hydrogen probably to give CH_2OH and H_2. The fact that hydrogen equals formaldehyde in the presence of scavengers and that the formaldehyde in the absence of scavengers is equal to the H_2 in the presence of scavengers shows that excess of hydrogen over (CH_2O + CO) must be due to reactions of hydrogen atoms produced in the primary process. The energy relationships are such that hot atoms could be expected from either primary process 2 or primary process 3.[17]

A logical interpretation of the data can be based on primary process 1 accompanied by primary process 2, followed by such reasonable reactions of the radicals and atoms as would be expected from earlier work. The arguments against some occurrence of (3) are strong but not absolutely conclusive. A more detailed discussion of the mechanism does not seem to be warranted at this time.

ROCHESTER, NEW YORK

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[17] P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956).

[CONTRIBUTION NO. 2454 FROM THE GATES AND GRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Shock Waves in Chemical Kinetics: The Thermal Decomposition of NO_2[1a]

BY ROBERT E. HUFFMAN AND NORMAN DAVIDSON

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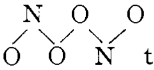
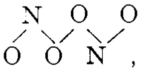
The thermal decomposition of NO_2 in argon–NO_2 mixtures has been investigated by the shock wave method, using both incident and reflected shocks. The argon:NO_2 ratio was varied from 360 to 5.6, and the temperature was varied from 1400 to 2300°K. The rate law is $-d(NO_2)/dt = k_u(M)(NO_2) + k_b(NO_2)^2$. (M) is the total (mainly argon) gas concentration, and $k_u = 3.06 \times 10^{13} \exp(-65{,}400/RT)$ mole^{-1} liter sec.$^{-1}$, $k_b = 2.5 \times 10^{10} \exp(-25{,}000\ (\pm 5000)/RT)$ mole^{-1} liter sec.$^{-1}$. The k_u term in the rate law is believed to be due to the unimolecular dissociation at its low pressure limit $M + NO_2 \xrightarrow{k_u/2} M + NO + O$ (6), followed by $O + ONO \rightarrow O_2 + NO$ (fast), and it is shown that measurements of the reverse of reaction 6 at low temperature are in agreement with our high temperature values for k_u. The k_b term is partly due to the "Bodenstein bimolecular path." However, the values of k_b are about eight times greater than the extrapolated values for the Bodenstein mechanism; there may be some other bimolecular path which contributes to the decomposition. The results illustrate a characteristic feature of high temperature chemistry: namely, that a number of reaction paths frequently contribute to an over-all chemical transformation.

The thermal decomposition of NO_2 is in many

$$2NO_2 \rightleftarrows 2NO + O_2 \qquad (1)$$

respects one of the classical examples of a bimolecular reaction. It was studied by Bodenstein and Ramstetter[1b] and later by others, including Rosser and Wise.[2] For the rate constant between 600 and 1000°K., the latter authors give

$$-\frac{1}{(NO_2)^2}\frac{d(NO_2)}{dt} = k_{1b} =$$
$$4.0 \times 10^9 \exp(-26{,}900/RT) \text{ mole}^{-1} \text{ l. sec.}^{-1} \qquad (2)$$

(Subscript b implies the belief that this constant is for the "Bodenstein mechanism," with the  transition state for reaction 1.) A transition state calculation, with reasonable values for the distances and vibration frequencies of the activated complex, which is assumed to be  , agrees rather well with the observed pre-exponential factor.[3] (At low temperatures, the reverse termolecular reaction has a small negative temperature coefficient which has been extensively studied; above 500°K., this rate constant is essentially constant in accordance with (2).)[4]

By observing the very early stages of the reaction, Ashmore and Levitt[5] discovered that the initial rate of pyrolysis near 700°K. is greater than that observed by previous investigators; this additional contribution to the rate is quenched as NO forms or if NO is added to the initial mixture. These phenomena are attributed to the new reaction path

$$NO_2 + NO_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} NO_3 + NO \qquad (3,4)$$

$$NO_3 + NO_2 \xrightarrow{k_5} NO_2 + O_2 + NO \qquad (5)$$

This proposal is consistent with the properties of NO_3 as determined in other investigations.[6,7]

We report here a shock tube study of the rate of the same reaction in NO_2–argon mixtures from 1400–2300°K. In addition to the bimolecular reaction path, there is a unimolecular dissociation path

$$A + NO_2 \longrightarrow A + NO + O \qquad (6)$$

$$O + ONO \longrightarrow O_2 + NO \text{ (fast)} \qquad (7)$$

There is available a brief preliminary report of another shock wave investigation.[8] The experimental results in the two studies agree rather well; the differences in interpretation will be considered below.

