_2O_5 , $A(M)$, have been obtained. $A(M)$ has been studied as a function of argon concentration near 520°K . and as a function of temperature near $[A] = 0.0076 \text{ mole/l.}$ Equilibrium constants for the reaction



have been calculated between 450 and 550°K . from the state of near equilibrium that obtains at the time of the maximum NO_3 concentration. All these measurements depend on values of the extinction coefficients of NO_2 and NO_3 extrapolated from the work at higher temperatures.

$A(M)$ is the first-order dissociation rate constant, which depends on the nature and amount of each of the gases present. Properly, $[M]$ is the weighted sum of the concentrations of all the gases in the system. The weighting factor for each gas is its efficiency, relative to some standard gas, in exchanging energy with the internal motions of N_2O_5 . In this work, the standard gas is argon and, for the present considerations, the differences between $[M]$ and the total gas concentration are ignored. These experiments have been performed in a region of argon concentration where $A(M)$ is nearly linear in $[M]$. Accordingly, it is of interest to compute the ratio of $A(M)$ to the total gas concentration, $[M]$.

Calling this ratio A' , the apparent second-order dissociation rate constant, we have the rate equa-

(25) R. A. Ogg, Jr., *J. Chem. Phys.*, **21**, 2079 (1953).

tion in the form

$$A' = \frac{(dD/d\tau)_0}{C_0^2 \phi L \Delta^3 (\epsilon_{\text{NO}_2} + \epsilon_{\text{NO}_3})} (\text{mole/l.})^{-1} \text{sec.}^{-1} \quad (14)$$

D , C_0 , ϕ , Δ and the ϵ 's are defined as in equation 2. τ is the time after the arrival of the shock wave at the stationary observation point. The subscripts zero on the numerator and on Δ indicate the values of these quantities immediately after the arrival of the shock.

$A(M)$ and A' have been calculated from the initial slopes of smoothed plots of D versus τ in twenty experiments. The values of the logarithm of A' at $[M] = 0.0076$ mole/l. are plotted against $(1/T)$ in Fig. 6. The least squares line is

$$\log(A'_{0.0076 \text{ mole/l.}}) = -(3607 \pm 150)/T + 13.681 \quad (15)$$

giving an activation energy of 16.5 ± 0.7 kcal./mole.

Figure 6 also contains measured values of A' near 0.003 mole/l. These experiments yield values of A' that are larger than the average values at 0.0076 mole/l. This trend is to be expected, since at any finite pressure, $A' < A'_0$, the low pressure limit of $A(M)/[M]$. The average deviation of the 0.003 mole/l. points from the line, equation 15, is $22 \pm 14\%$. Crude extrapolation to $[M] = 0$ indicates that A'_0 is about 30% greater than $A'_{0.0076 \text{ mole/l.}}$ in the temperature range of these experiments. On this basis, A'_0 at 500°K. is estimated as 3.84×10^6 (mole/l.) $^{-1}$ sec. $^{-1}$.

These data include measurements of photoelectric records at $366 \text{ m}\mu$ and at $650 \text{ m}\mu$. The data at $366 \text{ m}\mu$ have consistently given values of $D/(\epsilon_{\text{NO}_2} + \epsilon_{\text{NO}_3})$ at particular values of τ that are from 0 to 15% higher than those given by the $650 \text{ m}\mu$ data. Some excess absorption at $366 \text{ m}\mu$ is to be expected, since as the decomposition of NO_3 becomes significant, $[\text{NO}_2] > [\text{NO}_3]$. However, the values of $[\text{NO}_2] - [\text{NO}_3]$ indicated in several of the experiments are somewhat too large too early in the reaction. It is not known which of the measurements are more reliable, so the averages have been used.

