of benefit in interpreting the data relative to the exchange of Cl_2 and CCl_4 initiated by γ-radiation.

Acknowledgments.—The author wishes to thank Henry Taube for his many helpful suggestions. Some of the early experimental work was done by T. S. Piper. The assistance offered by A. H. Zeltmann and P. J. Bendt in deriving the modified rate expression is appreciated.

Appendix

Derivation of Modified Rate Law.—For the conditions in which the loss of CCl_4 by decomposition is very small compared to the initial $[CCl_4]$ and the $[Cl_2]$ is about 10^{-3} to $^{-4}$ *M*, then the following derivation is valid for any one stated flux.

The rate of exchange of Cl between Cl_2 and CCl_4 is expressed as

$$R = \frac{dN}{dt} \qquad \text{(A 1)}$$

where dN = the number of tagged chlorine atoms disappearing from the tagged phase in time dt, and R is a constant for any stated flux.

$$\frac{dP}{dt} = -C\frac{dN}{dt} \qquad \text{(A 2)}$$

where P = number Cl^{36} atoms present as Cl_2 at time t and $C = P/N$. But since N increases with time

$$N = N_0(1 + \alpha t) \qquad \text{(A 3)}$$

where N_0 = total number of Cl_2 atoms present at time 0 and

$$\alpha = \frac{dN/dt}{N_0}$$

$$\frac{dP}{dt} = \frac{-P}{N_0(1 + \alpha t)}\frac{dN}{dt} = -\frac{PR}{N_0(1 + \alpha t)} \qquad \text{(A 4)}$$

$$\int_{P_0}^{P}\frac{dP}{P} = \frac{-R}{N_0\alpha}\int_0^t \frac{\alpha\, dt}{(1 + \alpha t)} \qquad \text{(A 5)}$$

where P_0 = number of Cl^{36} atoms present as Cl_2 at time 0.

$$\ln\frac{P}{P_0} = \frac{-R}{\alpha N_0}\ln(1 + \alpha t) \qquad \text{(A 6)}$$

At $P/P_0 = {}^1/_2$, $t = t_{1/2}$ and

$$\ln 2 = \frac{R}{\alpha N_0}\ln(1 + \alpha t_{1/2}) \qquad \text{(A 7)}$$

$$R = \frac{N_0\alpha \ln 2}{\ln(1 + \alpha t_{1/2})} \text{ which is } \gtrapprox \frac{N_0 \ln 2}{t_{1/2}} \qquad \text{(A 8)}$$

which would be the case for a stable system. This expression is in agreement with the work of other investigators[16] who have derived equations to fit the general case of unstable systems in exchange reactions.

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(16) C. P. Luehr, G. E. Challenger and B. J. Masters, THIS JOURNAL, **78**, 1314 (1956).

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA,[a] AND DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY[b]]

The Kinetics of the NO–N_2O_5 Reaction[1]

BY I. C. HISATSUNE,[a] BRYCE CRAWFORD, JR.,[a] AND R. A. OGG, JR.[b]

RECEIVED APRIL 5, 1957

The decomposition of N_2O_5 in the presence of NO has been studied with a fast-scanning infrared spectrometer at total pressures of 57 and 400 mm. using N_2 as diluent and at temperatures of 20, 25 and 30°. By using an excess of N_2O_5 over NO, the unimolecular dissociation constant for N_2O_5 as well as the ratio of the rates for NO_3 reacting with NO_2 and with NO, respectively, was determined. The Arrhenius activation energies for these rate constants also were determined.

Introduction

In earlier reports from this Laboratory,[2] the applicability of our fast-scanning infrared spectrometer to kinetic studies of relatively fast gas-phase reactions has been described. One of these moderately fast reactions which can be studied conveniently with our instrument is the unimolecular decomposition reaction of N_2O_5 in the presence of NO. Not only is the half-life of this reaction within the limits of our scanning rates, but both N_2O_5 and NO_2 have intense infrared absorption bands around 6 μ so that we may follow both molecular species simultaneously through the course of the reaction. Furthermore, since extensive kinetic data for this reaction are available in the literature, we are able to compare our results to those obtained from other methods.