[1a] From the Ph.D. thesis by R. E. H., California Institute of Technology, 1958.

[1b] M. Bodenstein and H. Ramstetter, *Z. physik. Chem.*, **100**, 106 (1922).

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

[3] D. R. Herschbach, H. S. Johnston, K. S. Pitzer and R. E. Powell, *ibid.*, **25**, 736 (1956).

[4] H. J. Schumacher "Chemische Gasreaktionen," Theodor Steinkopf, Leipzig, 1938, pp. 311–320.

[5] P. G. Ashmore and B. P. Levitt, *Research (Correspondence)*, **9**, 525 (1956).

[6] N. Davidson and G. Schott, *J. Chem. Phys.*, **27**, 317 (1957); P. G. Ashmore and B. P. Levitt, *ibid.*, **27**, 318 (1957).

[7] G. Schott and N. Davidson, THIS JOURNAL, **80**, 1841 (1958).

[8] M. Steinburg and T. F. Lyon, abstract of paper presented before Inorganic and Physical Chemistry Section, 131st National Meeting, American Chemical Society, Miami, Florida, April, 1957.

Experimental

The shock tube is essentially as described before[9,10] but somewhat longer. The diameter was 15 cm.; the driving section was a 270 cm. length of aluminum pipe; the shock wave section consisted of a 140 cm. long aluminum pipe and two 150 cm. long sections of Pyrex pipe.

The principal experimental innovation in our present work was the observation of reaction rates behind reflected shocks in some instances. This was particularly convenient when high ratios of argon to NO_2 were desired (the range of NO_2 concentrations being to some extent fixed by light absorption considerations) at high temperatures. The high argon pressures and high temperatures are more conveniently produced in reflected shocks; furthermore, since there is no "time compression," very fast reaction rates are more readily measured behind reflected shocks. For experiments with reflected shock waves, a special end plate was used which placed the reflecting surface about 12 cm. in front of the end of the glass pipe. The clearance between the circumference of this plate and the inside glass wall was about one mm. A plunger arrangement allowed the portion of the shock tube behind the reflecting surface to be evacuated through a hole in the reflecting plate. This opening could then be closed immediately before the diaphragm was burst. The reflecting surface was about 3 cm. from the station at which observations of the reflected shock were made.

In all experiments, incident shock velocities were measured using *Schlieren* techniques as before.

The mercury arc light sources and filter combinations have been described before.[7,9,10] However, the Osram HBO 200 high pressure arc which was used with great success previously became unstable in operation, even with new lamps, and was not used very much. In most experiments, the NO_2 concentration was monitored using the Hg 405 or 436 mμ line. For experiments with high concentrations of NO_2, the 546 mμ line was isolated from a Hanovia arc with a Baird multilayer interference filter and a Corning 3486 cut off filter.

NO_2 was prepared as before.[7] Nitric oxide, NO (Matheson), with NO_2 as the principal impurity, was fractionally distilled twice from the liquid at $-150°$ into a trap at $-196°$; the resulting solid was a light gray material, which melted to give a light greenish-blue liquid.

Calculations.—Experiments with incident shocks were made with NO_2–argon mixtures with initial NO_2 mole fractions of 0.023 to 0.15. The methods described previously for calculating the temperature and density from the measured velocity and for correcting for the change in these parameters as the endothermic reaction proceeded were used. Appropriate small corrections for the enthalpy and composition of the unshocked gas due to the equilibrium, $N_2O_4 = 2NO_2$, were made. Initial rates were measured from plots of the photoelectric traces over about the first 15% of reaction.

The reflected shock experiments were done with NO_2 mole fractions of about 0.003, 0.007 and a few at 0.023. In this case, the calculations were made for pure argon. Only in the case of the 0.023 mole fraction would the corrections be significant. However, it would be very difficult to make a proper correction. If observations were made far from the end plate, so that reaction had gone to equilibrium at the end plate, and the reflected shock had reached an appropriate steady value, corrections could readily be made. However, it is undesirable to make observations at a great distance from the end plate because of boundary layer problems and because of possible disturbances due to the "contact surface." Observations are actually made close (3 cm.) to the end plate. Thus if the reaction is being observed, it has not yet gone to completion at the end plate and the rarefaction wave resulting from the endothermic reaction has not slowed down the reflected shock to its final steady value. That is, a steady state has not been achieved. Calculations for the non-steady situation would be very complicated. We have accordingly made calculations assuming the gas was pure argon.[11] The cooling would at most produce a temperature change of 100°K., and the initial rate constant would not be affected very much.