As the dissociation of N_2O_5 becomes appreciable, the recombination reaction and the decomposition of NO_2 become important. The expression for zero net formation of NO_3 derived from the mechanism, reactions A, B, e, f and g, is

$$\frac{[\text{NO}_2][\text{NO}_3]}{[\text{N}_2\text{O}_5]} = \frac{K_e}{1 + \frac{2(e + g[\text{NO}_3]/[\text{NO}_2])}{B(M)}} \quad (16)$$

This equation is formally equivalent to the steady-state approximation which determines the small NO_3 concentration in the room temperature first-order decomposition of N_2O_5 . It is invoked here not as an approximation but as the condition for the observed maximum in the NO_3 concentration. The data from the pairs of photoelectric records have been analyzed for the values of the NO_2 , NO_3 and N_2O_5 concentrations at the time of the maximum in the absorption at $650 \text{ m}\mu$. The equilibrium constants K_e have been calculated in those experiments where N_2O_5 was less than 90% dissociated at that time. The range of temperature of these determinations has been extended from 520 to 550°K. by experiments in which excess NO_2 was added to suppress the extent of dissociation. Figure 6 con-

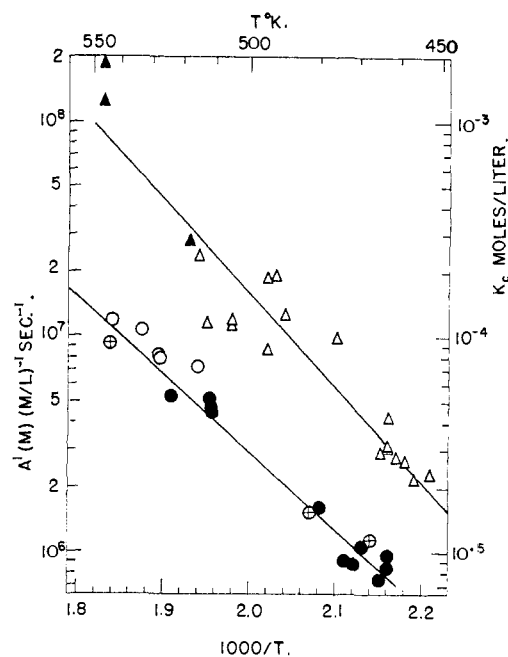


Fig. 6.—Equilibrium constants and rate constants for N_2O_5 dissociation: (Δ) K_e measured in pure N_2O_5 ; (\blacktriangle) K_e measured with NO_2 added: upper line, equation 17; (\bullet) $A'(M)$ measured at $[A] = 0.0076$ mole/l.; lower line, equation 15; (\circ) $[A] = 0.003$ mole/l.; (\oplus), $[A] = 0.009$ mole/l.

tains a plot of $\log K_e$ versus reciprocal temperature. It shows rather large scatter in the results at the higher temperatures. The most reliable data have been obtained near 460°K. , where 5×10^{-5} mole/l. N_2O_5 is only about half dissociated at equilibrium. The average value of K_e at 460°K. is 2.75×10^{-5} mole/l. The best linear relationship, shown in Fig. 6, is

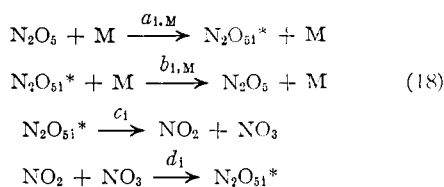
$$\log K_e = -(4383 \pm 232)/T + 4.967 \quad (17)$$

The energy change ΔE^0 for the dissociation of N_2O_5 is calculated to be 20.1 ± 1.1 kcal./mole. The fact that this reasonable temperature coefficient is measured indicates that there is no great error in the extrapolated extinction coefficients and other data used in interpreting the results. For it can be seen that a small error in the extinction coefficient of NO_2 or NO_3 produces a large percentage error in the calculated value of the N_2O_5 concentration in the experiments above 500°K. , where the degree of dissociation is large.

In the calculation of K_e by equation 16, the denominator of the right side is substantially unity under the conditions of high inert gas concentration used in these experiments. This does not imply that the extent of NO_3 decomposition is negligible in the time before the NO_3 concentration reaches its maximum value but merely that the rate of turnover in the NO_3 population is high at the maximum and thereafter.