Since the publication of our preliminary notes[3] on this reaction, we have been able to improve the sensitivity and stability of our spectrometer and also have been able to overcome some of the experimental difficulties involved in the present method. This paper reports our final results on this reaction.

A number[4] of investigators have studied this reaction and have found that their experimental data can be interpreted adequately in terms of the simple mechanism proposed by Smith and Daniels,[4] which is given below in equation 1. Our data ob-

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(1) This work was supported by the U. S. Navy, Bureau of Ordnance, through contract with the University of Minnesota.

(2) G. R. Cowan, E. Vincent and B. Crawford, Jr., *J. Opt. Soc. Am.*, **43**, 710 (1953); R. E. Nightingale, G. R. Cowan and B. Crawford, Jr., *J. Chem. Phys.*, **12**, 1398 (1953).

(3) G. R. Cowan, D. Rotenberg, A. Downie, B. Crawford, Jr., and R. A. Ogg, Jr., *ibid.*, **21**, 1397 (1953); I. C. Hisatsune, A. P. McHale, R. E. Nightingale, D. L. Rotenberg and B. Crawford, Jr., *ibid.*, **23**, 2467 (1955).

(4) W. F. Busse and F. Daniels, THIS JOURNAL, **49**, 1257 (1927); J. H. Smith and F. Daniels, *ibid.*, **69**, 1735 (1947); R. L. Mills and H. S. Johnston, *ibid.*, **73**, 938 (1951); H. S. Johnston and R. L. Perrine, *ibid.*, **73**, 4782 (1951); H. S. Johnston, *ibid.*, **75**, 1567 (1953); D. J. Wilson and H. S. Johnston, *ibid.*, **75**, 5763 (1953); R. A. Ogg, Jr., *J. Chem. Phys.*, **18**, 572 (1950); R. A. Ogg, Jr., W. S. Richardson and M. K. Wilson, *ibid.*, **18**, 573 (1950).

tained by using a fast-scanning infrared spectrometer also were found to fit this mechanism and the rate equation 2. Our work establishes the first

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO_2 + NO_3 \qquad (1)$$

$$NO + NO_3 \xrightarrow{k_6} 2NO_2$$

$$-d(N_2O_5)/dt = k_1(N_2O_5)/[1 + k_2(NO_2)/k_6(NO)] \qquad (2)$$

quantitative estimate of the inhibition constant k_2/k_6. Our values for the constant k_1 are of the same order of magnitude as those obtained by previous investigators,[4] but are consistently lower than the earlier results. The Arrhenius activation energy for k_1 from our work was found to be in excellent agreement with the earlier values of Johnston and his co-workers.[4]

Experimental

The gases NO, N_2O_5 and NO_2 were prepared according to the methods published recently.[5] Special precautions were taken to prevent the formation of HNO_3 which hindered our earlier work, and spectroscopic evidence was obtained for its absence. Brief descriptions of the experimental technique and the treatment of the data are given in the earlier reports.[3]

Previously, we had used a reaction cell where the reactants were expanded through two slightly off-centered jets from either side of the cell by opening the two taps with a mechanical crank. However, this system produced serious mixing difficulties and therefore a new reaction cell system shown schematically in Fig. 1 was used. The 10 cm. Pyrex absorption cell had a volume of 163 ml. and a surface-to-volume ratio of approximately 1.4. Silver chloride windows were sealed to the cell with a mixture of high-temperature Halocarbon grease and wax. The reactant bulbs on either side of the 3 mm., 3-way, hollow-T tap had approximately 100-ml. capacities. The T tap was connected to the absorption cell through a ball-joint and by 4 mm. i.d. Pyrex tubing of approximately 10 cm. length. The reactants which were diluted with oil-pumped nitrogen gas were expanded from bulbs A and B through the 3-way tap into the reaction cell. To test for reproducibility, N_2O_5 was placed either in bulb A or B and the 3-way tap was always opened clockwise from identical initial positions so that the reactant in A always emptied out from the same tap-hole. All of our runs were made in the above manner. For temperature coefficient measurements the entire laboratory was thermostated to 20, 25 and 30° with variation of not more than 0.5°.