It may be noted that the reflected shock velocities could be obtained from the experimental data (since the passage of both incident and reflected shocks are observed on the oscilloscope trace); these measured velocities agreed with the velocities calculated from the incident velocities.[1] However, because of the large error in the reflected shock velocity measurements, this is not a critical confirmation of the validity of the reflected shock experiments. The best confirmation comes from the agreement between rate data from incident and reflected shock experiments. The reflected shock pictures all looked good and in accordance with ideal shock tube theory.

Results

Extinction Coefficients.—Extinction coefficient data are determined as part of the kinetic records. They are not highly accurate. The results are summarized in Table I. They agree fairly well, but not perfectly, with those given by Schott.[7] As expected, the absorption coefficients near the maximum decrease with increasing temperature; at 546 mμ, on the edge of the absorption band, $d\epsilon/dT > 0$.

TABLE I

EXTINCTION COEFFICIENTS FOR NO_2[b]

T, °K.	300	800	1000	1500	2000
ϵ (405 mμ)[a]	164	140	130	113	95
ϵ (436 mμ)	144	118	112	100	87
ϵ (546 mμ)	29		55	63	

[a] $\epsilon = (1/cl) \log (I_0/I)$, mole^{-1} l. cm.$^{-1}$. [b] The average deviation of the results is about 10%.

Kinetics.—The principal experimental results are values of initial rate constants. Ten groups of reactions were done in which the NO_2 concentration, the argon concentration and their ratio were widely varied. The approximate conditions of each group of experiments are given in Table II where (M) = total gas concentration (argon plus NO_2). Since the compression ratio is a (slowly varying) function of the shock strength, concentrations in the shocked gas varied slightly for constant initial conditions. Exact conditions are given elsewhere.[1a]

TABLE II

RANGE OF EXPERIMENTAL CONDITIONS

Unshocked gas		Shocked gas			
Mole fraction NO_2 ($\times 10^2$)	Pressure (atm.)	(NO_2) mole/l. $\times 10^4$	(A), mole/l. $\times 10^3$	Temp. range, °K.	Wave region[b]
0.28	0.1	0.8	30	1700–2150	r
0.7	.04	0.8	11	1700–2400	r
2.3	.019	1.5	6	1600–2050	r
2.3	.04	1.5	6	1400–1800	i
5.0	.02	1.5	3	1500–2200	i
5.0[a]	.02	1.5	3	1400–1950	i
5.0	.04	3	6	1400–1850	i
10	.01	1.5	1.5	1700–2300	i
10	.02	3	3	1400–1900	i
15	.03	8	4	1350–1450	i

[a] 0.04 mole fraction NO added. [b] r = reflected, i = incident shock.

As we shall see, the evidence indicates that the rate law is

$$\frac{-d(NO_2)}{dt} = k_u(M)(NO_2) + k_b(NO_2)^2 \qquad (8)$$

The k_u term corresponds to a second-order process, first order in (M) (essentially argon) and first order

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[9] D. Britton, N. Davidson and G. Schott, *Disc. Faraday Soc.*, **17**, 58 (1954).

[10] D. Britton, N. Davidson, W. Gehman and G. Schott, *J. Chem. Phys.*, **25**, 804 (1956).

[11] The appropriate equations are given by F. W. Geiger and G. W. Mautz, "The Shock Tube as an Instrument for the Investigation of Transonic and Supersonic Flow Patterns," Engineering Research Institute, Univ. of Michigan, Ann Arbor, 1949 (ONR report).

in NO_2. As discussed later, we believe that it is the unimolecular dissociation of NO_2 at its low pressure, second-order limit. The k_b term is second order in NO_2 and is attributed to a true bimolecular reaction.

In order to plot the data at varying $(M)/(NO_2)$ ratios, an apparent "first order in NO_2" rate constant is defined. The results so calculated are

$$k_9 = -\frac{1}{(M)(NO_2)}\frac{d(NO_2)}{dt} \qquad (9)$$

displayed in Fig. 1. Note that if k_b were zero, $k_9 = k_u$, and k_9 would be an Arrhenius function of the temperature and independent of the gas composition. A similar plot of the defined rate constant could be made.

$$k_{10} = -(1/(NO_2)^2)d(NO_2)/dt \qquad (10)$$

An effort has been made in Fig. 1 to indicate the approximate argon and NO_2 concentrations for each point. This makes the plot necessarily rather complicated. Careful scrutiny of Fig. 1 and of the corresponding plot for k_{10} reveals that the points at low NO_2 mole fractions, 2.8×10^{-3} and 7.0×10^{-3}, at the higher temperatures fit the k_9 interpretation and indicate a high activation energy. For the 2.8×10^{-3} mole fraction points, this is 57 kcal. mole^{-1}. The points at high NO_2 mole fractions (0.05, 0.10, 0.15), particularly at lower temperatures, fit the k_{10} interpretation better and indicate a low (23 ± 4 kcal.) activation energy.