Correlation with Room Temperature Results

Unimolecular Dissociation of N_2O_5 .—The kinetics of dissociation and association of N_2O_5 has been formulated in eq. 18



This formulation considers the rates of dissociation and recombination of the critically excited states of N_2O_5 individually in steps c and d. Steps a and b include the dependence of the excitation and de-excitation rates of each of the activated states, i , on the nature and concentration of specific molecules as M . The special cases that are of particular interest involve limiting concentration conditions. These are

$$\begin{aligned}
 \lim_{[\text{M}] \rightarrow 0} (A(\text{M})/[\text{M}]) &= \sum_i a_{i,\text{M}} = A'_0(\text{M}) \\
 \lim_{[\text{M}] \rightarrow \infty} A(\text{M}) &= \sum_i a_{i,\text{M}}c_i/b_{i,\text{M}} = A_\infty \\
 \lim_{[\text{M}] \rightarrow \infty} B(\text{M}) &= \sum_i d_i = B_\infty
 \end{aligned} \quad (19)$$

Measurements of the rate of oxidation of NO by N_2O_5 have given considerable information on the unimolecular dissociation constants, $A(\text{M})$.⁷ The best data near the low pressure limit, $A'_0(\text{M})$, are in a temperature range about 50°, while the high pressure data have been measured at lower temperatures. Additional data at the low pressure limit have been derived from experiments on the decomposition of pure N_2O_5 at such low pressures (10⁻³ mm.) that equilibrium in the dissociation reaction is not maintained.²⁶ Selected data from recent sources are shown in Table II.

TABLE II

SELECTED DATA ON THE UNIMOLECULAR DISSOCIATION OF N_2O_5

Quantity	T , °K.	Value, (mole/l.) ⁻¹ sec. ⁻¹	E_{act} , kcal. mole ⁻¹	System	Source
$A'_0(\text{N}_2\text{O}_5)$	323.7	2250	N_2O_5 , NO	7a, 7b
$A'_0(\text{N}_2\text{O}_5)$	323.7	3500	18.3 ± 2	N_2O_5	26
$A'_0(\text{N}_2\text{O}_5 + \text{NO})$	323.3	1130 ± 30	19.3 ± .6	N_2O_5 , NO	7c
$A'_0(\text{argon})$	323.7	304 ± 24	N_2O_5 , NO	7a, 7b
$A'_0(\text{argon})_{0.0076 \text{ mole/l.}}$	500	2.9 × 10 ⁶	16.5 ± .7	N_2O_5	This work
$A'_0(\text{argon})$	500	3.8 × 10 ⁶	N_2O_5	This work
A_∞	300	0.29 sec. ⁻¹	21 ± 2	N_2O_5 , NO	7d
$A(\text{N}_2)_{0.0914 \text{ mole/l.}}$	300	0.06 sec. ⁻¹	21 ± 2	N_2O_5 , NO	8

One basis for comparison of the results near 500°K. obtained in the present investigation with those near room temperature is the Rice-Ramsperger-Kassel formulation of the unimolecular dissociation rate.²⁷ This theory allows definite values of $A(\text{M})$ to be calculated at any value of $[\text{M}]$ and T by specifying the form of $a_{i,\text{M}}$, $b_{i,\text{M}}$ and c_i in terms of four parameters which may be adjusted, within certain limits, to fit the available experimental data. The model of the reacting molecule is a system of s lightly coupled harmonic oscillators all having the frequency $\nu = E_c/hm$. The frequency factor J measures the rate at which energy

(26) R. A. Ogg, Jr., *J. Chem. Phys.*, **18**, 572 (1950), has analyzed, in terms of recent developments, the data of E. F. Linhorst and J. H. Hodges, *This Journal*, **56**, 836 (1934).