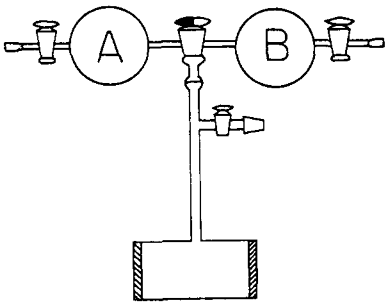

Fig. 1.—Schematic diagram of the reaction-absorption cell system; path length = 10 cm., volume = 163 ml. Silver chloride windows were sealed on with a mixture of high-temperature Halocarbon wax and grease.

The reaction was followed by observing the time variation of the two neighboring intense absorption bands of N_2O_5 and NO_2 in the 6 μ region with our fast-scanning spectrometer. A single cycle of the photographic record of the oscilloscope signal is shown in Fig. 2. Optical densities of the two species were read from these films and plotted against the reaction time, which was calculated from the known film speed of the recording camera and the scanning speed of the spectrometer. A portion of the optical density *vs.* time plot for a typical run is shown in Fig. 3.

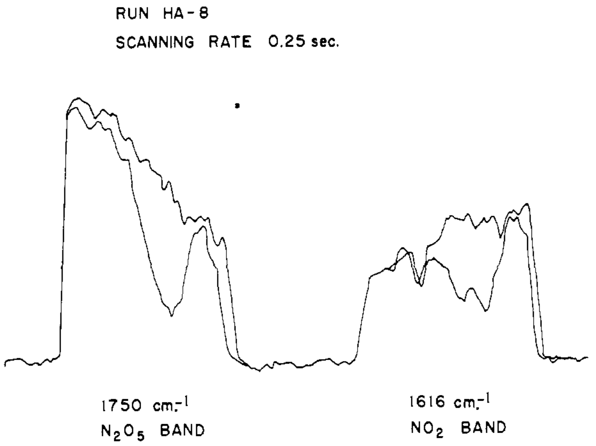

Fig. 2.—A single cycle of the photographic record with blank superimposed.

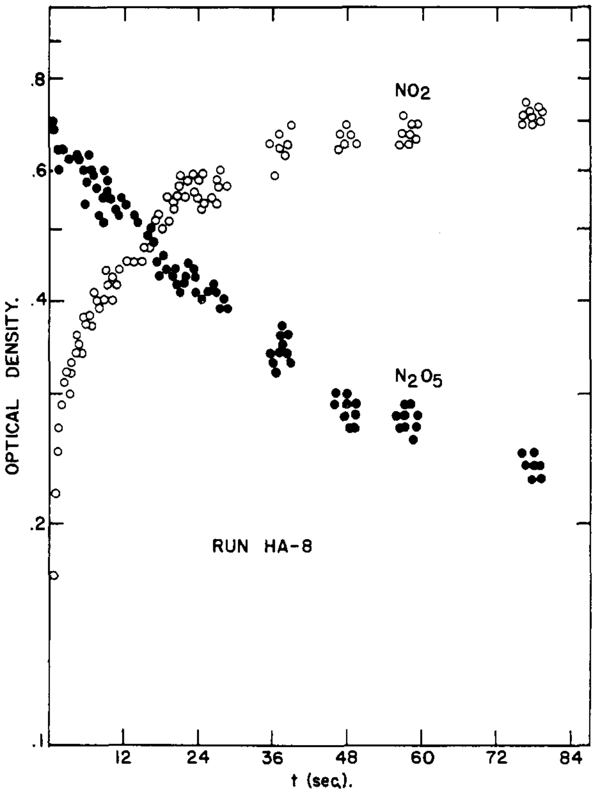

Fig. 3.—An optical density *vs.* time plot for a typical run.

