sole product, and its presence was demonstrated up to 325°. It is conceivable that more refined experimental methods would detect it at even higher temperatures. The annealing experiments show that the transition from ϵ- to χ-carbide *in vacuo* is sufficiently rapid to account for the absence of ϵ-carbide from most fully carbided iron catalysts, especially since the rate of carbiding decreases rapidly with the extent of carbiding. Moreover, the decreasing ratio of ϵ- to χ-carbide with increasing temperature may be accounted for on the basis that much, if not all, of the χ-carbide found at higher temperatures was originally ϵ-carbide.

Merkel and Weinrotter[9] found ϵ-carbide as the initial carbide in copper-containing iron catalysts that had been used in synthesis at 220°. They also observed that the ϵ-carbide was transformed to χ-carbide as the synthesis proceeded: Between 3.5 and 10 hours, about 10% of the ϵ-carbide was converted to χ-carbide. Their rate of transition from ϵ- to χ-carbide is not much different from the rates observed in the present study of copper-free catalysts, indicating that in their catalyst, at least, copper did not appreciably affect the rate of transition. Furthermore, the fact that they found ϵ-carbide under conditions where the transition took place indicates that ϵ-carbide may be the precursor of χ-carbide not only in an atmosphere of carbon monoxide but also in synthesis gas.

As mentioned in footnote *b* of Table I, the catalyst treated for 0.5 minute at 350° could not be analyzed magnetically for ϵ-carbide because of the presence of cementite. The synthesis of cementite from higher iron carbide and free iron is known to proceed at that temperature[8]; hence it is reasonable to assume that χ-carbide (and, indirectly, ϵ-carbide) is a precursor of cementite during the carbiding of iron.

The mechanism of the carbiding of iron catalysts may be closely related to the mechanism of the tempering of martensitic steels. ϵ-Carbide has been found[10] as an intermediate in the decomposition of martensite, which is therefore a precursor of ϵ-carbide in that reaction. It is conceivable that martensite, or a martensite-like substance, is also a precursor of ϵ-carbide in the carbiding reaction. If, as is likely, carbide nuclei are formed in the interior of crystallites of α-iron, carbon must diffuse from the surface through α-iron. It is known that carbon diffuses through α-iron only as carbon atoms. The solid solution of carbon in iron resulting from such diffusion cannot deposit carbon in ϵ-carbide unless it is supersaturated with respect to ϵ-carbide. Since martensite is a solid solution of carbon in α-iron which can contain enough carbon to deposit ϵ-carbide and which decomposes in about the right temperature range, martensite may be the precursor of ϵ-carbide in carburization.

Acknowledgment.—Thanks are due to Mrs. W. C. Peebles for X-ray diffraction analyses.

BRUCETON, PA.

[9] H. Merkel and F. Weinrotter, *Brennstoff-Chem.*, **32**, 289 (1951).

[10] K. H. Jack, *Acta Cryst.*, **3**, 392 (1950).

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

Kinetics of the Exchange of N^{15} between $N^{15}O_2$ and N_2O_5[1]

BY ALEXANDER R. AMELL AND FARRINGTON DANIELS

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The rate of the exchange reaction $N^{15}O_2 + N_2O_5 \rightarrow NO_2 + N^{15}NO_5$ in the gas phase has been followed at −9, 0 and 10° using chemical separations and a mass spectrometer. The equation $k = 6.0 \times 10^{12}\, e^{-19,000/RT}$ can be used to express the experimental data. The agreement between this reaction rate and that for the reaction between nitrogen pentoxide and nitric oxide leads to the conclusion that the first step in both reactions is the bond-breaking step $N_2O_5 \rightarrow NO_2 + NO_3$. No effect of total pressure on the specific rate constants for isotopic exchange at low pressures was found, but no conclusions can be drawn concerning the existence of a pressure effect. Qualitative experiments are described in which the rate of decomposition of nitrogen pentoxide is increased by several gaseous reducing agents, as well as by nitric oxide.

