cancel. In the hydrolysis two hydroxide ions are involved and besides the addition of one to the carbonyl and the displacement of the CH_2-N ⟨structure⟩ there is an additional loss of a proton to the second hydroxyl (see reference 1 for the complete mechanism). The effect of a substituent may again cancel for the first two processes but the loss of the proton

will be aided by a bromine substituent and hindered by the electron donating methoxyl. Consequently the observed changes in the rate will occur.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Some Azeotropes of Bromine

BY WILLIAM M. SPICER AND LEON H. MEYER

Vapor–liquid equilibria were investigated at 1 atm. pressure for four systems involving bromine and suitable solvents. Homogeneous azeotropes were observed to exist in three of the systems studied—$Br_2-CF_2ClCFCl_2$, $Br_2-CCl_3CClF_2$, $Br_2-C_6H_5CF_3$. A two-phase azeotope was found to exist in the system composed of the partially miscible liquids bromine and $CF_3CCl_2CF_2Cl$. Liquid–liquid equilibrium data were also obtained for this system between 0° and the azeotropic boiling point. The investigation of another system, Br_2-CS_2, was not carried to completion due to evidence of a reaction occurring between the components. No evidence of reaction between the components of the other systems could be detected. As a further indication of the deviations of the systems from ideality, volume changes occurring on mixing the two components of each system were determined.

I. Introduction

As a continuation of an investigation to prepare binary azeotropes consisting of one colored and one colorless component,[1] it was decided to study further possibilities in systems of bromine and colorless bromine solvents. Azeotropes of this general type are valuable in the study of the methods employed to separate azeotropic mixtures, since separation can be observed visually.

Due to the inert character and the availability of certain of the completely halogenated saturated hydrocarbons, it was felt that certain of these compounds would be suitable as second components of the systems to be studied. Spicer and Kruger[1] proved the existence of an azeotrope in the system bromine–carbon tetrachloride. To go higher in this series, however, it was necessary to use fluorine containing compounds in order that the boiling point of the second component should not be excessively high, a condition which would be unfavorable for azeotrope formation. Three systems involving bromine solvents of this general type were studied—$Br_2-CF_2ClCFCl_2$, $Br_2-CCl_3CClF_2$ and $Br_2-CF_3CCl_2CF_2Cl$.

Two other systems were investigated. One of these employed benzotrifluoride ($C_6H_5CF_3$) as the bromine solvent, for it was deemed probable that no reaction would occur between the components in the absence of a catalyst, due to the inhibiting effect of the trifluoromethyl group.[2,3] The final system studied involved bromine and carbon disulfide, a commonly employed bromine solvent.

II. Experimental

Merck and Co., Inc., analyzed C.P. bromine was used in all investigations without further purification. One of the solvents—CCl_3CClF_2, a low melting solid at room temperature (m.p. 40.6°)—was furnished pure by the General Chemical Division of the Allied Chemical and Dye Corporation. The $CF_2ClCFCl_2$ was obtained from Kinetics

Chemicals, Inc., and purified by fractionation in a five-foot glass helix packed column. A middle cut was taken, boiling point range 46.6–46.8° at 739.6 mm. pressure. The carbon disulfide was purified by the method of Chenevier,[4] fractionation being performed in the same column. A middle cut, boiling point range 45.2–45.4° at 740 mm., was retained.

It was not possible to purify further the $CF_3CCl_2CF_2Cl$ and the $C_6H_5CF_3$, since they were obtained in insufficient quantity to permit this. These compounds were furnished by Halogen Chemicals, Inc., and by the Hooker Electrochemical Company, respectively. Purity of both was listed as approximately 98%. This impurity was tolerated since it was felt probable that it was of similar chemical constitution.