To test for heterogeneity in the reaction, we packed the absorption cell with Pyrex glass rods, 3 mm. diameter by 25 mm. length. However, we were only able to increase the surface-to-volume ratio to 2.7 (compared to 1.4 in the unpacked cell) without blocking out the infrared beam. Two runs were made with this packed cell at 20° and at total pressures of 400 and 57 mm., respectively; in both cases

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

an excess of NO was used so that only the rate constant k_1 was obtained. The results were as follows

	Unpacked cell	Packed cell
400 mm.	0.028 sec.$^{-1}$	0.027
57 mm.	0.016	0.018

In the high pressure runs, the difference in the two values of k_1 is within the limits of experimental uncertainties. However, in the low pressure runs, the difference is probably significant, although not large. It is reasonable for us to conclude that no heterogeneity affects our k_1 values beyond the limits indicated below.

Treatment of the Data.—Smooth curves were drawn through the optical density *vs.* time plots and readings from these curves were used for the following calculations. These smoothed optical densities were converted into pressures by using calibration curves which were obtained for N_2O_5 and NO_2 at every different temperature and total pressure used in the runs. Corrections were made for the NO_2–N_2O_4 equilibrium, using the constant given by Verhoek and Daniels,[6] and for the slight overlap of the N_2O_4 and N_2O_5 absorption bands. For every run a "stoichiometry plot" of N_2O_5 *vs.* total NO_2 (*i.e.*, $NO_2 + 2N_2O_4$) was made; Fig. 4 represents such a plot for a typical run. In every case the slope was found to be $^1/_3$ as predicted by the over-all equation for the reaction, within the limits of experimental uncertainties.

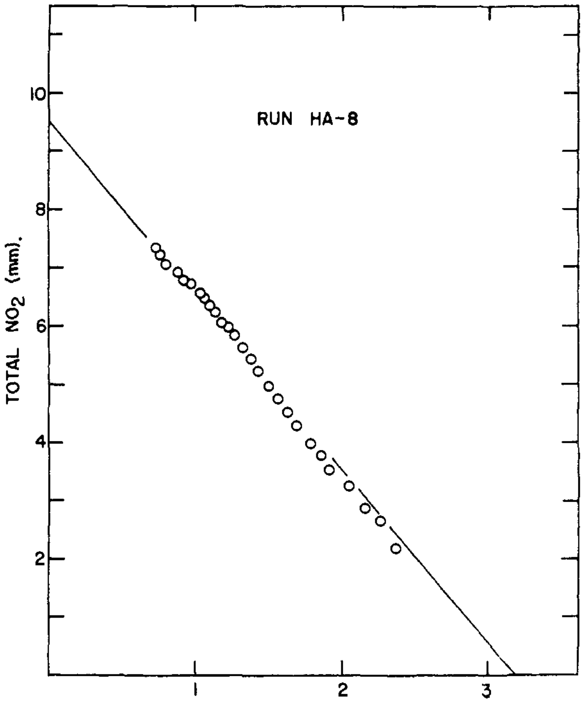

Fig. 4.—A stoichiometry plot for a typical run. Total NO_2 refers to $NO_2 + 2N_2O_4$. The line is of slope 1/3.