(27) L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., 1932, pp. 93-105.

is exchanged among the oscillators. Dissociation occurs when the critical energy E_c (m quanta) is present in a particular one of the oscillators. The theory has the important qualitative feature that the specific dissociation rates of the excited states, c_i , increase with the energy, $ih\nu$, in excess of the critical energy. This is in agreement with the usual observation that the activation energy is less at low pressures than at the high pressure limit. The great simplifying approximation is that the deactivation rate constants, $b_{i,\text{M}}$, are independent of the degree of activation, i . In the simplest RRK formulas, b is equated to the kinetic theory collision number. The collision number contains some dependence on the nature of M , but additional dependence of b on M , independent of i , easily can be incorporated as the average collisional efficiency factor, \bar{f}_M . The frequency factor and the critical energy alone determine the high pressure limit.

$$A_\infty = J e^{-E_c/RT} \text{ sec.}^{-1} \quad (20)$$

In these terms

$$\begin{aligned}
 a_{i,\text{M}} &= b_M \binom{m+i+s-1}{s-1} (1 - e^{-h\nu/kT})^s e^{-(m+i)h\nu/kT} \\
 b_M &= \bar{f}_M (8\pi kT/\mu)^{1/2} \sigma^2 N \times 10^{-23} (\text{mole/l.})^{-1} \text{ sec.}^{-1}
 \end{aligned} \quad (21)$$

and

$$c_i = J \binom{i+s-1}{s-1} \binom{m+i+s-1}{s-1}^{-1} \text{ sec.}^{-1}$$

$$A(\text{M}) = \sum_i \frac{a_{i,\text{M}}c_i[\text{M}]}{b_M[\text{M}] + c_i} \quad (22)$$

The calculations made here have used the fixed values of J and E_c indicated by the high pressure limiting results, $A_\infty = 6.85 \times 10^{15} e^{-21.0/RT}$, in spite of the uncertainty in these values. Various integral values of s and m have been selected to fit the low pressure limit, $A'_0(\text{N}_2\text{O}_5) = 2250$ at 323.7°K. The

maximum allowed value of s is taken as fifteen, the number of vibrational modes of the N_2O_5 molecule. The minimum value of s , seven, is the one that comes closest to the experimental $A'_0(\text{N}_2\text{O}_5)$ in the classical limit of the RRK summation as $\nu \rightarrow 0$.

Though it is known that the collisional excitation efficiency, \bar{f}_M , averaged over i , is substantially less than unity for several monatomic and diatomic gases,^{7a} the approximation $\bar{f}_{\text{N}_2\text{O}_5} = 1$ is believed to be more nearly correct. For definiteness, it has been used, and \bar{f}_{argon} is taken as 0.154,^{7a} independent of i and of the translational temperature of the argon. This simplification is probably incorrect, but as yet there is not enough information to contradict it.^{7a} It is probably no worse an approximation than setting $\bar{f}_{\text{N}_2\text{O}_5} = 1$ and the arbitrariness of the RRK formulations of the $a_{i,\text{M}}$ and c_i .

In performing the computations of the low pressure limits, the approximate summation formulas, equations 12 and 13 of ref. 7c, have been used. The computation for 0.0076 mole/l. argon used similar formulas for all but the first two terms of the sum, equation 22, since these are the only terms seriously affected by that value of $[M]$. The collision radii quoted in ref. 7a have been adopted. The results of computations, showing the fitting of the RRR parameters to the 51° data on $A'_0(\text{N}_2\text{O}_5)$ and the values of $A'_0(\text{argon})$ at 500°K. predicted by these parameters, are shown in Table III.

TABLE III
UNIMOLECULAR DISSOCIATION RATES COMPUTED BY RRR
THEORY

<i>s</i>	<i>m</i>	At 323.7 °K.		At 500 °K.		$A'_{0,0076}/A'_0$
		A'_0 (N_2O_5) (mole/l.) ⁻¹ sec. ⁻¹ × 10 ⁻³	E_{act} , kcal./ mole	A'_0 (argon) (mole/l.) ⁻¹ sec. ⁻¹ × 10 ⁻⁶	E_{act} , kcal./ mole	
15	10	1.95	20.1	10.6	17.3	
10	20	2.55	18.9	7.5	16.3	0.83
7	∞	3.30	17.5	4.6	15.5	
Experiment		2.25	19	3.8	16.5	0.77 ± 0.13