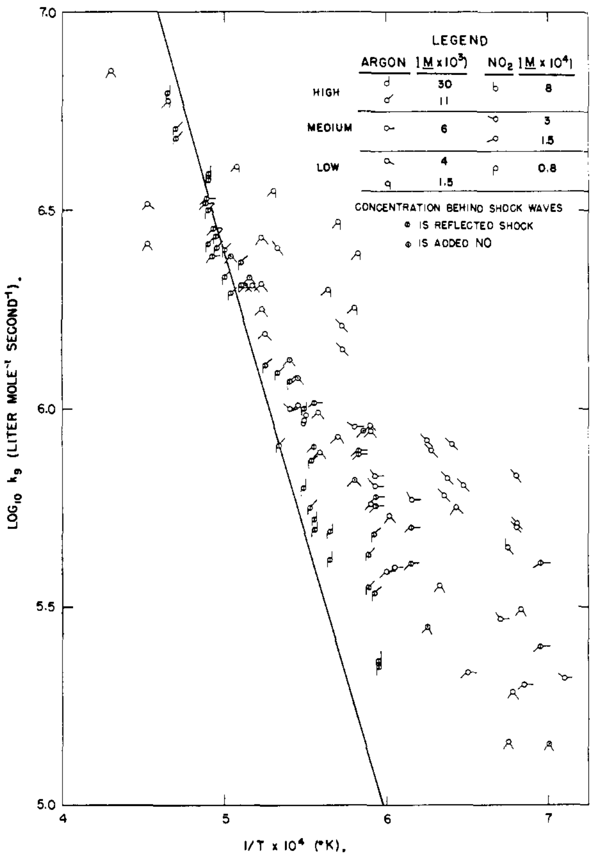


Fig. 1.—Observed rate constants calculated assuming $-d(NO_2)/dt = k_9(M)(NO_2)$.

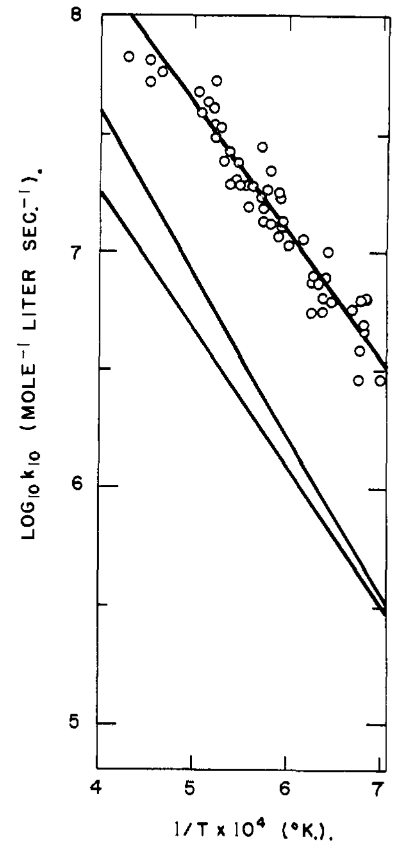


Fig. 2.—Values for k_b from $-d(NO_2)/dt = k_b(NO_2)^2$ for high NO_2 mole fraction experiments.

Theory indicates that the local activation energy for the unimolecular process (k_u) should be about 65.4 kcal. mole^{-1} near 2000°K. Once k_u is known, values of k_b can be calculated from the data in Fig. 1 by the relation, $k_b = ((M)/(NO_2))(k_9 - k_u)$. By a trial process, a line for k_u with a slope corresponding to an activation energy of 65.4 was chosen so as to give a good fit for k_b. This expression is

$$k_u = 3.06 \times 10^{13} \exp(-65{,}400/RT) \text{ mole}^{-1}\text{ l. sec.}^{-1} \qquad (11)$$

and is the straight line in Fig. 1. Clearly the value of k_u affects only the high temperature results. The points on the Arrhenius plot for the values of k_b thus calculated show a fair amount of scatter, but it is significant that the points with low NO_2 mole fractions (0.0028, 0.007, 0.023) are now much more consistent with the data from the high NO_2 mole fractions. When the points at high NO_2 mole fractions (0.05, 0.10, 0.15) are graphed by themselves, they give a quite good straight line plot (Fig. 2) from which

$$k_b = 2.5 \times 10^{10} \exp(-25{,}000(\pm 5000)/RT) \text{ mole}^{-1}\text{ l. sec.}^{-1} \qquad (12)$$

