[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide. II. Details at Low Pressures

BY HAROLD S. JOHNSTON AND RICHARD L. PERRINE

The decomposition of nitrogen pentoxide in the presence of nitric oxide has been re-studied in a 22-liter flask at pressures from 0.05 to 10 mm. and at three temperatures: 27.0, 50.1 and 71.3°. The previous work of Mills and Johnston was found to be slightly heterogeneous at very low pressures. In the 22-liter flask any heterogeneity is less than experimental error. These results have been analyzed in terms of collisional theories of the low-concentration limit for unimolecular reactions. Comparison of these results with those of Linhorst and Hodges for pure nitrogen pentoxide shows that the second-order rate of activation at low concentrations becomes the same for these two systems, except for the slightly greater activating efficiency of pure nitrogen pentoxide as compared to an equimolar mixture of nitric oxide and nitrogen pentoxide.

Mills and Johnston[1] recently completed an extensive kinetic study of the decomposition of nitrogen pentoxide in the presence of nitric oxide. They confirmed the mechanism proposed by Smith and Daniels[2] for the reaction, and that for the decomposition of nitrogen pentoxide alone proposed by Ogg.[3] The mechanisms predicted that the two reactions should become essentially the same at very low pressures, yet there appeared to be a small discrepancy between the results of Mills and Johnston, and those of Linhorst and Hodges[4] with pure nitrogen pentoxide. The reaction has been reinvestigated in detail from about 0.05 to 10 mm. total pressure at three temperatures: 27.0, 50.1 and 71.3° in a 22-liter Pyrex flask to minimize heterogeneity.

Experimental

The apparatus used was very similar to the low pressure apparatus of Mills and Johnston,[1] and the preparation of reagents was the same. However, in this study the pipet system led to the 22-liter flask, which was enclosed in an air-bath built with plywood, lined inside with copper foil, and covered outside with 3 inches of plumber's magnesia insulation. This air-bath was heated electrically, thermostated, and stirred by a fan. The four pipets used to inject reagents into the flask were designed to have volumes one-hundredth or one-thousandth that of the 22-liter flask. The relative volumes were calibrated both by the pressure-drop when dry air was admitted successively to the pipets and flask, and absorptiometrically with pure nitrogen dioxide. The data of Verhoek and Daniels[5] were used to calculate the nitrogen dioxide–nitrogen tetroxide equilibrium concentrations.

The absorptiometric system was calibrated against pure nitrogen dioxide measured from the pipet system, and against a known nitrogen dioxide–air mixture with the pressure in the 22-liter flask measured directly. The result was an extinction coefficient of 0.0192 mm.$^{-1}$ cm.$^{-1}$ at 27°. The reaction was followed by the absorption by nitrogen dioxide of the 436 mμ line from a mercury arc, isolated by glass filters and focused by a quartz converging lens on an electron-multiplying photoelectric tube inside the air-bath. The output of the photoelectric tube was placed directly across the terminals of an electronic voltmeter.

The flask was evacuated for several hours before a run, while thermal equilibrium was obtained. The pipets were filled to the proper concentration of each reagent, and air-bath and room temperatures recorded. The run was timed by stopwatch and clock, the latter so that any drift of the initial intensity reading, or I_0, could be interpolated back to zero time. Voltmeter readings, or I, were corrected for "dark current" of the photoelectric circuit, and I_0/I values computed. From the absorptiometric calibration, corresponding concentrations of nitrogen dioxide were obtained, and the concentration of nitrogen pentoxide calculated. The logarithm of the nitrogen pentoxide concentration plotted *versus* the time gave an essentially straight line in all cases throughout most of the reaction. Empirical rate constants were obtained on multiplying the slopes of these lines by −2.303.

Carbon dioxide was added in order to extend rate studies to pressures above one mm. and still use only low pressures of nitrogen pentoxide, while maintaining an approximate one-to-one ratio of nitric oxide and nitrogen pentoxide. Rate measurements in the region where carbon dioxide and pure reagent runs overlapped indicated that carbon dioxide was equal in efficiency to the reagents in maintaining the rate.

Results

All empirical first-order rate constants are listed in tables which are available on microfilm,[6] and are plotted in Fig. 1. As was noted by Mills and Johnston,[1] the first-order rate constant varies markedly with total concentration (M). Below 10^{-8} mole/cc. the rate constants are proportional to the variable (M), as is seen from the 45° slope of Fig. 1.