In an effort to clear up some of the unanswered questions on the decomposition of N_2O_5, Smith and Daniels studied the rapid bimolecular reaction between NO and N_2O_5. As a result of this study Smith, in his Ph.D. thesis,[2] proposed the following mechanism for the N_2O_5 decomposition:

$$N_2O_5 \longrightarrow NO_2 + NO_3 \qquad (1)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \qquad (2)$$

$$NO_3 \longrightarrow NO + O_2 \qquad (3)$$

$$NO_3 + NO \longrightarrow 2NO_2 \qquad (4)$$

Smith pointed out that this mechanism leads to a rate equation in which the decomposition of N_2O_5 is dependent on the concentration of NO_2, while the experimentally found decomposition is independent of the NO_2 concentration. Smith and Daniels proposed the same mechanism with the elimination of equation (3) as fitting the experimental data for the $NO + N_2O_5$ reaction.[2-4]

In 1947, Ogg offered a clever explanation for the independence of the rate of decomposition of N_2O_5 on NO_2.[5] By the addition of NO_2 to both sides of equation (3) above (which then becomes $NO_3 + NO_2 \rightarrow NO + O_2 + NO_2$) he obtained a mechanism leading to a rate equation in which the decomposition of N_2O_5 is independent of the concentration of NO_2. Ogg also reported the exchange of N^{13} between N_2O_5 and $N^{13}O_2$ in CCl_4 solution as the first experimental evidence of the reversibility of the first step, *i.e.*, $N_2O_5 \rightarrow NO_2 + NO_3$.

It seemed desirable to use the stable isotope N^{15}

[1] Further details of this investigation may be obtained from the Ph.D. thesis of Alexander R. Amell, filed in the Library of the University of Wisconsin, September, 1950.

[2] J. H. Smith, Ph.D. Thesis, University of Wisconsin, June, 1941.

[3] J. H. Smith, St. Louis Meeting, Am. Chem. Soc., April 9, 1941.

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

[5] R. A. Ogg, *J. Chem Phys.*, **15**, 337, 613 (1947)

to check the reversibility of this step in the gas phase, and also to study the kinetics of the initial step $N_2O_5 \rightarrow NO_2 + NO_3$. If the proposed mechanism is correct, the rate equation for this step should be the same as the rate equation obtained for the $NO + N_2O_5$ reaction on the theory that NO would react with NO_3 very rapidly, preventing the reverse reaction; and thus the rate determining step for the $NO + N_2O_5$ reaction would be the initial bond-breaking of the N_2O_5.

Experimental

The reaction was carried out in a Pyrex reaction vessel fitted with a side-arm, acting as an $N^{15}O_2$ reservoir and connected to a manometer. A second arm with a stopcock led to an N_2O_5 reservoir. A third side-arm connected by a stopcock led to a reservoir from which a solution of sodium hydroxide was admitted after a specified time interval. The N_2O_5 was prepared from the oxidation of NO_2 with ozone. The NO_2 was obtained from commercial tanks of the liquefied gas. The $N^{15}O_2$ was obtained from $KN^{15}O_3$ (purchased from the Eastman Kodak Co.) in the following manner: A sample of $KN^{15}O_3$ was dissolved in 85% H_3PO_4 and a coil of Cu wire dropped in. The gases evolved were pumped through a trap immersed in liquid air. When the reaction had stopped, air was admitted to the trap which was warmed to room temperature to oxidize any NO formed. About 90% of the theoretical yield of $N^{15}O_2$ was obtained.