Discussion

The Unimolecular Dissociation.—The term in the rate law, $k_u(A)(NO_2)$, is reasonably attributed to the mechanism

$$A + NO_2 \underset{k_{6r}}{\overset{k_{6d}}{\rightleftharpoons}} A + NO + O \qquad (6)$$

$$O + ONO \xrightarrow{k_7} O_2 + NO \qquad (7)$$

At high temperatures, the reverse of (6) is unimportant. Ford and Endow[12] give $k_7 = 2 \times 10^9$ mole^{-1} l. sec.$^{-1}$ at 300°K. A simple transition state argument suggests that k_7 increases approximately as either $T^{1/2}$ or T, so we guesstimate $k_7 = 5 \times 10^9$ mole^{-1} l. sec.$^{-1}$ at 2000°K. With $(NO_2) = 10^{-4}$ mole l.$^{-1}$, the average lifetime of an O atom for reaction 7 is therefore 2 μsec. With $k_{6d} = 3 \times 10^6$ mole^{-1} l. sec.$^{-1}$ and $(A) = 3 \times 10^{-2}$, which corresponds to the fastest reaction rates measured (*cf.*, Fig. 1), the mean reaction time is about 10 μsec. Thus possibly for the very fastest reactions measured, reaction 7 was not quite but almost in a steady state with respect to (6). For all other cases, (7) was certainly adequately fast, so that $k_u = 2k_{6d}$. Therefore

$$k_{6d} = k_u/2 = 1.5 \times 10^{13} \exp(-65{,}400/RT) \text{ mole}^{-1} \text{ l. sec.}^{-1} \quad (13)$$

We may compare this result with an extrapolated, calculated value based on the measurement of the reverse rate by Ford and Endow. They give $k_{6r} = 1.8 \times 10^{10}$ mole^{-2} l.^{2} sec.$^{-1}$ at 300°K. with N_2 as the "third body" M. The classical version of the Rice, Ramsperger, Kassel theory suggests for a reaction like (6)

$$k_{6d} = Z\left(\frac{E_0}{RT}\right)^{s-1} \frac{1}{(s-1)!} \exp(-E_0/RT) \quad (14)$$

where Z is a collision number and s is the number of effective oscillators—in this case three. For E_0 we take $\Delta E_0{}^0 = 71{,}400$ cal. The term in front of the exponential varies as $1/T^{3/2}$. (The Slater theory of unimolecular reactions gives a similar expression, perhaps with a smaller value of s. It is plausible that an available energy treatment such as that of RRK is better than the critical coördinate treatment of Slater for a simple molecule.)

The equilibrium constant for reaction 6 can be expressed in the form

$$K_6 = \frac{Q_O Q_{NO}}{Q_{NO_2}} \exp(-\Delta E_0{}^0/RT) \quad (15)$$

where the Q's are partition functions. The vibrational partition function for NO_2 is due to two stretches and one bend. Assume that for the stretching frequencies, $Q_{vib} \sim 1$; for the bend, $Q = kt/h\nu$. Considering the contributions of rotation and translation, the equilibrium constant is of the form $K_6 = F \exp(-\Delta E_0{}^0/RT)$, where F is temperature independent. In view of (14), $k_{6r} \sim 1/T^{3/2}$. Assume that argon is about one-half as effective as N_2 as a third body; therefore

$$k_{6r}\,(300°, \text{A}) = 1.0 \times 10^{10} \text{ mole}^2 \text{ l.}^{-2} \text{ sec.}^{-1} \text{ and}$$

$$k_{6r}\,(\text{A}) = 5.2 \times 10^{13}/T^{3/2} \text{ mole}^2 \text{ l.}^{-2} \text{ sec.}^{-1} \quad (16)$$

From standard thermodynamic data,[13-15] the equilibrium constant for (6) at 2000°K. is 1.15×10^{-3} mole l.$^{-1}$, and we may write $K_6 = 7.3 \times 10^4 \exp(-71{,}400/RT)$. We therefore calculate from the low temperature value of k_{6r}

$$k_{6d} = (3.8 \times 10^{18}/T^{3/2}) \exp(-71{,}400/RT) \text{ mole}^{-1} \text{ l. sec.}^{-1} \quad (17)$$

The expression 13 for the high temperature rate data in the neighborhood of 2000°, when recast in the form expressed by equation 14, gives

$$k_{6d} = (6.0 \times 10^{18}/T^{3/2}) \exp(-71{,}400/RT) \quad (18)$$

Thus the extrapolated (17) and experimental (18) high temperature data agree remarkably well. Equation 14 above can be rewritten as

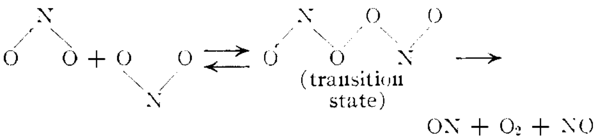
$$k_{6d} = Z_{1000}\left(\frac{T}{1000}\right)^{1/2}\left(\frac{E_0}{RT}\right)^2\left(\frac{1}{2}\right) \exp(-E_0/RT)$$

where Z_{1000} is the collision number at 1000°. Numerical evaluation from (18) gives $Z_{1000} = 2.9 \times 10^{11}$ mole^{-1} l. sec.$^{-1}$, which is quite reasonable.