Vapor–liquid equilibrium data were obtained using an equilibrium still similar to that described by Jones, Schoenborn and Colburn.[5] A constant pressure control maintained pressure at 760 mm. It consisted of a large (approximately 25 l.) air reservoir, equipped with a $^1/_6$ horsepower compressor, to which the system was open. The pressure in the reservoir was set by manual operation and checked approximately every 20 minutes during a run (estimated accuracy of pressure control ± 1 mm.). Equilibrium temperatures, which were measured by means of a calibrated copper-constantan thermocouple using a potentiometer reading to one microvolt, were accurate to approximately 0.1°. Composition of equilibrium liquid and vapor phases were determined in all cases, except for a few runs made on the system $Br_2-CF_3CCl_2CF_2Cl$, by titrating samples, withdrawn from the still into concentrated potassium iodide solutions, with standardized sodium thiosulfate solution to a starch indicator end-point. This followed, of course, determination of the weight of each sample. The liquids bromine and $CF_3CCl_2CF_2Cl$ were found to be only partially miscible and to complete the phase diagram above 0° the liquid–liquid equilibria were determined for the two layers. These determinations were carried out by allowing the system to equilibrate in a water-bath equipped with an automatic temperature control capable of maintaining regulation within approximately ±0.1°, and then analyzing samples from each layer in the usual manner. Not before this information was available, was it possible to obtain complete vapor-liquid equilibria data from the equilibrium still, since the composition of the vapor phase in the region in which the condensed vapor separated into two liquid layers could not be determined by the usual method. To perform the analyses within this region, the following method was used. The entire vapor condensate was withdrawn into a separatory

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(1) W. M. Spicer and J. Kruger, THIS JOURNAL, **72**, 1855 (1950).

(2) J. H. Simons and E. O. Rambler, *ibid.*, **65**, 391 (1943).

(3) J. H. Simons, *Ind. Eng. Chem.*, **39**, 240 (1947).

(4) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford University Press, London, 1935, p. 170.

(5) C. A. Jones, E. M. Schoenborn and A. P. Colburn, *Ind. Eng. Chem.*, **35**, 666 (1943).

funnel and allowed to equilibrate at 0°, after which the layers were separated and the weight of each determined. From these data it was possible to compute the over-all composition.

For each system exhibiting azeotrope formation, the azeotrope itself was prepared by fractionating at 760 mm. pressure a liquid mixture of very nearly the azeotropic composition in a small glass helix-packed column (packed section 40 cm. in length and 2 cm. in diameter). After the column had reached equilibrium, the azeotropic temperature was read directly and the composition of the azeotrope determined by analyzing small samples of the condensed vapor, using the method of titration with standard sodium thiosulfate solution.

The volume change occurring on mixing the components for each system was determined, by direct volumetric means, to obtain an indication of the extent to which the mixtures deviate from Raoult law behavior. With the exception of the system involving the partially miscible liquids bromine and $CF_3CCl_2CF_2Cl$ this determination was made using approximately equal volumes of the two constituents. In the excepted case, however, it was possible to prepare a mixture of only about one to six (bromine to solvent) volumetric ratios and still retain a single liquid phase, which was necessary to obtain a valid indication of non-ideality.

To test the systems for evidence of reaction, although the likelihood of such was considered small, approximately 10% (by weight) bromine solutions were fractionated, the bromine being distilled off in the azeotrope. After removal of the bromine the refractive index of the residue in the still pot was determined and compared with that of the pure solvent at the same temperature.

III. Results

Data for the vapor–liquid equilibria of all the systems studied, except that of bromine and carbon disulfide, are given in Tables I–V below, as well as the liquid–liquid equilibrium data for the system Br_2–$CF_3CCl_2CF_2Cl$.