The N_2O_5 was introduced into the reaction vessel by warming the solid crystals, and the pressure of the gas determined with a mercury manometer. The stopcock to the $N^{15}O_2$ reservoir was opened and the $N^{15}O_2$ admitted to the reaction vessel to start the reaction. The amount of $N^{15}O_2$ in the reservoir had been previously determined by pressure measurements, and checked by the weight loss of the trap from which the $N^{15}O_2$ had been admitted to the reservoir. The exchange reaction was stopped after a suitable period of time by introducing NaOH solutions into the reaction vessel. This procedure gives a solution of $NaNO_3$ and $NaNO_2$. All of the N_2O_5 gives $NaNO_3$ while approximately one-half of the NO_2 gives $NaNO_3$ and the other half, $NaNO_2$. The $NaNO_2$ is removed by the addition of sulfamic acid. The $NaNO_3$ remaining is reduced by Devarda alloy to NH_3 which is then decomposed to N_2 by NaOBr. The ratio of N^{15} to N^{14} was obtained with a mass spectrometer in the laboratory of Professor R. G. Burris, given to the University of Wisconsin by the Thomas E. Brittingham Foundation.

The atomic fraction of excess N^{15} in the N_2O_5 at the end of the reaction is the desired quantity. This is obtained as follows

D = total moles of N^{15} used in the reaction, as obtained from the initial concentration of $N^{15}O_2$ and the isotopic analysis of the $N^{15}O_2$

F = moles of N^{15} in the nitrate as obtained from the total concentration of nitrate (*i.e.*, twice the moles of N_2O_5 plus one-half the moles of NO_2) and the isotopic analysis of the nitrate

Then $D - F = G$ = moles of N^{15} in the nitrite = moles of N^{15} in the nitrate coming from the NO_2

Also, $D - 2G$ = moles of N^{15} in nitrate coming from N_2O_5

In order to use this method of separation it is necessary that no exchange of N^{15} between nitrate and nitrite occur in solution. Experiments were performed in which solutions of $KN^{15}O_3$ and KNO_2 were mixed and allowed to stand for 30 minutes. This is a much longer time than needed to perform the nitrate–nitrite separation described above. The nitrogen from the nitrite was then analyzed and found to be isotopically normal, indicating that no exchange of nitrogen occurred during the separation.

There is one serious objection to using this method of separation and analysis. To get the N^{15} concentration in the N_2O_5 the difference between two numbers of the same magnitude is being taken $(D - 2G)$. Thus, a small percentage error in the original measurements is magnified to give a very large possible error in the final result. However, since these initial errors are random errors the average of a series of experiments should give a good approximation of the rate constant desired. Other methods of separation were tried but discarded because isotopic exchange was found to occur during the separation.

Once it had been determined that the exchange of N^{15} did occur (indicating that the equilibrium $N_2O_5 \rightleftarrows NO_2 + NO_3$ does exist in the gas phase) the rate of the initial bond-breaking step $N_2O_5 \rightarrow NO_2 + NO_3$ could be determined by measuring the rate of appearance of N^{15} in the N_2O_5, as determined by isotopic analysis of the nitrate. The equation used for this is[a]

$$-k = \frac{2.303}{t}\,\frac{2b}{2a+b}\log\left(1 - \frac{x}{x_\infty}\right)\ \text{sec.}^{-1} \qquad (5)$$

where k = rate constant for the step $N_2O_5 \rightarrow NO_2 + NO_3$; t = time in seconds; a = total concentration of N_2O_5; b = total concentration of NO_2; x = concentration of N^{15} in N_2O_5 at time t; x_∞ = concentration of N^{15} in N_2O_5 at equilibrium.