The results are best presented as parameters in the mechanism confirmed by Mills and Johnston, who found the initial rate of disappearance of nitrogen pentoxide to be

$$k = \frac{\text{rate}}{(\text{N}_2\text{O}_5)} = \sum_i \frac{a_i c_i (M)}{b_i(M) + c_i} \qquad (1)$$

in which a_i is the second-order rate constant for the activation of nitrogen pentoxide molecules to the energy state i above the critical energy, b_i is the second-order rate constant for the de-activation of excited nitrogen pentoxide molecules in the state i, and c_i is the specific first-order rate constant for the unimolecular decomposition of excited molecules in state i.

Expansion of Equation 1 subject to the condition $b_i(M) < c_i$ for all i gives

$$k = \sum_i a_i(M) - \sum_i \frac{a_i b_i (M)^2}{c_i} + \sum_i \frac{a_i b_i^2 (M)^3}{c_i^2} - \cdots \qquad (2)$$

This relationship describes the low-concentration region. The low-concentration limit occurs when $b_i(M) \ll c_i$ for all i and is

$$k_0 = (M) \sum_i a_i = a(M) \qquad (3)$$

In Equation 2 it can be seen that there are no terms in the low-concentration region which are independent of (M). However, a first-order heterogeneous reaction would give a constant term in

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

(2) J. H. Smith and F. Daniels, *ibid.*, **69**, 1735 (1947).

(3) R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 337, 613 (1947).

(4) J. H. Hodges and E. F. Linhorst, THIS JOURNAL, **56**, 836 (1934).

(5) F. H. Verhoek and F. Daniels, *ibid.*, **53**, 1250 (1931).

(6) Order Document 3256 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

Equation 2. Thus if all data below the low-concentration limit are fitted by the method of least squares to the relation

$$k = a(M) + H \tag{4}$$

the presence or absence of a first-order heterogeneous reaction can be determined by whether H is large, or essentially zero. The region over which k is proportional to (M) was determined by graphical inspection. Thus at each temperature all experimental rate constants for concentrations up to 10^{-8} mole/cc. were fitted to Equation 4 by the method of least squares. The values of the rate constants for activation a, the intercept H, and their standard errors of estimate are listed in Table I. In all cases the intercept is very small compared with the lowest measured rate constant. Thus within experimental error the intercepts are all zero, and there is no observable first-order heterogeneous reaction in the 22-liter flask.

TABLE I

RATE CONSTANTS FOR ACTIVATION OF NITROGEN PENTOXIDE MOLECULES

T, °C.	Number of points	Slope from Eq. 4, $a \times 10^{-5}$, cc. moles^{-1} sec.$^{-1}$	Intercept, Eq. 4, $H \times 10^4$, sec.$^{-1}$
27.0	13	1.27 ± 0.48	− 0.08 ± 2.6
50.1	12	11.3 ± 0.3	+ 1.9 ± 1.7
71.3	9	79.3 ± 14.6	−24 ± 68

The slopes listed in Table I are the second-order rate constants of activation for nitrogen pentoxide molecules. On fitting these rate constants to the Arrhenius equation by the method of least squares, there is found

$$\log_{10} a = 19.109 - \frac{E_0 \times 10^3}{(2.303)(1.987)(T)} \tag{5}$$

in which E_0, the energy of activation at the low-concentration limit, is 19.27 ± 0.63 kcal./mole.

By introducing the assumption that every collision of a molecule with energy above the critical energy results in its deactivation,[7] there is obtained a physical interpretation of the higher order terms in Equation 2. The assumption gives

$$b_i = b = \text{kinetic collision factor} \tag{6}$$
$$a_i = bP_i, \sum_i a_i = a = b\sum_i P_i$$

where P_i is the probability of the existence of the molecule in the ith excited energy state in the hypothetical absence of reaction. Then Equation 2 becomes, on division by (M)

$$k/(M) = bP - b(bP)(M)\overline{(1/c)} + b^2(bP)(M)^2\overline{(1/c^2)} - \cdots \tag{7}$$

where

$$P = \sum_i P_i, \overline{(1/c)} = \frac{\sum_i P_i/c_i}{\sum_i P_i}, \text{etc.} \tag{8}$$