TABLE I

VAPOR–LIQUID EQUILIBRIA DATA FOR SYSTEM BROMINE-1,1,2-TRIFLUORO-1,2,2-TRICHLOROETHANE

Temperature, °C.	Mole fraction bromine	
	In vapor	In liquid
47.6	0.000	0.000
45.7	.105	.049
44.2	.197	.103
43.4	.248	.132
42.5	.307	.200
41.0	.455	.455
41.2	.523	.669
42.0	.551	.839
43.4	.590	.889
46.1	.630	.919
51.6	.791	.973
58.9	1.000	1.000

TABLE II

VAPOR–LIQUID EQUILIBRIA DATA FOR SYSTEM BROMINE-1,1,1,2-TETRACHLORO-2,2-DIFLUOROETHANE

Temperature, °C.	Mole fraction bromine	
	In vapor	In liquid
91.6	0.000	0.000
89.0	.149	.027
77.6	.461	.138
71.0	.600	.238
64.8	.726	.389
61.5	.778	.508
57.9	.889	.872
57.8	.908	.908
57.9	.925	.935
58.4	.981	.991
58.9	1.000	1.000

TABLE III

VAPOR–LIQUID EQUILIBRIA DATA FOR SYSTEM BROMINE-1,1,1,3,3-PENTAFLUORO-2,2,3-TRICHLOROPROPANE

Temperature, °C.	Mole fraction bromine	
	In vapor	In liquid
72.5	0.000	0.000
66.6	.217	.049
62.7	.342	.087
59.5	.434	.126
58.1	.443	.146
51.0	...	.375
49.1	.695	...
53.0	.71[a]	.961
55.7	.80[a]	.978
56.5	.81[a]	.981
56.8	...	.985
57.6	...	.995
58.9	1.000	1.000

[a] Analyses performed gravimetrically (as described above).

TABLE IV

LIQUID–LIQUID EQUILIBRIA DATA FOR SYSTEM BROMINE-1,1,1,3,3-PENTAFLUORO-2,2,3-TRICHLOROPROPANE

Temperature, °C.	Mole fraction bromine	
	In upper layer	In lower layer
0.0	0.270	0.974
20.3	.354	.971
35.3	.434	.954
40.1	.468	.942
45.4	.504	.935
48.0	.529	.926

TABLE V

VAPOR–LIQUID EQUILIBRIA DATA FOR SYSTEM BROMINE-BENZOTRIFLUORIDE

Temperature, °C.	Mole fraction bromine	
	In vapor	In liquid
103.9	0.000	0.000
96.5	.249	.040
90.2	.386	.080
80.1	.578	.175
71.1	.736	.298
61.0	.865	.630
58.4	.942	.934
58.1	.967	.967
58.5	.978	.988
58.9	1.000	1.000

Study on the system bromine–carbon disulfide was discontinued when a definite reaction was observed to occur between the components. Several runs were made on charges of low bromine content, preliminary data indicating that no azeotrope would be formed for this system. When a charge of relatively high bromine content, however, was introduced into the equilibrium still and a run attempted, a high boiling residue was observed to be formed. The investigation was thus carried no further. No attempt was made to identify the reaction products.

Azeotrope formation was observed in the other four systems studied. Azeotropic boiling points and compositions for these systems were found to be as follows: Br_2–$CF_2ClCFCl_2$, 41.0°, 45.5 mole % bromine; Br_2–CCl_3CClF_2, 57.8°, 90.8 mole % bromine; Br_2–$CF_3CCl_2CF_2Cl$ (two-phase azeotrope), 49.1°, 69.5 mole % bromine; Br_2–$C_6H_5CF_3$,