The complete calculations for one typical experiment are

Temperature of experiment, °C.	0.0
Volume of cylindrical reaction vessel, ml.	138
Pressure of N_2O_5, mm.	25
Mole of N_2O_5	2.00×10^{-4}
Mole of $N^{15}O_2$	3.43×10^{-4}
Atomic fraction of excess N^{15} in NO_2	0.306[b]
Total mole of N^{15}	1.05×10^{-4}
Total mole of N	7.43×10^{-4}
Atomic fraction of excess N^{15} in N_2O_5 at equilibrium	0.141[b]
Total mole of nitrate formed	5.71×10^{-4}
Atomic fraction of excess N^{15} found in nitrate	0.125[b]
Mole of N^{15} in nitrate	7.14×10^{-5}
Mole of N^{15} in nitrite	0.34×10^{-4}
Mole of N^{15} in N_2O_5	0.37×10^{-4}
Atomic fraction of N^{15} found in N_2O_5	0.0930
Ratio: (atomic fraction N^{15} found in N_2O_5)/(atomic fraction at equilibrium)	0.666
Time of reaction, seconds	125
k (from equation (5)), sec.$^{-1}$	0.0081

The initial bond-breaking step $N_2O_5 \rightarrow NO_2 + NO_3$ was found to be a very rapid reaction. Experiments were performed at −9, 0 and at 10° as recorded in Tables I, II and III. Assuming no entropy of activation for this bond-breaking step,

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[a] FOOTNOTE: The derivation of equation (5) follows: In addition to the symbols above: y = concentration of N^{15} in NO_2 at time t; w = concentration of N^{15} in NO_3 at time t; u = total concentration of NO_3; then dx/dt = (rate of formation of N_2O_5) (atomic fraction of N^{15} in $NO_2 + NO_3$) − (rate of decomposition of N_2O_5)(atomic fraction N^{15} in N_2O_5).

The atomic fraction of N^{15} in the NO_2 and NO_3 is $(y + w)/(b + u)$ but since there is very little NO_3 as compared to NO_2, w and u are small compared to y and b, respectively, and we can use y/b instead of $(y + w)/(b + u)$. The atomic fraction of N^{15} in the nitrogen of N_2O_5 is $x/2a$. Equilibrium between N_2O_5 and its dissociation products NO_2 and NO_3 is quickly reached (although the time required for isotopic exchange equilibrium is longer) and so the rate of formation, R, of N_2O_5 equals the rate of decomposition of N_2O_5. Also, $R = ka$. Then the rate of change of N^{15} in the N_2O_5 is given by the expression

$$\frac{dx}{dt} = R\left(\frac{y}{b}\right) - R\left(\frac{x}{2a}\right)$$

Integrating and evaluating the integration constant

$$\frac{-Rt}{2ab} = \frac{1}{2a+b}\ln\left(1 - x\Big/\frac{2az}{2a+b}\right)$$

where $z = x + y$ = total N^{15}. The quantity $z/(2a + b)$ is the fraction of the total nitrogen which is N^{15}, and since N_2O_5 is only slightly dissociated $2az/(2a + b)$ is the amount of N^{15} in the N_2O_5 after the equilibrium with the N^{15} has been established. Signifying this by x_∞ and since $R = ka$

$$-k = \frac{2.303}{t}\,\frac{2b}{2a+b}\log\left(1 - \frac{x}{x_\infty}\right) \qquad (5)$$

[b] All data on N^{15} are given as excess N^{15}, obtained by subtracting the atomic fraction of N^{15} in normal nitrogen from the total atomic fraction of N^{15} in the nitrogen of the sample.

TABLE I

Temperature 0°; 138-ml. cylindrical reaction vessel; 30.6 atom % N^{15} in NO_2

Total pressure, mm.	Moles N_2O_5 × 10^4	Moles NO_2 × 10^4	Atom % N^{15} in nitrate	Atom % N^{15} in N_2O_5	Time, sec.	k × 10^3, sec.$^{-1}$
53	2.00	3.43	12.5	9.30	125	8.1
44	1.60	3.03	13.4	10.5	205	5.8
63	3.26	2.80	7.30	4.69	196	2.3
56	3.19	2.03	7.14	6.80	153	8.0
65	3.14	3.16	7.50	3.41	161	1.7
57	3.09	2.26	7.50	6.57	159	5.4
66	1.82	3.78	14.2	11.4	285	5.0
					Av.	5.2 ± 0.8[a]

[a] Errors are given as probable errors.