In the interpretation above, we have not attempted to consider the effect of possible differences between NO_2 itself and A as energy transfer agents for reaction 6. Because of the low $(NO_2)/(A)$ ratios, it is unlikely that any special effects due to NO_2 would be evident.

Thus we may say that the interpretation of the high temperature, high dilution, $k_u(M)(NO_2)$ term in the rate law as being due to the unimolecular dissociation of NO_2 at its low pressure limit followed by reaction 7 is quite satisfactory.

The Bimolecular Path.—It is natural to try to attribute the bimolecular term in the rate law, $k_b(NO_2)$,^{2} to the "Bodenstein mechanism," which we picture in detail as



In ref. 3 (HJPP), a detailed transition state analysis for this reaction is given. The empirical rate law around 570°K. is $k_{1b} = 4.0 \times 10^9 \exp(-26{,}900/RT)$ mole^{-1} sec.$^{-1}$. This is the lowest straight line in Fig. 2. The middle curve in the figure is calculated from the transition state theory using the frequency assignment and structure for the transition state given by HJPP. It too is lower than the experimental curve.

The transition state expression is

$$k_{1b}/2 = \frac{kT}{h} \frac{Q(N_2O_4{}^*)}{Q(NO_2)^2} \exp(-E_0/RT) \quad (19)$$

where the Q's are partition functions. The assignment of HJPP gives $E_0 = 25{,}900$ cal. mole^{-1}. A simple approximate argument in which vibrational partition functions are cancelled when their frequencies are close and are taken as having the limiting form, $kT/h\nu$, for low frequencies, indicates that k_{1b} can be approximately represented by $k_{1b} \sim T^{3/2} \exp(-E_0/RT)$ at the higher temperatures, which explains why the transition state extrapolation lies above the simple Arrhenius extrapolation. (However the transition state extrapolation in Fig. 2 is based on an exact calculation of the partition functions using the HJPP frequencies and not on the approximate representation given above.)

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(12) H. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1156 (1957).

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

(14) H. W. Wooley, "The NBS-NACA Tables of Thermal Properties of Gases," National Bureau of Standards, Washington, D. C., Tables 15.10 and 15.11, 1950.

(15) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., Circular 500, Series 1, 1952.

The question now is whether there is some other bimolecular reaction path since the extrapolated k_{1b} rate constants are less than the experimental ones (k_b) by a factor of about 8 (at *ca.* 1667°K.).

One such possibility is the Ashmore and Levitt (AL) path (reactions 3, 4, 5). The rate law for this is

$$-\frac{1}{(NO_2)^2}\frac{d(NO_2)}{dt} = \frac{2k_3}{1 + k_4(NO)/k_5(NO_2)} \quad (20)$$

According to AL, at 707°K., $2k_3 = 26$ mole^{-1} l. sec.$^{-1}$ and $k_4/k_5 = 60$, whereas $2k_{1b} = 19.4$. Thus the two mechanisms contribute approximately equally to the initial rate.

The ratio $k_4/k_5 = 60$ implies that when NO has accumulated so that $(NO)/(NO_2) > 1/60$, the NO_3 reaction path is suppressed compared to the Bodenstein path.

The available information from studies of other reactions[6,7] (mainly $N_2O_5 = NO_2 + NO_3$) indicates that ΔE for reaction 3 is 23,000 cal. Kinetic information about the reverse rate constant, k_4, indicates an activation energy close to zero.[16] Thus the indirect evidence indicates that $E_3 - E_{1b} = -4$ to 0 kcal. However, AL report[17] from direct experiments, $E_3 - E_{1b} = 3 \pm 3$ kcal. The direct experiments are difficult and we are inclined to accept the evidence from the other studies on NO_3 that the activation energy for (3) is slightly less than or at most equal to that for reaction 1. Since the two rates are comparable at 707°*K*., it is probable that the NO_3 process would make at most an equal contribution with the Bodenstein mechanism at high temperatures, but the possibility that the NO_3 process contributes more than this is not absolutely excluded.