Thus $\overline{(1/c)}$ is the average value of the reciprocals of the specific rate constants with respect to decomposition. A reasonable value for the collisional diameter is 3 ± 0.5 Å., which gives 9×10^{13} cc. moles^{-1} sec.$^{-1}$ for b at 27°, but the range of values due to estimated error in collisional diameter is from 6 to 13 × 10^{13} cc. moles^{-1} sec.$^{-1}$. Thus quantitative interpretations which depend on the value of b have an uncertainty at least as large as a factor of two. By computing b and finding bP from the intercept, then dividing them into $b^2P\overline{(1/c)}$, one obtains $\overline{(1/c)}$. The average half-life of the molecules with respect to decomposition is $(0.693)\overline{(1/c)}$. The higher order terms in Equation 7 can similarly be made to give $\overline{(1/c^2)}$, $\overline{(1/c^3)}$, etc., which are the moments of the function $1/c_i$.

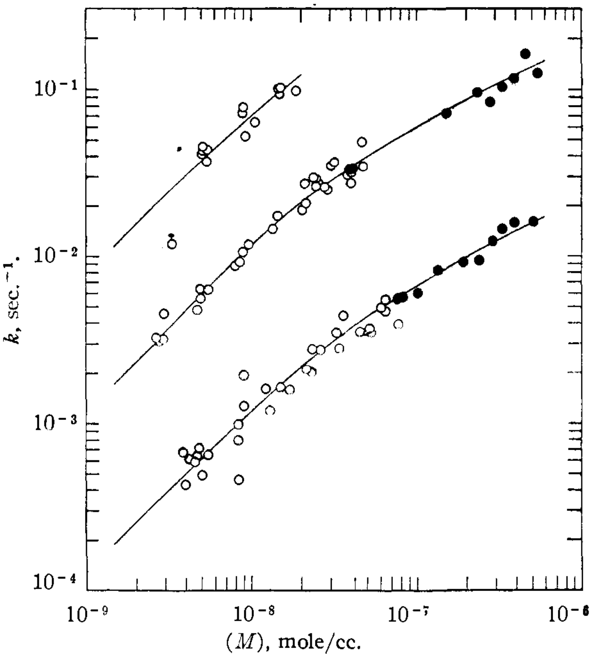

Fig. 1.—log k plotted *versus* log (M) at 27.0, 50.1 and 71.3°; logarithmic scale: ○, obtained with pure reagents; ●, obtained with carbon dioxide added.

It is apparent that the value of $\overline{(1/c)}$ obtained by this method will depend on the range of (M) used. To find $\overline{(1/c)}$ and test the expected error due to uncertainty in choice of the range of (M), parameters in the equation

$$k/(M) = bP - b(bP)\overline{(1/c)}(M) \tag{9}$$

were found for several ranges of (M). The results are shown in Table II. The range over (M) for which the two-parameter expression above seems adequate from graphical inspection of the points and the calculated curves is 0 to 4 × 10^{-8} moles cc.$^{-1}$. For this range the average half-life for molecules with respect to decomposition is 6 × 10^{-8} sec. at 27°, 4 × 10^{-8} at 50°, and 8 × 10^{-8} at 71°. The uncertainty in this figure due to choice of b is a factor of 2 as discussed above, and the additional uncertainty due to choice of range of (M) is seen from Table II to be almost another factor of 2. Thus the estimate from these data of the average half-life of an excited molecule by the method of moments is only slightly better than an order of magnitude calculation. Even so the calculation is of considerable value in giving a quantitative interpretation independent of an

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[7] R. C. Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1927, p. 263. L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1932, p. 99.

assumed form for the functions c_i and P^i. Thus the average half-life of excited nitrogen pentoxide molecules with respect to decomposition is 6 × 10^{-8} sec. In view of the uncertainties in the first moment of $1/c_i$, it is obvious that the data are not sufficiently detailed to permit evaluation of the higher moments in Equation 7. The values of the low concentration limit a or bP as found by Equation 7 are very stable with respect to uncertainties in range of (M) as is seen in Table II, and they are in satisfactory agreement with values given in Table I.