TABLE II

Temperature 10°; 138-ml. cylindrical reaction vessel; atom % N^{15} in NO_2: 8.18% in first four, 9.71% in second four

Total pressure, mm.	Moles N_2O_5 × 10^4	Moles NO_2 × 10^4	Atom % N^{15} in nitrate	Atom % N^{15}in N_2O_5	Time, sec.	k × 10^3, sec.$^{-1}$
131	7.22	4.09	1.42	0.945	63	5.2
118	5.97	4.40	2.03	1.71	71	15.5
104	4.46	5.03	2.76	2.48	63	23.0
88	4.19	3.59	2.31	2.10	53	21.7
109	5.51	4.08	2.21	1.62	62	8.5
133	6.65	5.18	2.44	2.05	53	14.9
134	6.90	4.95	2.06	1.38	56	7.3
113	5.61	4.45	2.57	2.32	59	17.7
					Av.	14.2 ± 2[a]

[a] Errors are given as probable errors.

TABLE III

Temperature −9°[b]; 226-ml. spherical reaction vessel; atom % N^{15} in NO_2: 9.17% in first three, 7.25% in next five, 11.6% in last one

Total pressure, mm.	Moles N_2O_5 × 10^4	Moles NO_2 × 10^4	Atom % N^{15} in nitrate	Atom % N^{15} in N_2O_5	Time, sec.	k × 10^4, sec.$^{-1}$
35	1.54	5.22	4.66	0.682	297	5
39	2.79	3.97	3.44	2.37	303	24
40	2.95	4.17	2.96	1.14	260	11
45	2.94	5.35	2.91	1.80	242	29
37	2.38	4.32	2.56	0.78	238	10
35	1.54	5.27	3.63	1.04	241	14
40	2.59	4.60	3.00	2.20	227	43
38	2.53	4.32	2.52	1.11	236	16
46	3.78	3.97	3.37	2.41	308	21
					Av.	19 ± 4[a]

[a] Errors are given as probable errors. [b] Temperature of individual experiments varied by as much as one degree but all constants are corrected to a common temperature of −9°.

a frequency factor of RT/Nh (or 6 × 10^{12} sec.$^{-1}$) is obtained which is normal for a simple unimolecular reaction. Using this frequency factor, it is possible to express the data reasonably well with the equation

$$k = 6 \times 10^{12}\, e^{-19{,}000/RT} \text{ sec.}^{-1}$$

This equation agrees within the limits of experimental accuracy with the data obtained by Smith and Daniels,[4] and with later data obtained by Mills and Johnston for the NO + N_2O_5 reaction.[6] This is to be expected for the reasons mentioned above. It is also in agreement with the limited data published by Ogg.[7] The activation energy calculated by the Arrhenius equation is 16,000 calories but the data are so discordant that the value of 19,000 is probably more accurate.

According to the Rice–Ramsperger–Hinshelwood–Kassel theory of unimolecular reactions,[8] if this reaction is a true unimolecular reaction, the rate constant should show a total pressure effect at low pressures. Such an effect has been reported by Ogg for the decomposition of N_2O_5[7] and by Mills and Johnston in the NO + N_2O_5 reaction.[6] To determine whether or not such a pressure effect existed in the experiments described here, large excesses of CO_2 were added to the reaction vessel in a series of experiments. No detectable change in the rate constant was noted (Table IV). No final conclusions can be drawn, however, concerning the pressure effect. Additional theoretical studies are needed on the effect of pressure on isotopic exchange in the gas phase and more accurate experimental measurements at the beginning of the reaction as well as under conditions, such as described here, in which the isotopic exchange is approaching equilibrium.