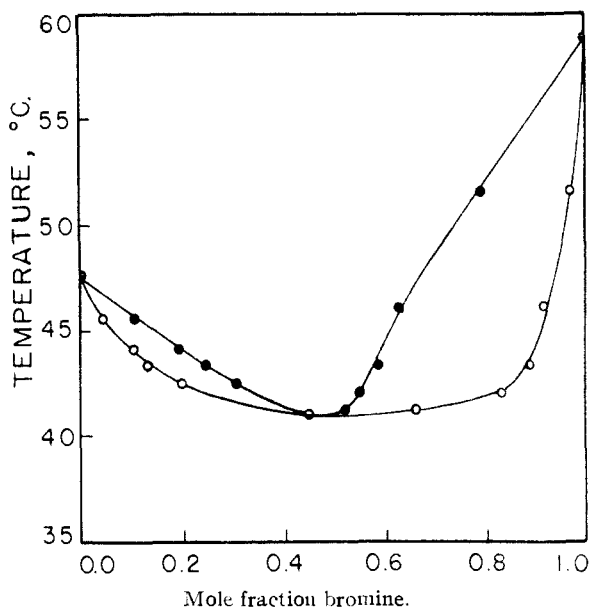58.1°, 96.7 mole % bromine. The equilibrium data are plotted in the usual manners in the figures shown.

Fig. 1.—Temperature-composition diagram for system Br_2–$CF_2ClCFCl_2$ at 760 mm. pressure: ●, vapor; O, liquid; ◐, vapor and liquid.
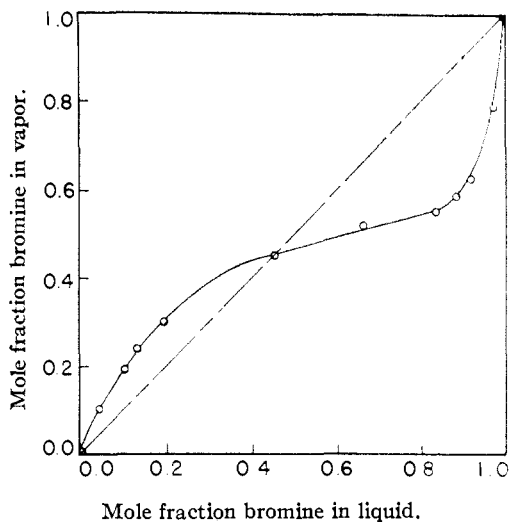

Mole fraction bromine in liquid.

Fig. 2.—Vapor-liquid equilibrium diagram for system Br_2–$CF_2ClCFCl_2$ at 760 mm. pressure.

Results of the experiments performed to determine the volume change of mixing are listed in Table VI. The largest per cent. volume increase

TABLE VI

DATA ON VOLUME CHANGES OBSERVED ON MIXING

Temperature, °C.	Solvent	Vol. of bromine, ml.	Vol. of solvent, ml.	Ideal vol. of mixture, ml.	Actual vol. of mixture, ml.	Vol. increase, %
30	$CF_2ClCFCl_2$[a]	1.52	1.70	3.22	3.42	6.2
44.5	CCl_3CClF_2[a]	3.20	3.87	7.07	7.40	4.7
28	$CF_2CCl_2CF_2Cl$	0.50	3.00	3.50	3.57	2.0
23	$C_6H_5CF_3$[a]	2.00	2.10	4.10	4.28	4.4

[a] Considerable cooling noted on mixing with bromine.
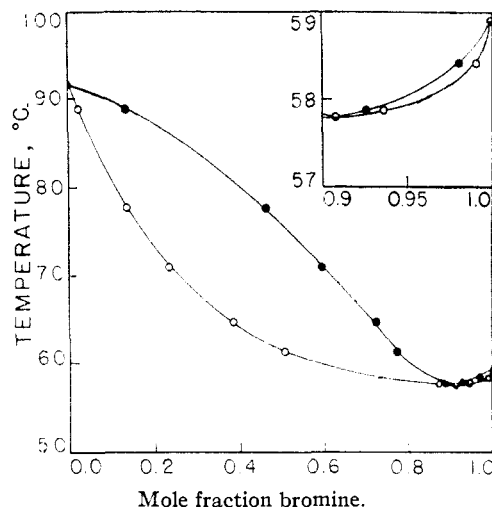
Fig. 3.—Temperature-composition diagram for system Br_2–CCl_3CClF_2 at 760 mm. pressure· ●, vapor; O, liquid; ◐, vapor and liquid.
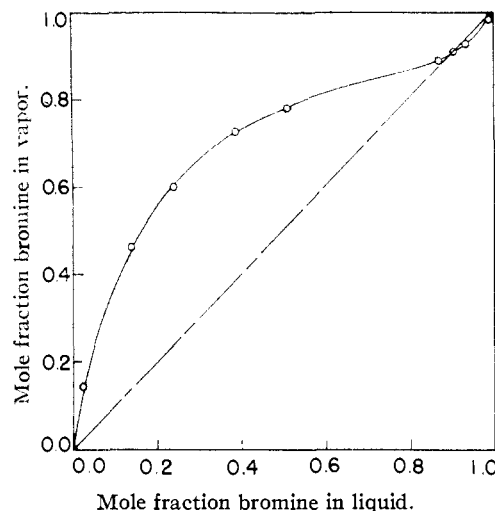