The activation energy difference $E_5 - E_4$ is at most the value of E_5 of 3900 cal. so that at 1750, $k_4/k_5 \geq 12$. Thus NO should still be a potent inhibitor for the NO_3 reaction path at the high temperatures of the present investigation. It is possible, however, that some other reaction faster than (5) destroys NO_3 at the high temperatures. An attractive possibility is the unimolecular decomposition of NO_3 at its low pressure limit.[7]

$$NO_3 + M \underset{k_{21r}}{\overset{k_{21d}}{\rightleftarrows}} NO_2 + O + M \quad (21)$$

Consideration of the nature of the partition functions suggests that the equilibrium constant for reaction 21 can be approximately represented as $K_{21} = AT^{-1/2}\exp(-\Delta E_0^0/RT)$. The low temperature data[7] then give $K_{21} = 1.9_5 \times 10^7\ T^{-1/2}\exp(-49{,}600/RT)$ mole l.$^{-1}$, or $K = 0.29$ (1750°K.). Ford and Endow report $k_{21r} = 10^{11}$ mole^{-2} l.^{2} sec.$^{-1}$ at 298°K., and we surmise $k_{21r} \sim T^{-3/2}$, so that $k_{21r} = 5.2 \times 10^{14}\ T^{-3/2}$. This gives a reasonable expression for k_{21d}

$$k_{21d} = 10^{22}\ T^{-2}\exp(-49{,}600/RT)\ \text{mole}^{-1}\ \text{l. sec.}^{-1} \quad (22)$$

or $k_{21d} = 2 \times 10^9$ at 1750°K.

If reaction 21 replaces (5), the rate law for the NO_3 path is

$$-\frac{1}{(NO_2)^2}\frac{d(NO_2)}{dt} = \frac{2k_3}{1 + k_4(NO)/k_{21d}(A)} \quad (23)$$

From the estimate of Schott and Davidson,[7] $k_4 = 4 \times 10^{10}$ mole^{-1} sec.$^{-1}$ at 1750°K. Using the values of (NO) and (A) present in the experiments with added NO (where no significant inhibition was observed), $k_4(NO)/k_{21d}(M) \sim 1$ at 1750°K. Thus indeed, as regards the absence of inhibition by NO, the NO_3 reaction path might be important at 1750°. At the lowest temperature of this investigation (1400°K.), k_{21d} is about 1/50 of its value at 1750°K. This is still large enough to be a fast follow reaction for reaction 3, but NO would now certainly be a potent inhibitor. Unfortunately, this important point was recognized after the experimental work was concluded and this crucial test of the modified NO_3 reaction path has not been adequately performed.

Comparison with Other Work.—As previously noted, the results of Steinburg and Lyon[8] on the same system over the same temperature range are somewhat different. They find all their data may be accounted for by the rate expression

$$k_{SL} = -\frac{1}{(NO_2)(A)}\frac{d(NO_2)}{dt} = 3.82 \times 10^{11}\exp(-46{,}000/RT)\ \text{mole}^{-1}\ \text{l. sec.}^{-1} \quad (24)$$

Near 2000°K., the results are in agreement. The expression above gives $k_{SL} = 3.4 \times 10^6$ mole^{-1} l. sec.$^{-1}$, whereas in Fig. 1, we give $k = 2.7 \times 10^6$. If our interpretation of the data is correct, the activation energy of 46,100 observed by SL is an average of the activation energies of the high temperature $k_u(A)(NO_2)$ term with an activation energy of 65,000 cal. and the low temperature $k_b(NO_2)^2$ term with an activation energy of 25,000 (±5000) cal.

The bright yellow-orange light emission observed by Steinburg and Lyon[8] also was observed in all of our experiments. This emission was distinctly seen under normal laboratory lights. An extensive study was not made. A few photoelectric oscilloscope traces indicated that the light emission decreased as (NO_2) decreased. This emission interfered with the light absorption measurements only at 546 mμ where appropriate small corrections were made.

Conclusion.—In summary, then, it is believed that the most reasonable interpretation of the shock tube experiments, taking into account the experimental data, extrapolation of other results and general theoretical considerations, is that NO_2 is decomposing by two paths. One is the unimolecular decomposition of NO_2 into NO and O with a rate law $-d(NO_2)/dt = k_u(NO_2)(M)$ and an activation energy of about 65 kcal. The second is a bimolecular decomposition, $-d(NO_2)/dt = k_b(NO_2)^2$, with an activation energy of 25 ± 6 kcal. It should be re-emphasized that the random error in our shock tube experiments is rather large, so that the above conclusions have not been established with as much certainty as is desirable. However, the data do strongly support the interpretation given.

The phenomenon encountered is characteristic of high temperature reactions, namely, that a high activation energy, high steric factor reaction path replaces a low activation energy, low steric factor path as the temperature is raised.