Consideration of the values of the rate constants and the observed local activation energies leads to the choice of about ten oscillators with frequencies near 10^{13} sec.⁻¹ as the best over-all description. That was the conclusion reached over the smaller temperature range from the measurements in N_2O_5 plus NO mixtures.^{7c} On this basis, the observed rate constant at 500°K. in argon agrees within a factor of two with that calculated solely on the basis of measurements near room temperature. The over-all change is a factor of 10^3 . In view of the approximate nature of the theory and the uncertainty of the value of the critical energy, this agreement is satisfactory. Closer examination shows that all the values calculated at 500°K. are higher than the measured value and that there is really little to choose between large *s* with large vibrational quanta and small *s* and nearly classical behavior. Also, additional calculations have shown that small changes in the critical energy do not greatly affect the predicted constants at 500°K. when agreement with those at 324°K. is maintained. It is not possible to say how much of this inadequacy of the theory lies in the variation of the excitation efficiencies $f_{i,M}$ with *i* and *M* and how much depends on other things.

It is also of interest to compare the room temperature results with the high temperature shock wave results by the simple Arrhenius equation. Comparison of A'_0 (argon) between 323.7 and 500°K. gives an average activation energy of 17.3 kcal./mole. This value is intermediate between the two measured local activation energies. Direct comparison of the values of $A(M)$ in 0.0076 mole/l. argon between 300 and 500°K. is also possible. The computed average activation energy is 18.6 kcal./mole. The value of $A(M)$ at 300°K. used for this comparison was not actually measured in argon but in other gases.^{7d} However, at 0.0076 mole/l. at 300°K. (144 mm.), $A(M)$ is closer to its high pressure limit than to its lower pressure limit, and the differences between different inert gases are

small. At 500°K., A' at 0.0076 mole/l. is a much greater fraction of A'_0 than at room temperature, and the distinction between gases is important.

The present experiments near 500°K. definitely show that the activation energy of the dissociation of N_2O_5 near the low pressure limit decreases with temperature. They also show that the transition between low pressure and high pressure behavior occurs at higher concentrations as the temperature is increased. Both these facts indicate that the specific rate constants c_i increase with the energy of the molecule. The fact that the low pressure activation energy is less than the high pressure activation energy at 300°K. is also a consequence of this property of the c_i 's.^{7d} The present experiments are over too small a range of total pressure and $\text{N}_2\text{O}_5/\text{argon}$ ratio to contribute significantly to our understanding of the activation and deactivation processes. Nor do they reduce the existing uncertainty about the activation energy of the high pressure limiting rate. However, they do confirm the interpretation of the rate measurements made at room temperature by showing that the unimolecular rate of production of NO_3 can be observed directly at suitably high temperatures.

Thermodynamics of N_2O_5 Dissociation.—The equilibrium between N_2O_5 , NO_2 and NO_3 is the key to the kinetics of many reactions of N_2O_5 at room temperature. The deduction of the equilibrium constant K_c and the internal energy change ΔE^0 for reaction 13 at 300°K. from the results of the present high temperature experiments and other available information is presented here. Four estimates of ΔE^0 are made on the basis of the present work and compared with Johnston's previous estimate.³

The equilibrium measurements between 450 and 550°K. give $\Delta E^0_{500} = 20.1 \pm 1$ kcal./mole. An estimate of $\overline{\Delta C_V}$ for reaction 13 between 300 and 500°K. as -4 cal./mole degree leads to $\Delta E^0_{300} = 20.9 \pm 1$.