Mole fraction bromine in liquid.

Fig. 4.—Vapor-liquid equilibrium diagram for system Br_2–CCl_3CClF_2 at 760 mm. pressure.

was observed for the system Br_2–$CF_2ClCFCl_2$ (6.2%). Increases of 4.7% for the system Br_2–CCl_3CClF_2 and 4.4% for the system Br_2–$C_6H_5CF_3$ were measured. The proportionally small volume increase (2%) observed for the system Br_2–$CF_3CCl_2CF_2Cl$ is not felt to be a fair indication of the deviation from ideality for this mixture, obviously the greatest for any of the systems studied, but is attributed to the impossibility of preparing a single-phase solution of more than relatively low volume per cent. bromine.

The tests performed for evidence of reaction between the components of all systems, except for the Br_2–CS_2 system, were negative, the solvents exhibiting no significant changes in refractive index before and after contact with bromine. In the case of the solvents $CF_2ClCFCl_2$, CCl_3CClF_2 and $C_6H_5CF_3$, no change whatsoever in the measurements could be ascertained by the Bausch and Lomb Refractometer used, which could be read to five significant figures. A slight change was noted in the fifth significant figure for the solvent CF_3-
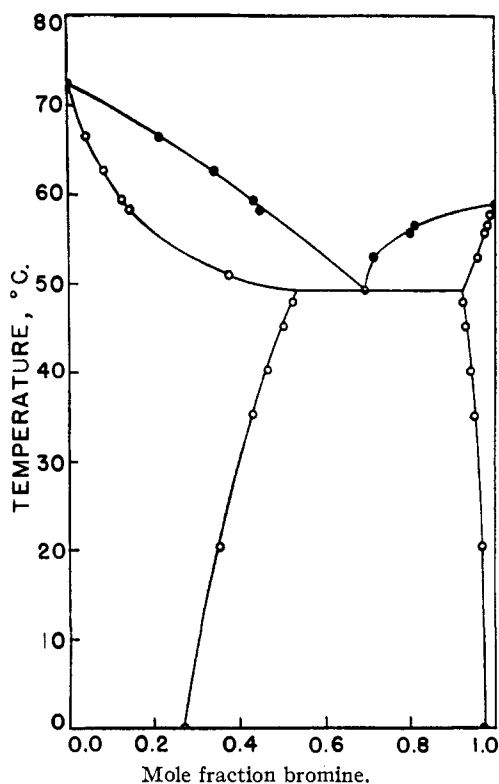
Fig. 5.—Temperature–composition diagram for system Br₂-CF₃CCl₂CF₂Cl at 760 mm. pressure: ●, vapor; O, liquid; ◐, vapor and liquid.

Fig. 6.—Vapor–liquid equilibrium diagram for system Br₂-CF₃CCl₂CF₂Cl at 760 mm. pressure.

Fig. 7.—Temperature–composition diagram for system Br₂-C₆H₅CF₃ at 760 mm. pressure: ●, vapor; O, liquid; ◐, vapor and liquid.