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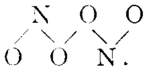
[16] I. C. Hisatsune, B. Crawford and R. A. Ogg, THIS JOURNAL, **79**, 4648 (1957).

[17] Private communication.

The observed bimolecular rate constants are greater by a factor of eight than extrapolated values for the bimolecular "Bodenstein" mechanism, for which the transition state is believed to be



It seems unlikely, but not entirely excluded, that this is due to an error in extrapolation. Possibly a simple extension of the Ashmore and Levitt NO_3 mechanism, including reaction 21, can account for the additional reaction path. However, the data now available indicate that this should increase the extrapolated rate only by a factor of two. Possibly there is some other as yet unrecognized reaction path. Possibly the discrepancy is in the present work. This question requires further work, but the present investigation has fairly definitely established the occurrence of both unimolecular and bimolecular reaction paths.

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PASADENA, CALIFORNIA

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

The Effect of Deuterium on the Kinetics of Reactions Involving Neptunium(IV), (V) and (VI) Ions[1]

BY J. C. HINDMAN, J. C. SULLIVAN AND DONALD COHEN

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The rate of neptunium(IV)–neptunium(VI) reaction is markedly decreased in both sulfate and perchlorate solutions by the addition of deuterium. The ratio of the observed rate constants for perchlorate solutions at 25° is $k_H/k_D = 5.0$. The similarity of the effect in both sulfate and perchlorate solutions lends support to the previous suggestions that the mechanism is the same in both media. The disproportionation rate of neptunium(V) in sulfate solution is increased by deuterium. The interpretation of the isotope effect in terms of possible pre-equilibria and reaction intermediates is discussed.

Introduction

As a result of studies on the kinetics of the reactions involving Np(IV), Np(V) and Np(VI) in both perchlorate[2] and sulfate[3] media, it has been suggested that the mechanism of the reaction is governed by the tendency of the reacting ions to attain and maintain a configuration close to the O–M–O structure. With this basic assumption, strong arguments can be made against mechanisms which involve either oxygen or hydroxyl atom transfer. Either an electron transfer or a hydrogen atom transfer process would be possible mechanisms.

To shed further light on this problem we have undertaken an investigation of the reactions of the Np(IV), (V) and (VI) ions in deuterium solutions. A large isotope effect has been observed. The magnitude of the isotope effect is essentially the same in either perchlorate or sulfate media. This lends support to the suggestion that the mechanism of reaction is probably the same in the two media.[3]

Experimental

The preparation of stock solution of neptunium and the general experimental techniques have been described in previous publications.[2,3] The deuterio-sulfuric acid used in the present investigation was obtained through the courtesy of Dr. J. J. Katz of this Laboratory. The deuterioperchloric acid was prepared as previously described.[4]

Results

I. The Np(IV) + Np(VI) → 2Np(V) Reaction.—The order of the reaction with respect to each of the metal ions has been determined previously.[2,3] The reaction is bimolecular both in perchlorate and sulfate media. The rate constant, k_{obsd}, in the present work therefore was calculated by means of the integrated equation for a bimolecular reaction.

The Effect of Acid Concentrations.—Table I summarizes the data on the effect of acid concentration on the rate of the reaction. Least squares analysis yields a value for n in the equation

$$k_{obsd} = k[H^+]^n \qquad (1)$$

of -2.140 ± 0.022 (99% confidence level) for the hydrogen containing solutions and of -2.154 ± 0.022 (99% confidence level) for the 95% deuterium solutions. Within experimental error there is no significant effect of deuterium on the acid dependence of the reaction. The data in perchlorate solution may be analyzed in terms of more than a single reaction path. Least squares treatment of the data yields values of the rate constants for the equation

$$k_{obsd} = k_1[H^+]^{-2} + k_2[H^+]^{-3} \qquad (2)$$

in the hydrogen medium, $k_1 = 4.27 \times 10^{-2}$ mole liter^{-1} sec.$^{-1}$ and $k_2 = 5.04 \times 10^{-3}$ mole^2 liter^{-2} sec.$^{-1}$. In the deuterium solutions, $k_1 = 8.56 \times 10^{-3}$ mole liter^{-1} sec.$^{-1}$ and $k_2 = 1.02 \times 10^{-3}$ mole^2 liter^{-2} sec.$^{-1}$.

The Effect of Deuterium Concentration.—Examination of Table I shows that there is a significant effect of deuterium on the reaction rate. Table II illustrates this in more detail. A plot of the observed rate against the percentage of deute-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, **76**, 3278 (1954).

[3] J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **79**, 4029 (1957).

[4] J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **79**, 3672 (1957).