TABLE II

PARAMETERS FITTED TO EQUATION 9

T, °C.	No. of points	Including up to $(M) \times 10^8$, moles/cc.	From the slope, $\overline{(1/c)} \times 10^8$ sec. $^{-1}$	The intercept, $a \times 10^{-5}$ cc. moles^{-1} sec.$^{-1}$
27.0	21	2.5	12.7	1.35
	26	4.5	9.3	1.31
	31	6.5	8.2	1.29
	35	10.0	7.6	1.28
50.1	18	2.5	4.1	12.0
	22	2.9	5.5	12.2
	25	3.2	5.0	12.1
	28	4.0	6.2	12.3
	33	5.0	7.5	12.4
71.3	14	2.0	11.1	77.9

If we assume that a real molecule of n non-linear atoms can be replaced by an array of $s = 3n - 6$ lightly coupled classical oscillators,[8]

$$a = be^{-\epsilon_c/RT} \sum_{r=0}^{r=s-1} \frac{(\epsilon_c/RT)^r}{r!} \tag{10}$$

and the energy of activation is

$$E_0 = \epsilon_c - (s - 3/2)RT \tag{11}$$

By substituting various integers for s, the calculated value for b, and experimental values for the other quantities in Equations 10 and 11 we may solve for a and see which number of effective oscillators best fits the experimental results. If the critical energy ϵ_c is large compared with sRT, only a few terms contribute significantly to the result. The results of computations with various values of s using the last three terms of the series are summarized in Table III. In view of the estimated error in b, the number of oscillators computed this way is 10 ± 1, and the critical energy per mole is 24.7 ± 0.9 kcal.

TABLE III

NUMBER OF CLASSICAL OSCILLATORS EFFECTIVE IN THE DECOMPOSITION

T, °C.	Number of oscillators	$a \times 10^{-5}$, by Eq. 10 cc. moles^{-1} sec.$^{-1}$	$a \times 10^{-5}$ observed cc. moles^{-1} sec.$^{-1}$
	9	.561	
27.0	10	1.11	1.27
	11	6.81	
	9	5.84	
50.1	10	11.6	11.3
	11	62.7	
	9	37.1	
71.3	10	73.7	79.3
	11	365	

For a molecule with s quantized oscillators of the same natural frequency υ where $mh\upsilon$ is the critical energy per molecule, the low-concentration limit of the rate constant can be approximated by

$$a = \frac{b(m + s - 1)!\,(1 - e^{-h\nu/kT})^s\, e^{-mh\nu/kT}}{m!\,(s - 1)!\left(1 - \frac{m + s}{m + 1}\, e^{-h\nu/kT}\right)} \tag{12}$$

and the energy of activation is

$$E_0 = 1/2RT + Nh\upsilon \left(m - \frac{s}{e^{h\nu/kT} - 1} + \frac{1}{\frac{m + s}{m + 1} e^{h\nu/kT} - 1}\right) \tag{13}$$

The results of computations with various values of m and s are summarized in Table IV, assuming frequencies of 0.5, 1 and 2 × 10^{13} sec.$^{-1}$.

TABLE IV

NUMBER OF QUANTIZED OSCILLATORS EFFECTIVE IN THE DECOMPOSITION

T, °C.	Frequency, $\nu \times 10^{-13}$ sec.$^{-1}$	m	s	$a \times 10^{-5}$, calculated, Eq. 12 cc. moles^{-1} sec.$^{-1}$	$a \times 10^{-5}$, observed, cc. moles^{-1} sec.$^{-1}$
27.0	0.5	46	9	1.0	1.27
	0.5	48	10	1.0	
	1.0	22	10	1.4	
	1.0	23	11	1.1	
	2.0	10	11	1.6	
	2.0	11	15	1.3	
50.1	0.5	46	9	9.5	11.3
	0.5	48	10	9.9	
	1.0	22	10	14	
	1.0	23	11	11	
	2.0	10	11	12	
	2.0	11	15	12	
71.3	0.5	46	9	57	79.3
	0.5	48	10	60	
	1.0	22	10	86	
	1.0	23	11	73	
	2.0	10	11	63	
	2.0	11	15	72	

For a frequency of 3 × 10^{13} sec.$^{-1}$ it is not possible to fit the rate constants with s = 15 or less. For frequencies below 0.5 × 10^{13} sec.$^{-1}$ the results are almost the same as those found with the classical formula. The best fit appears to be that with a frequency of 1 × 10^{13} sec.$^{-1}$ and 10 or 11 oscillators. For this frequency and 10 oscillators the critical energy is 20.9 kcal./mole. According to Kassel's theory[9] of the variation of the relative values of the specific rate constants c_i with energy, the critical energy should be the energy of activation at the high-concentration limit. Mills and Johnston[1] observed 21 ± 2 kcal. for this energy of activation. Their results at high concentrations should be checked before conclusions are drawn from this apparent agreement.