The most reliable measurements of K_c are at 460°K. and give $\Delta F^0_{460} = 6.3$ kcal./mole. An independent estimate of ΔS^0_{460} provides another approach to the heat of dissociation of N_2O_5 . The standard entropies of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_5(\text{g})$ at 300°K. taken from the literature are 57.5 e.u.¹⁸ and 82 ± 3 e.u.,²⁸ respectively. The entropy of NO_3 has been estimated in two ways, from estimated molecular parameters and by analogy with other compounds. The NO_3 molecule is the nitrate free radical, which we have assumed to be planar with symmetry D_{3h} and to have N–O distances of 1.33 Å., a doublet electronic ground state, and vibrational frequencies somewhat lower than those of the nitrate ion. S^0_{300} for this model is 60.7 e.u. Adding $S^0_{300}(\text{SO}_3) - S^0_{300}(\text{SO}_2) = 1.9$ e.u.²⁹ to $S^0_{300}(\text{NO}_2)$ gives an estimate $S^0_{300}(\text{NO}_3) = 59.4$ e.u. Taking the average of these estimates as 60 ± 2 e.u. and combining it with $S^0_{300}(\text{N}_2\text{O}_5) = 82$ e.u. and $S^0_{300}(\text{NO}_2) = 57.5$ e.u. gives $\Delta S^0_{300} = 35.5$ e.u. and $\Delta S^0_{460} = 34.6$. With $\Delta F^0_{460} = 6.3$ kcal./mole, this

(28) K. K. Kelley, "Entropies of Inorganic Substances. Revision (1948) of Data and Methods of Calculation," U. S. Bur. Mines Bull. No. 477 (1950).

(29) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., Series III 1954.

TABLE IV
 DEDUCTION OF ΔE_{300}^0 FROM HIGH TEMPERATURE RESULTS

Result	Temp., °K.	Other known or assumed quantities	ΔE_{300}^0 , kcal./mole
$K_e = 9.26 \times 10^4 e^{-20,1/RT}$ mole/l.	Near 500	$\overline{\Delta C_v}$	20.9 ± 1
$\Delta F^0 = +6.3$ kcal./mole	At 460	$\Delta C_p, \Delta S_{300}^0$	21.9 ± 1
$e = 2.26 \times 10^8 e^{-4.42/RT}$ (mole/l.) ⁻¹ sec. ⁻¹	Near 820	$(E_{820} - E_{300})_e, (E_e + \Delta E^0)_{300}$	20.8 ± 1
$g = 2.63 \times 10^9 e^{-7.70/RT}$ (mole/l.) ⁻¹ sec. ⁻¹	Near 820	$(E_{820} - E_{300})_g, (1/2 E_g + \Delta E^0)_{300}$	20.4 ± 2.5
		Johnston (1951) ³	20 ± 3
		"Best value" average	21.0 ± 1

leads to $\Delta E_{460}^0 = 21.3$ kcal./mole and $\Delta E_{300}^0 = 21.9$ kcal./mole.

The values of C_p for NO_3 at 300°K. estimated by the above two methods are $5.76R$ and $5.77R$, respectively.

The high temperature rate measurements of reactions e and g also provide estimates of ΔE_{300}^0 when combined with the results of room temperature kinetics work. We use the collision theory formula $E_{\text{act}} = E_0 + 1/2 RT$ to adjust the observed activation energies from 820 to 300°K. The relationships $(E_e + \Delta E^0)_{300} = 24.7 \pm 0.1$ kcal./mole⁹ and $(1/2 E_g + \Delta E^0)_{300} = 24 \pm 2$ kcal./mole³ then give the estimates of $\Delta E_{300}^0 = 20.8 \pm 1$ and 20.4 ± 2.5 kcal./mole, respectively.

These computations are summarized in Table IV. They are all in agreement with Johnston's previous estimate.

Using $\Delta E_{300}^0 = 21.0$, the estimated $\overline{\Delta C_v} = -4$ cal./mole degree, and the measurement $\Delta F_{460}^0 = 6.3$ kcal./mole, one obtains $\Delta H_{460}^0 = 21.3$ kcal./mole, $\Delta S_{460}^0 = 32.7$ e.u., $\Delta F_{300}^0 = 11.5$ kcal./mole, $\Delta H_{300}^0 = 21.6$, $\Delta S_{300}^0 = 33.6$ e.u., $K_{e,300} = 1.65 \times 10^{-10}$ mole/liter.

We believe K_{460} to be good to $\pm 50\%$, or about 0.2 in log K . Translation of this value to 300°K. with uncertainty of about 1 kcal./mole in ΔH^0 introduces an additional $\delta \Delta \log K = \delta \Delta H^0 / 4.57 \Delta(1/T) = 0.25$. Thus K_{300} is known to within a factor of three or better and ΔF_{300}^0 to within 0.6 kcal./mole.