Fig. 8.—Vapor–liquid equilibrium diagram for system Br₂-C₆H₅CF₃ at 760 mm. pressure.

CCl_2CF_2Cl. This was not felt to be due to any reaction, however, but perhaps to the presence of some trace of lower boiling constituent in the

TABLE VII

DATA ON TESTS FOR EVIDENCE OF REACTION

| | Temp. of measurements, °C. | Refractive index | |
Solvent		Before contact with bromine	After contact with bromine
CF₂ClCFCl	35.0	1.3512	1.3512
CCl₃CClF₂	45.0	1.4032	1.4032
CF₃CCl₂CF₂Cl	35.0	1.3453	1.3458
C₆H₅CF₃	35.0	1.4073	1.4073
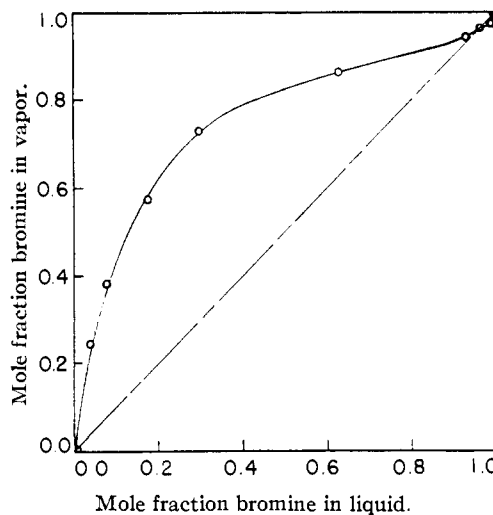
original solvent. Data for these determinations are listed in Table VII.

IV. Discussion

The experimental results are in good accord with internal pressure differences existing between the components of each system. Using Hildebrand's method[6] for estimating internal pressures for the liquids involved, the 'following values are obtained: Br₂, 5390 atm.; CS₂, 4360 atm.; C₆H₅-CF₃, 2650 atm.; CCl₃CClF₃, 2430 atm. and CF₂-ClCFCl₂, 2220 atm. When these values are viewed in conjunction with the boiling-point, differences existing between the components of each system, the boiling-point depressions ex-

(6) J. H. Hildebrand, "Solubility of Non-Electrolytes," second edition, Reinhold Publishing Corporation, New York, N. Y., 1936, pp. 98-106.

hibited in the azeotropes formed seem to be in at least semi-quantitative agreement with the extent of deviation from ideal behavior, as is to be expected.

No conclusions are drawn concerning the reaction observed in the study of the bromine–carbon disulfide system. A survey of the literature revealed no mention of the occurrence of a reaction between these two components below 180°.[7] It is not beyond the realm of possibility that the reaction was promoted by the presence of some impurity in small amount in the carbon disulfide, although this is considered unlikely due to the fact that tests made for the detection of impurities

in this solvent[8] were all negative. Furthermore, refractive index and boiling point measurements gave excellent agreement with values recorded in the literature.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation, whose financial assistance made this investigation possible, and to both the General Chemical Division of the Allied Chemical and Dye Corporation and the Hooker Electrochemical Company, who furnished without charge some of the chemicals.

(7) R. Gerstl, Ber., 3, 508 (1870).

(8) B. L. Murray, "Standards and Tests for Reagent and C. P. Chemicals," second edition, D. Van Nostrand Company, New York, N. Y., 1927, pp. 192–194.
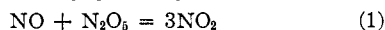

Decomposition of Nitrogen Pentoxide in the Presence of Nitric Oxide[1]
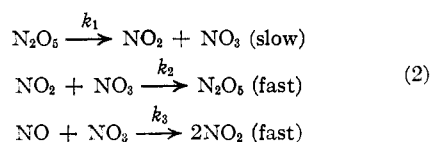
BY ROBERT L. MILLS AND HAROLD S. JOHNSTON

The rate of the initial reaction between nitrogen pentoxide and nitric oxide is that of the elementary unimolecular decomposition $N_2O_5 \rightarrow NO_2 + NO_3$.