Comparisons with Other Studies

Mills and Johnston[1] studied this reaction over this pressure range in a 33-mm. internal diameter

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(8) R. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, 1949, p. 496.

(9) L. S. Kassel, *ibid.*, p. 98.

quartz cylinder. By drawing the best straight line through their lowest points and the origin at 27°, they obtained 2.3×10^5 cc. moles^{-1} sec.$^{-1}$ for the low-concentration limiting rate constant. This value is in disagreement with the present value of 1.3×10^5 cc. moles^{-1} sec.$^{-1}$. Their energy of activation was 14.5 ± 2 kcal./mole, again in serious disagreement with 19.3 ± 0.6 kcal./mole. When their data are fitted to Equation 4 by the method of least squares, the slope is found to be $1.41 \pm 0.30 \times 10^5$ cc. moles^{-1} sec.$^{-1}$, which agrees with the present value. Their intercept is then $3.6 \pm 1.8 \times 10^{-4}$ sec.$^{-1}$, which indicates a heterogeneous first-order reaction in their system. If this heterogeneous reaction has a low energy of activation, it also explains the low value of the energy of activation they observed. By subtracting the first-order intercept from each rate constant observed by Mills and Johnston, there are obtained the points of Fig. 2. The curve in Fig. 2 is taken from Fig. 1, based on the present study. It can be seen that this method of correcting for heterogeneity is only fairly good in this case.[10]

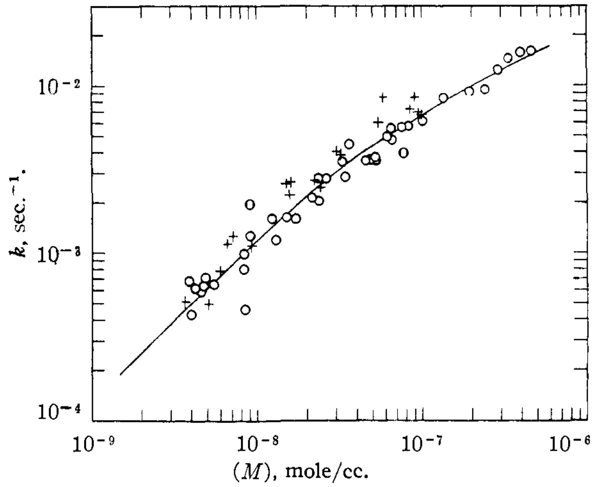

Fig. 2.—Comparison with the present data of the low-concentration data of Mills and Johnston corrected for heterogeneity; O, the present data; +, Mills and Johnston (corrected).

The apparatus of Smith and Daniels[2] used in studying this reaction was of comparable surface-volume ratio to the low-pressure cell of Mills and Johnston, and the values of the rate constants found by these two investigations were in substantial agreement. Thus the discussion above should apply equally well to the results of Smith and Daniels.

At some extremely low concentration the rate of decomposition of pure nitrogen pentoxide should become identical with that for nitrogen pentoxide in the presence of nitric oxide.[1] The best low pressure work on nitrogen pentoxide alone appears to have been done by Linhorst and Hodges.[4] They followed the rate of decomposition of pure nitrogen pentoxide in a 22-liter flask from about 7.5×10^{-11} to 4.5×10^{-9} mole/cc. at 35°, and at about 1×10^{-10} mole/cc. at 45, 55 and 65°. A plot of the first-order rate constant against total concentration for the 35° runs was linear and proportional to the total concentration below 1×10^{-10} mole/cc. Thus for each temperature a least-squares fit to Equation 4 was made for points taken below 1×10^{-10} mole/cc. Since Linhorst and Hodges had so few experimental points, the origin was included as if it were an experimental result. The slopes, giving the second-order rate constant for the activation of nitrogen pentoxide molecules, are listed in Table V, and in parallel columns are presented the same quantity found in this study as interpolated by Equation 5. The values found by Linhorst and Hodges are consistently higher than those of the present study, averaging 50% greater. This difference is readily explained in that pure nitrogen pentoxide should be more efficient for exciting molecules than an equimolar mixture of nitric oxide and nitrogen pentoxide. Linhorst and Hodges reported an energy of activation of 20 ± 2 kcal./mole, and the rate constants in Table V give 20.8 kcal./mole. Within their experimental error, this agrees with the present value, 19.3 kcal./mole. Thus this investigation greatly strengthens the assertion[1] that these two kinetic systems become identical at extremely low pressures, except for the slight difference in what constitutes M in the two cases.