The heat of formation of NO_3 indicated by this work is $\Delta H_f^0(\text{NO}_3)$ at 300°K. = 17.1 ± 1 kcal./mole, based on the values 3.6 and 8.1 kcal./mole for N_2O_5 and NO_2 , respectively.¹⁰ The standard entropy of NO_3 computed from the entropy data referred to above is $S_{300}^0(\text{NO}_3) = 58 \pm 4$ e.u. A significant part of the uncertainty in this entropy value lies in the uncertainty in $S_{300}^0(\text{N}_2\text{O}_5)$, and we believe our computed values of $S_{300}^0(\text{NO}_3) = 60 \pm 2$ e.u. and $C_p^0(\text{NO}_3) = 5.77R$ are as reliable as any.

The recently published data of Ray and Ogg¹¹ on the thermodynamic properties of $\text{N}_2\text{O}_5(\text{g})$ yield the values 16.6 ± 1 kcal./mole and 61 ± 2 e.u. for the standard heat of formation and entropy of NO_3 at 300°K., lending support to our calculation of the entropy of NO_3 .

Room Temperature Rate Constants Based on K_e .—Relationships between K_e and the bimolecular rate constants B_∞ , e , f and g are available from room temperature kinetics studies. These relationships are presented in Table V.

(10) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circ. 500, 1952.

(11) J. D. Ray and R. A. Ogg, Jr., *J. Chem. Phys.*, **26**, 984 (1957). See also J. D. Ray, Thesis, Stanford University, 1955.

TABLE V

 RELATIONSHIPS BETWEEN BIMOLECULAR RATE CONSTANTS AND K_e

Quantity	Value at 300°K.	E_{act} , kcal./mole	Source
$A_\infty = B_\infty K_e$, sec. ⁻¹	0.29	21 ± 2	7d
$e K_e$, sec. ⁻¹	4.1×10^{-5}	24.7 ± 0.1	9
$f K_e$, sec. ⁻¹	1.0	22.4 ± 2	8
$g^{1/2} K_e$, (mole/l.) ^{1/2} sec. ^{-1/2}	1.9×10^{-9}	24 ± 2	3

These relationships, with the exception of the value of $f K_e$ which has been determined only recently, were used by Johnston to deduce the values of K , B_∞ and e and their activation energies on the basis of information on g , namely, the value $E_g = 8.1 \pm 2$ kcal./mole and the assumed pre-exponential factor for g of 1×10^9 (mole/l.)⁻¹ sec.⁻¹. Those results are presented together with the ones deduced from the present results on the dissociation equilibrium in Table VI.

In Table VI, two entries appear for the pre-exponential factors and activation energies of reactions e and g. The first entries are deduced from K_e and the information in Table V and hence are local values near 300°K. The second entries represent the Arrhenius equation relating the values of e and g at 300°K. to those at 820°K. (equation 10). Allowing a possible error of a factor of three in the ratio of the constants at 820° to those at 300°K. leads to an uncertainty in the activation energies of 1.0 kcal./mole. The agreement among these values and those based on the local measurements of the activation energies near 300°K. (first entries) and 820°K. (Table IV) is striking. The apparent small positive temperature coefficient of these activation energies is probably not significant.

One conclusion that can be drawn is that the collision and steric factor in reaction g is comparable to the recombination rate B_∞ and is an order of magnitude greater than the corresponding property of reaction e. This is unexplained, since reactions e and g are very similar processes and should have similar activated complexes. Reaction f is of a different type from reactions e and g, since only one N-O bond is broken, an N-O bond rather than an O-O bond is formed, and two molecules rather than three emerge. Its pre-exponential factor is a factor of ten greater than that of reaction g.