The experimental pressures are substituted into the integrated form of the rate equation given below, valid for $(N_2O_5)_0 > (NO)_0$.

$$y = -k'(1 - 3k')^{-1}w + k_1(1 - 3k')^{-1} \qquad (3)$$

where $k' = k_2/k_6$

$$y = (t - t_0)^{-1} \ln[(N_2O_5)_0(N_2O_5)^{-1}]$$

and

$$w = (t - t_0)^{-1}(NO_2)_\infty (N_2O_5)_\infty{}^{-1} \ln [(NO)_0(N_2O_5)(NO)^{-1}(N_2O_5)_0{}^{-1}]$$

The subscripts "0" and "∞" denote pressures at some initial time t_0 and at the end of the reaction, respectively. The pressure of NO is calculated from the relation $(NO) = (N_2O_5) - (N_2O_5)_\infty$. The values of t_0 and pressures corresponding to the completion of the reaction were chosen to give the best linear y–w plots. The intersection of the experimental y–w plot with a line $y = w/3$ gives k_1 and the w-intercept gives k_1k_6/k_2. A typical example of such y–w plots is shown in Fig. 5.

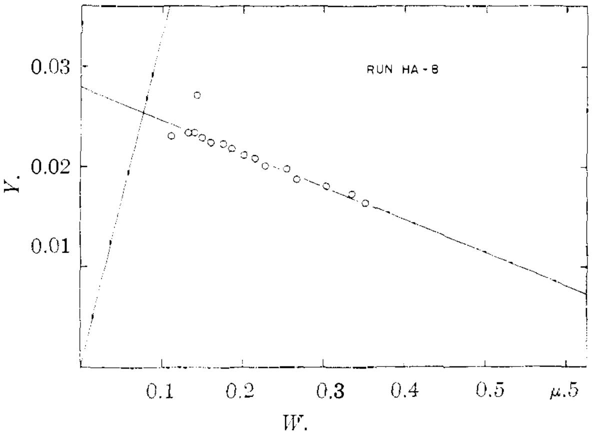

Fig. 5.—A y–w plot for a typical run. The line through the origin is $y = w/3$.

Results

The average values of the rate constants obtained in the above manner are given in Table I.[7] The estimated errors are average errors. For k_1 the maximum deviation from the mean value was approximately 20%. However, for k_1k_6/k_2 and the calculated constant k_2/k_6 this deviation was approximately 50%, since the w-intercept involves larger uncertainties. The inhibition constants k_2/k_6 listed in Table I are the averages of the values calculated from the separate runs.

TABLE I

EXPERIMENTAL RATE CONSTANTS AT VARIOUS TOTAL PRESSURES

t, °C.	No. of runs	k_1 (sec.$^{-1}$)	k_1k_6/k_2 (sec.$^{-1}$)	k_2/k_6
(a) 400 mm.				
20	20	0.0281 ± 0.0029	0.492 ± 0.086	0.0635 ± 0.0124
25	13	.0538 ± .0036	1.06 ± .12	.0535 ± .0086
30	12	.0921 ± .0160	1.53 ± .17	.0667 ± .0081
(b) 57 mm.				
20	14	0.0156 ± 0.0009	0.461 ± 0.122	0.0398 ± 0.0113
25	13	.0269 ± .0010	0.910 ± .209	.0328 ± .0100
30	12	.0482 ± .0020	1.69 ± .25	.0253 ± .0081

The activation energies and frequency factors calculated for k_1 and k_1k_6/k_2 from a least-square treatment of the entire data are listed in Table II. The Arrhenius plots for these constants are shown in Fig. 6. It would be difficult to estimate the temperature coefficients for k_2/k_6 from the values in Table I because of the large uncertainties (see Fig. 7). Hence, the final values of this constant were calculated from those of k_1 and k_1k_6/k_2, both from Table II. These values were found to be

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[6] F. H. Verhoek and F. Daniels, THIS JOURNAL, **53**, 1250 (1931)

[7] Tables of complete data have been deposited as Document number 5196 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance by check or money order payable to: *Chief, Photoduplication Service, Library of Congress*