TABLE V

COMPARISON OF LIMITING LOW-CONCENTRATION SECOND-ORDER RATE CONSTANTS FOR NITROGEN PENTOXIDE ALONE, AND FROM THIS STUDY

	Linhorst and Hodges, experimental data		Present data, interpolated by Eq. 5	
T, °C.	Number of exptl. points	(A), $a \times 10^{-5}$ cc. moles^{-1} sec.$^{-1}$	(B), $a \times 10^{-5}$ cc. moles^{-1} sec.$^{-1}$	Ratio (A)/(B)
35	3	3.66	2.79	1.3
45	2	11.4	7.50	1.5
55	3	28.8	19.0	1.5
65	3	76.6	45.4	1.7

Defining the empirical rate constant for the decomposition of nitrogen pentoxide alone as k, the constant at the low-concentration limit as k_0, the constant at the high concentration limit as k_∞, Mills and Johnston showed that the mechanism predicts for any concentration

$$k = \frac{k_0\,(M)}{1 + k_0\,(M)/k_\infty} \tag{14}$$

Using the Linhorst and Hodges value of k_0 and the generally accepted value for k_∞, one obtains the curve in Fig. 3. The only experimental results

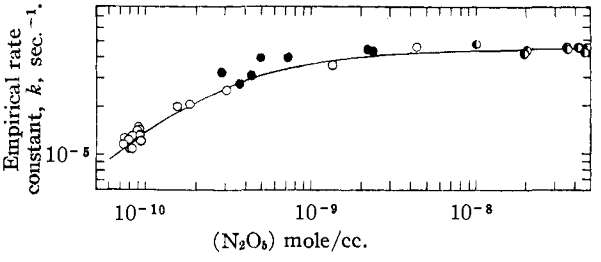

Fig. 3.—Prediction of low-concentration behavior of the decomposition of pure nitrogen pentoxide from the mechanism, 27°: O, Linhorst and Hodges[4]; ●, Ramsperger and Tolman[11]; ◐, Ramsperger, Nordberg and Tolman.[12]

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[10] Compare *J. Chem. Phys.* **19**, 663 (1951).

plotted are those obtained in bulbs 22 liters or larger. The rate constants were extrapolated to 27° using the appropriate energy of activation. By excluding measurements made in small bulbs and by using the appropriate value of k_0, one finds in Fig. 3 an even better description of low-pressure results than is given by Mills and Johnston in their Fig. 7. Thus the slight heterogeneity encountered by Mills and Johnston does not alter their conclusion that Ogg's[3] mechanism predicts the observed behavior of nitrogen pentoxide at all concentrations.[11,12]

Acknowledgment.—This investigation was conducted under the sponsorship of the Office of Naval Research, Contract N6onr-25131, Project NR 058 246.

(11) H. C. Ramsperger and R. C. Tolman, *Proc. Natl. Acad. Sci.*, **16**, 6 (1930).

(12) H. C. Ramsperger, M. E. Nordberg and R. C. Tolman, *ibid.*, **15**, 453 (1929).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Exchange Studies with Complex Ions. II. The Kinetics of the Exchange of Radiocyanide Ion with Potassium Hexacyanomanganate(III) in Aqueous Solution[1]

BY ARTHUR W. ADAMSON, JOAN P. WELKER[2] AND W. B. WRIGHT

The results of a kinetic study of the exchange in aqueous solution between potassium hexacyanomanganate(III) and potassium radiocyanide are reported. The exchange rate is found to be first order in complex ion concentration, and to be independent of the cyanide concentration, of *p*H over the range 9.0 to 10.8, and of ionic strength. It is not photocatalyzed but is slightly dependent upon extent of glass surface. The first order rate constant at 0° is 2.64×10^{-2} min.$^{-1}$ and the activation energy is found to be *ca.* 8.5 kcal./mole. It is proposed that the rate-determining step involves the hepta-coördinated ion $Mn(CN)_6H_2O^{-3}$. The general applicability of a mechanism of this type to the exchange results reported for various tetra and hexa-coördinated cyanides is discussed.