TABLE IV

Temperature 0°; 226-ml. spherical reaction vessel; atom % N^{15} in NO_2 7.25% in first two, 8.68% in remainder

Total pressure, mm.[a]	Moles N_2O_5 × 10^4	Moles NO_2 × 10^4	Atom % N^{15} in nitrate	Atom % N^{15} in N_2O_5	Time, sec.	k × 10^3, sec.$^{-1}$
520	3.85	3.99	1.74	1.35	50	3.9
620	4.24	2.05	0.88	0.22	58	1.2
530	3.58	4.54	2.69	1.59	61	8.1
535	6.63	5.77	2.17	1.61	72	7.2
540	6.63	5.09	2.00	1.44	67	7.5
540	6.63	3.96	1.67	1.24	69	6.5
530	5.04	4.34	1.73	0.48	65	1.9
					Av.	5.2 ± 1

[a] Total pressure increased by adding CO_2 to the reaction vessel.

If the exchange reaction were carried out in the presence of NO so as to disturb the chemical equilibrium, a pressure effect could perhaps be observed. A series of such experiments were carried out as

TABLE V

Exchange in presence of NO; 138-ml. reaction vessel; temperature 0°; atom % N^{15} in NO_2: 11.9% in first three, 13.8% in last two

Moles NO × 10^4	Moles N_2O_5 × 10^4	Moles NO_2 × 10^4	Atom % N^{15} in nitrate	Atom % N^{15} in N_2O_5	Time, sec.	k × 10^2, sec.$^{-1}$
2.38	3.65	2.45	1.71	1.71	61	1.6
2.11	3.40	1.86	1.69	1.69	68	1.7
1.85	4.05	1.50	1.27	1.27	68	1.2
2.47	4.05	2.56	2.08	2.08	65	1.9
2.52	3.97	2.18	1.95	1.95	77	1.8
					Av.	1.6 ± 0.2

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(6) R. L. Mills and H. S. Johnston, THIS JOURNAL, **73**, 938 (1951).

(7) R. A. Ogg, *J. Chem. Phys.*, **18**, 572, 573 (1950).

(8) L. Kassel, "Kinetics of Homogeneous Gas Reactions," Chem. Cat. Co., New York, N. Y., 1932.

shown in Table V.[9] The analytical difficulties in the presence of the excess of NO were so great that the exact numerical value of the rate constant given is doubtful.

If the same frequency factor is assumed for this reaction as for the primary, single-step decomposition of N_2O_5 into NO_2 and NO_3 the data can be expressed by the equation

$$k = 6 \times 10^{12}\, e^{-18{,}500/RT} \text{ sec.}^{-1}$$

A comparison of the limiting value of the rate constant found from the data of the authors extrapolated to 27°, and the accurate constants reported by Johnston[10] can be made. The data were extrapolated by using the equations obtained assuming the frequency factor of 6×10^{12}. The limiting value of the rate constant was calculated by dividing the extrapolated rate constant by an average concentration. Values of 0.25×10^5 cc. moles^{-1} sec.$^{-1}$ for the N_2O_5 decomposition and 0.5×10^5 cc. mole^{-1} sec.$^{-1}$ for the $NO + N_2O_5$ reaction were obtained. These values are to be compared to the values of 1.5×10^5 and 1.27×10^5 cc. mole^{-1} sec.$^{-1}$ given by Johnston for these reactions. If the rate constant is approaching its high pressure limiting value the method described for determining the limiting value is not valid. The comparison should then be made with the high pressure value obtained by Johnston, *i.e.*, 0.009 sec.$^{-1}$ compared with the value 0.016 sec.$^{-1}$ given in Table V.