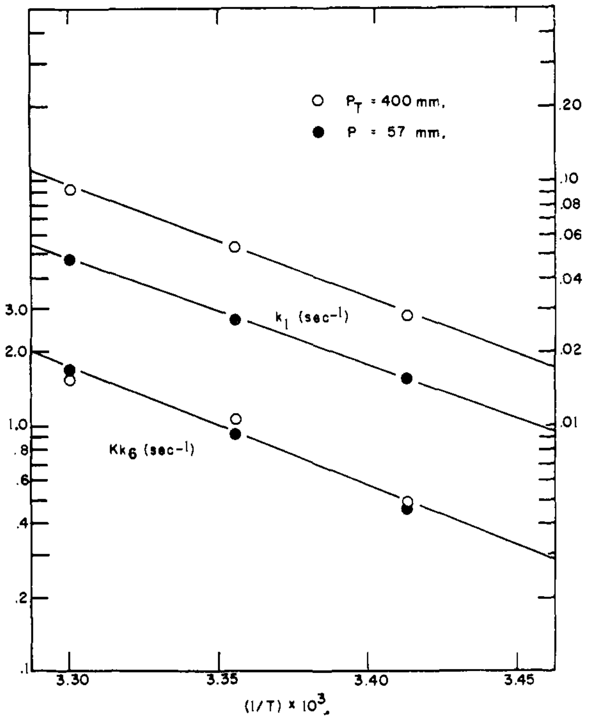

Fig. 6.—Arrhenius plot for k_1 and k_1k_6/k_2 at total pressures of 57 and 400 mm.

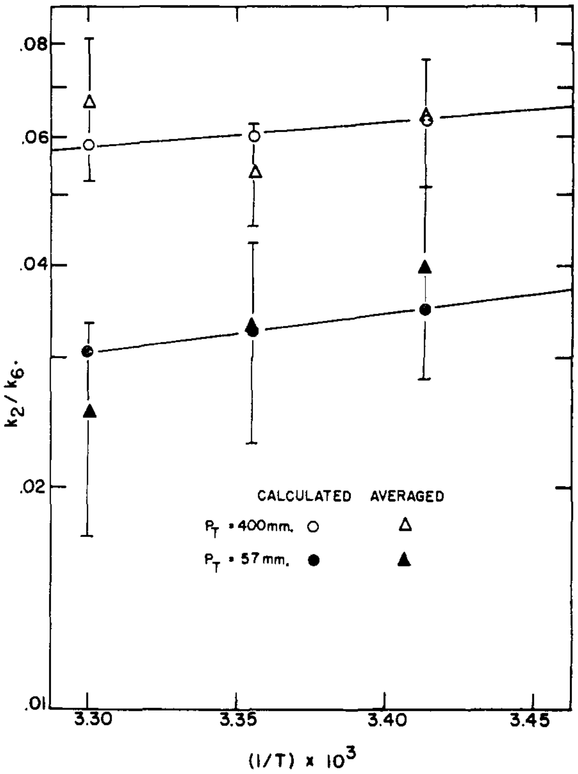

Fig. 7.—Arrhenius plot for k_2/k_6; see text.

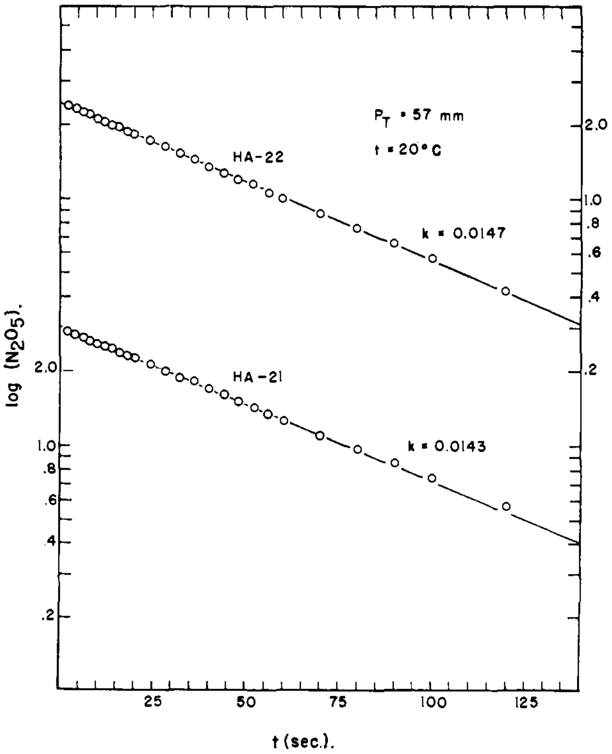

Fig. 8.—First-order rate plot for two typical runs where (NO) > (N_5O_2).

within the limits of the errors in Table I, as shown in Fig. 7.