Previous work in these laboratories, comprising determinations of the qualitative exchange behavior of a number of complex ions with respect to radiocyanide ion in aqueous solution,[3] led to the observation of an exchange with the hexacyanomanganate(III) complex which was unexpectedly rapid, if judged by the rates for the corresponding complex ions of Cr(III) and Fe(III). The present paper presents the results of a kinetic study designed to yield information concerning the kinetics, and, if possible, the mechanism for this system.

Experimental

Preparation and Purity of the $K_3Mn(CN)_6$.—Analyses of the compound prepared by the addition of solid manganese-(III) orthophosphate to warm potassium cyanide solution[4] indicated that the complex was only approximately 92% pure, due to the presence of MnO_2.[4] Repeated recrystallizations of the compound from warm 10% potassium cyanide solution did not improve the quality. Because of this difficulty, a different method of preparation,[5] involving the formation and subsequent air oxidation of potassium hexacyanomanganate(II) was employed for the present work. The product was recrystallized once from 10% potassium cyanide solution, washed with alcohol, and then ether, and stored in a vacuum desiccator.

The compound was analyzed by fuming with sulfuric acid, and determining the manganese by the sodium bismuthate method. The result for manganese was 16.67% (calculated for $K_3Mn(CN)_6$, 16.73%).

Counting and Tracer Techniques.—Potassium radiocyanide was prepared from $BaC^{14}O_3$ by the sodium azide method.[6,7] The same counting procedure was employed as that described in the previous paper,[3] except that a windowless, flow type counter (using a 98.7% He, 1.3% butane mixture) was employed instead of a mica end-window tube. The coincidence correction was determined by the same method as before, and since the samples were uniformly about 2 mg./cm.^{2} in thickness it was considered adequate to correct for self-absorption by means of the same curve as previously given.

Exchange Experiments.—The following general procedure was employed for the exchange runs. Solid complex was dissolved in inactive potassium cyanide solution of concentration about 90% of the desired final value, and the mixture brought to and kept at the desired temperature for one-half hour before the addition of sufficient potassium radiocyanide solution to give the indicated final concentrations of free cyanide and of complex. After the lapse of the desired exchange time, the complex was precipitated as the cadmium salt, and the specific activity of the remaining free cyanide determined in the manner previously described.[3] These exchange times were measured from the moment of addition of the tracer until the end of the *ca.* two-minute period of centrifugation of the precipitated complex.

Color Changes.—The solution obtained upon dissolving the complex in dilute potassium cyanide solution initially is an orange-red color, and fades to a pale yellow over a period of 10 to 15 minutes, at room temperature, and of several hours at 0°. Most of the exchange results were obtained with the yellow solution. The effect has been noticed before; Christensen[8] thought it was due to reduction to $Mn(CN)_6^{-4}$ by the free cyanide, an energetically favorable reaction, while Myer[5] supposed the red coloration to be due to small amounts of $Mn(CN)_3$. If an explanation of the first type were correct, namely, that the red form is the actual $Mn(CN)_6^{-3}$ which then undergoes reaction to give an entirely different, yellow species, then the interpretation of any exchange data would be seriously affected. Since Myer did not exhaust alternatives of this nature, it was desirable to study the color change in somewhat more detail than had been done previously.

The absorption spectrum of the yellow solution is given in Fig. 1, and shows a band at 330 mμ as the principal feature, in agreement with a previous report.[9] The spectrum of the

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(1) The work here described was conducted under contract N6 onr 23809 between the University of Southern California and the Office of Naval Research. It was presented in part at the Symposium on "Equilibrium and Rate Behavior of Complex Ions in Solution" held at the University of Chicago, February, 1951.

(2) This paper is in part based on portions of a dissertation submitted by Joan P. Welker in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.

(3) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

(4) W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 213.

(5) J. Meyer, *Z. anorg. Chem.*, **81**, 385 (1913).

(6) A. W. Adamson, THIS JOURNAL, **69**, 2564 (1947).

(7) The $BaC^{14}O_3$ was obtained from the Isotopes Division of the Atomic Energy Commission.

(8) O. T. Christensen, *J. prakt. Chem.*, **139**, 163 (1885).

(9) L. Szego and P. Ostinelli, *Gazz. chim. ital.*, **60**, 946 (1930).