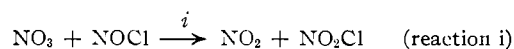
Another approximate check on the values of K_e and g at 300°K. can be obtained from the optical densities due to NO_3 absorption in the N_2O_5 catalyzed decomposition of ozone. Sprenger¹⁰ has reported the product $\epsilon_{\text{NO}_3}[\text{NO}_3]$ at the wave length of maximum absorption, 660-664 $m\mu$, together with the other conditions of his experiments. Using the

TABLE VI
 RATE CONSTANTS BASED ON K_0

Quantity	Johnston (1951)		Value at 300°K.	Present status Pre-exponential	E_{act} , kcal./mole
	Value at 300°K.	E_{act} , kcal./mole			
K_0 (mole/l.)	0.6×10^{-10}	20 ± 3	1.65×10^{-10}	3.3×10^5	21.0 ± 1
B_∞ (mole/l.) $^{-1}$ sec. $^{-1}$	4×10^9	1 ± 4	1.8×10^9	1.8×10^9	0.0 ± 2.5
e , (mole/l.) $^{-1}$ sec. $^{-1}$	7×10^6	5 ± 3	2.5×10^6	1.3×10^8	3.7 ± 1
				1.66×10^8	3.9 ± 1
f , (mole/l.) $^{-1}$ sec. $^{-1}$	$\geq 1 \times 10^{10}$	6×10^9	6×10^{10}	1.4 ± 2.5
g , (mole/l.) $^{-1}$ sec. $^{-1}$	1×10^3	8.1 ± 2	1.3×10^4	3.1×10^9	6.0 ± 2.5
				1.95×10^9	7.1 ± 1

values of the constants proposed here, one can calculate the appropriate extinction coefficient as 1200 (mole/l.) $^{-1}$ cm. $^{-1}$ near 300°K. The crude estimate derived from the present work is 3000 ± 1000 (mole/l.) $^{-1}$ cm. $^{-1}$ near 600°K.

The present results are in substantial agreement with the 1951 estimates of Johnston.³ The precision of the present values is considerably greater. The information on reaction h is of course not affected by the present results. The value of the rate constant for the process



which has been found⁴ in the N_2O_5 catalyzed oxidation of NOCl by O_3 can be revised. Its value at 40° is computed to be 2.3×10^4 (mole/l.) $^{-1}$ sec. $^{-1}$.

Other Rates and Equilibria.—From the thermodynamic properties of NO_3 deduced here and the rate constants of reactions e, f, g, h and i, one can compute the equilibrium relationships and the reverse reaction rate constants. This is done in Table VII.

The reverse rate constant e_{-1} recently has been measured by Ray and Ogg,³¹ who report the value 6.6×10^1 (mole/l.) $^{-2}$ sec. $^{-1}$, which is in good agreement with the value computed here. The thermodynamic properties of NO_2Cl used in the computations about reaction i were taken from that work. The other reverse reactions are inherently very slow and probably never will be observed at room

TABLE VII

EQUILIBRIUM AND REVERSE RATE CONSTANTS					
Re- ac- tion	ΔH° , kcal./ mole	ΔS° , e.u.	$K_{300^\circ\text{K.}}$	k_{300} (rev.)	E_{act} (rev.)
e	5	39	7×10^3 mole/l.	3×10^1 (mole/l.) $^{-2}$ sec. $^{-1}$	0
f	-23	5	3×10^{17}	2×10^{-8} (mole/l.) $^{-1}$ sec. $^{-1}$	23
g	-18	44	2×10^{21} mole/l.	7×10^{-18} (mole/l.) $^{-2}$ sec. $^{-1}$	25
h	-25	-5	1×10^{17}	4×10^{-10} (mole/l.) $^{-1}$ sec. $^{-1}$	32
i	-19	1	1×10^{13}	2×10^{-9} (mole/l.) $^{-1}$ sec. $^{-1}$	25^a

^a 40°, E_1 is estimated as 6 kcal./mole.

temperature. The role of the reactions f_{-1} and e in the decomposition of NO_2 near 700°K. has been discussed elsewhere.³²

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(32) N. Davidson and G. Schott, *J. Chem. Phys.*, **27**, 317 (1957); P. G. Ashmore and B. P. Levitt, *Research (Corr.)*, **9**, S25 (1956); *J. Chem. Phys.*, **27**, 318 (1957).