In view of the proposed initial step for the decomposition of N_2O_5, NO should not be unique in increasing the over-all rate of decomposition of N_2O_5. Any gaseous reducing agent which would react with the NO_3 (an excellent oxidizing agent) and thus prevent the step $NO_3 + NO_2 \rightarrow N_2O_5$ from occurring, should increase the rate of decomposition of the N_2O_5. A qualitative test of this theory was made by mixing N_2O_5 with various gases normally considered to be reducing agents. An increased rate of decomposition was indicated by the rapid appearance of the brown color NO_2. With CH_3OH the rate was followed by pressure measurements since CH_3OH reacts very rapidly with NO_2 to form methyl nitrite[11] and so no brown color appears. The following gases were used: HCl, H_2S, SO_2, HBr, NH_3, HCHO, HI and CH_3OH. All except the SO_2 and the NH_3 appeared to increase the rate of decomposition. Quantitative work is planned on these reactions to compare the rates with the rate of the $NO + N_2O_5$ reaction and with the bond-breaking step as determined by the exchange reaction. Such a series of rate constants would offer a means of comparing the reducing efficiencies of gases.

Conclusions

It is generally accepted that the first step in the N_2O_5 decomposition is the splitting of a nitrogen–oxygen bond to form NO_2 and NO_3. For years it has been recognized as being the rupture with the least energy requirements. The exchange of isotopic nitrogen observed by the authors and previously by Ogg leads to the conclusion that this step is reversible. While the experimental, chemical procedure used may introduce large errors, the average of the several experiments should give a fair value of the rate constant for the initial bond-breaking step.

The agreement between the rate constant for the step $N_2O_5 \rightarrow NO_2 + NO_3$ and the rate equation obtained by Smith and Daniels, by Ogg, and by Mills and Johnston for the $NO + N_2O_5$ reaction indicates that this bond-breaking step is the initial step in both the N_2O_5 decomposition and the $NO + N_2O_5$ reaction, and is the rate-determining step in the latter.

The failure to find a falling-off of the rate constant at low pressures in the over-all decomposition of N_2O_5 as predicted by the collision theory of unimolecular reactions has been an objection to the collision theory of Rice–Ramsperger–Hinshelwood–Kassel. This failure can be explained by the mechanism given by Ogg. The pressure effect reported by Ogg and by Mills and Johnston for the initial bond-breaking step would overcome this objection in the case of the nitrogen pentoxide. Great efforts should be made to find true unimolecular steps in other reactions and to study the effect of pressure on them at low concentrations.

The findings of this investigation are not able to contribute to our understanding of a possible pressure effect. Additional experimental and theoretical studies are needed on the pressure effect in isotopic exchange in gaseous reactions at low pressures.

MADISON, WISCONSIN

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(9) FOOTNOTE: Two things are to be noted in connection with these experiments. In the equation used for the calculation of k

$$-k = \frac{2.303}{t}\,\frac{2b}{2a + b}\,\log\left(1 - \frac{x}{x_\infty}\right) \qquad (5)$$

the term $b/(2a + b)$ has a different significance than in the original experiments. "b" is now the sum of the NO_2 and NO concentrations instead of the NO_2 concentration. This result is reached in the same manner as is the original equation.

The experimental procedure was varied slightly also. The assumption was made that an equimolar mixture of NO and NO_2 will give a solution of only nitrite when dissolved in NaOH. The NO was added to the NO_2 reservoir and the mixture admitted to the reaction vessel to start the reaction. In all experiments the NO concentration was either greater than or substantially equal to the NO_2 concentration. As a result, all of the NO_2 was assumed to form nitrite; and the nitrate in the solution came only from the N_2O_5. Because of the reaction between NO and N_2O_5 some NO_2 is formed while the exchange reaction is going on and this NO_2 will give some additional nitrate. However, a calculation shows that the N^{15} introduced into the nitrate from the NO_2 thus formed is not sufficient to introduce an appreciable error. Mass spectrometric analysis of the nitrogen from nitrate gives directly the atomic fraction of N^{15} in the nitrogen of the N_2O_5.

(10) H. S. Johnston, THIS JOURNAL, **73**, 4542 (1951).

(11) J. Treacy, forthcoming publication.