TABLE II

FREQUENCY FACTORS AND ACTIVATION ENERGIES (KCAL./MOLE)

Constant	Total pressure 400 mm.	57 mm.
k_1 (sec.⁻¹)	$10^{14.1}\,e^{-21.0/RT}$	$10^{13.1}\,e^{-20.0/RT}$
k_1k_6/k_2 (sec.⁻¹)	$10^{16.3}\,e^{-22.4/R}$	
k_2/k_6	$10^{-2.2}\,e^{+1.4/RT}$	$10^{-3.2}\,e^{+2.3/RT}$

Discussion

In our earlier work[3] we encountered serious difficulties arising from the mixing of the reactants in the absorption cell. The values of the constant k_1 were of the right order of magnitude but the calculated activation energy was found to be anomalously low. In the present work we feel that this difficulty has been removed. As another precaution, we made at least two runs at each total pressure and temperature in which an excess of NO was used. In these runs the plot of log(N_2O_5) against time gave straight lines over the entire period of the reaction. Two of these plots are shown in Fig. 8. The values of k_1 obtained from the slopes of these plots were found to be in good agreement with those calculated from the y–w plots. From these agreements and from the fact that the stoichiometry plots all gave slopes of $^1/_3$, we can reasonably assume that the mixing effect of the reactants has not been serious.

The activation energy obtained from this work for the rate constant k_1 is in excellent agreement with those obtained by Johnston and his coworkers.[4] These investigators found that the energies of activation for the high pressure and low pressure limits were, respectively, 21 ± 2 and 19.3 kcal./mole. Our values fall gratifyingly within these limits. Although we probably cannot claim significance in the difference of the two values at

400 and 57 mm., nevertheless, the decrease in the energy is in the correct direction. As for the frequency factors, we can only conclude that they are reasonable, since a rather limited temperature range was used in their evaluation.

The constant k_1k_6/k_2 is found to be independent of the total pressure within the precision of our measurements. This result is in complete agreement with the proposed mechanism. From this value one could estimate the equilibrium constant for the dissociation of N_2O_5 into NO_2 and NO_3 if one knew the value for k_6, or *vice versa*.

It is interesting to note that the temperature coefficient for k_2/k_6 is small and negative. This of course means that the activation energy E_2 associated with k_2 is slightly less than E_6 associated with k_6. Our accuracy is such that we can with confidence say only that $(E_2 - E_6)$ is small, and that if we regard E_2 as probably small because the reaction is merely a recombination, then E_6 must also be small. It is however interesting to note that the trend of activation energies with pressure, like that found for k_1 by Johnston, *et al.*,[4] is consistent with the prediction of unimolecular rate theory[8] that the activation energy of a unimolecular decomposition should fall off at low pressures, and that a bimolecular association with no activation energy at high pressures will have a negative "activation energy" at low pressures. Thus if we assume that the high pressure limit of E_2 is zero, we may interpret the data to mean that the high pressure limit of E_1, 21.0 kcal./mole, represents the dissociation energy of N_2O_5; that E_6 is also nearly zero; and that the negative quantity $(E_2 - E_6)$ essentially measures the predicted "negative activation energy" of the association of NO_2 and NO_3 at low pressures.

Conclusion.—We have investigated the unimolecular decomposition reaction of N_2O_5 in the presence of NO with our fast-scanning infrared spectrometer. The results obtained from this method were found to be consistent with those obtained from other methods. In addition, we have been able to obtain for the first time a quantitative estimate of the inhibition constant k_2/k_6. Finally, we can reasonably conclude that this spectroscopic method can be applied equally well to other relatively fast gas-phase reactions.

Acknowledgment.—We wish to thank Mr. David Rotenberg for preparing the ozone samples used in this work and Miss Ann McHale for undertaking the tedious but critical task of processing our photographic data. Our discussions on this problem with Professor Harold S. Johnston have been a pleasure.

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STANFORD, CAL.

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[8] L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," New York, N. Y., 1932, pp. 95–100; A. F. Trotman-Dickenson, "Gas Kinetics," New York, N. Y., 1953, pp. 62–64.

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

Solvents Having High Dielectric Constants. VI. Diffusion in N-Methylacetamide[1,2]

BY WILLIAM D. WILLIAMS, JAMES A. ELLARD AND LYLE R. DAWSON

RECEIVED APRIL 18, 1957

The self-diffusion coefficients of N-methylacetamide over the temperature range 35 to 60°, and the sodium ion in sodium chloride solutions in N-methylacetamide at 40°, have been determined. Concentrations of the salt varied from 2.5×10^{-3} to 0.25 molar. The capillary method was employed with stirring accomplished by rotating the capillary holder. For the pure solvent the diffusion coefficient increases from 4.11×10^{-6} to 7.33×10^{-6} cm.²/sec. as the temperature is raised. The value for the sodium ion decreases from 2.58×10^{-6} to 1.97×10^{-6} cm.²/sec. as the salt concentration is increased one hundred fold. The activation energy for self-diffusion in the amide is equal to that for viscous flow. Also it is equal to the activation energy for the self-diffusion of water.

Interest in N-methylacetamide as a solvent to be used in diffusion studies arises from its unusual properties. It dissolves readily both organic and inorganic solutes. At 40° its dielectric constant is 165.5 and its viscosity is 0.03019 poise.[3] Sodium chloride was chosen as the solute for this study because the literature contains diffusion data for this salt in water[4] and its conductance and transference numbers in N-methylacetamide have been calculated from measurements in this Laboratory.[5]

Wang[6] has discussed the theory and described the procedure for measuring diffusion coefficients by the capillary method. Mills and Kennedy[7] and Mills and Adamson[8] reported studies of probable experimental errors in this method and have described some improvements in techniques. These procedures together with a technique modified for viscous media have been used in the present work.

Experimental

Materials.—Reagent grade sodium chloride was recrystallized and fused.

Sodium-22 chloride was obtained from the Isotopes Division, U.S.A.E.C., Oak Ridge, Tennessee.

N-Methylacetamide was prepared by the method described in an earlier paper from this Laboratory.[3] The solvent which was used froze above 29° and had a specific conductance of 2×10^{-6} ohm^{-1} cm.$^{-1}$ at 40°.

Active N-methylacetamide was prepared from C^{14}-enriched $BaCO_3$, obtained from Oak Ridge, by first synthesizing acetic acid-1-C^{14}. This synthesis was accom-

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[1] Abstracted from a dissertation submitted by William D. Williams as a part of the requirements for the Ph.D. degree at the University of Kentucky.

[2] This work was supported in part by a contract with the Office of Ordnance Research.

[3] L. R. Dawson, P. G. Sears and R. H. Graves, THIS JOURNAL, **77**, 1986 (1955).

[4] J. H. Wang and S. Miller, *ibid.*, **74**, 1611 (1952).

[5] E. D. Wilhoit, Dissertation, University of Kentucky, 1956.

[6] J. H. Wang, THIS JOURNAL, **74**, 1182 (1952).

[7] R. Mills and J. W. Kennedy, *ibid.*, **75**, 5696 (1953).

[8] R. Mills and A. W. Adamson, *ibid.*, **77**, 3454 (1955).