This reaction has been studied over a 10^5-fold range of total pressure, and both the high-pressure first-order limit and the low-pressure second-order limit of the unimolecular reaction have been essentially attained. Foreign gases, notably carbon dioxide, sustain the high value of the first-order constant almost as well as the reactants themselves. Previously proposed mechanisms for this reaction and that for the decomposition of nitrogen pentoxide alone have been confirmed experimentally and extended to account explicitly for the effect of inert gases. Detailed analysis of these two closely similar mechanisms has brought out quantitative relations between the kinetic systems. The anomalies long associated with the low-pressure decomposition of nitrogen pentoxide are explained and removed by this study and these mechanisms.

The gaseous reactants nitrogen pentoxide and nitric oxide were first brought together by Busse and Daniels[2] who described the reaction as being "immeasurably fast." Subsequently the reaction was assumed to be a rapid secondary step in mechanisms proposed for the decomposition of nitrogen pentoxide alone. However, Daniels[3] raised a question regarding the possibility that this supposedly bimolecular reaction might be slow enough at low pressures to limit the rate of decomposition of nitrogen pentoxide. Smith and Daniels[4] studied the kinetics of the reaction at pressures from 0.1 to 20 mm. They found the reaction to be homogeneous, quantitatively given by the relation

$$NO + N_2O_5 = 3NO_2 \tag{1}$$

and first order with respect to nitrogen pentoxide and essentially zero order with respect to nitric oxide. They proposed the mechanism

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3 \text{ (slow)}$$

$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5 \text{ (fast)} \tag{2}$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2 \text{ (fast)}$$

From this mechanism the rate expression can be derived

$$R = -d(N_2O_5)/dt = k_1(N_2O_5) \frac{k_3(NO)}{k_3(NO) + k_2(NO_2)} \tag{3}$$

where parentheses denote concentration. Thus the initial rate, when the concentration of nitrogen dioxide is about zero, is that for the primary unimolecular dissociation of nitrogen pentoxide. The apparent experimental error reported by Smith and Daniels could be explained in terms of their study having been made in the so-called "falling-off" region of a unimolecular reaction. It was thus of considerable interest to study this reaction over a very large pressure range. The present study reports the rate of this reaction over a 100,000-fold range of total pressure, and the results and mechanism are compared with those for the decomposition of nitrogen pentoxide alone.

Experimental

Materials.—The reactants, nitrogen pentoxide and nitric oxide, were freshly prepared prior to the various kinetic studies. Pure anhydrous nitrogen pentoxide was made by the action of excess ozone on nitrogen dioxide. Nitric oxide was generated by the addition of sulfuric acid to a solution of potassium iodide and sodium nitrite, after which the gas was purified.[5] In addition to the reactants, various other gases were required to complete the studies. These were obtained from commercial tanks and included nitrogen dioxide, which was used for calibrations, and nitrogen, hydrogen, argon, nitrous oxide, carbon dioxide and Freon, which were used at different times to dilute the reactants.

Apparatus.—Smith and Daniels[4] have shown that a visual colorimetric method for following the progress of the nitrogen pentoxide–nitric oxide reaction is ideal for total pressures below about 20 mm. In order to extend kinetic studies of this reaction to higher pressures, it has been necessary to employ the absorptiometric technique for following fast reactions which was developed by Johnston and Yost.[6] The present studies encompass the pressure range 7×10^{-2} to 7×10^3 mm. To complete the measure-

(1) Abstracted from a dissertation by Robert L. Mills in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Stanford University, 1950. Shell Fellow 1949.

(2) W. F. Busse and F. Daniels, THIS JOURNAL, 49, 1257 (1927).

(3) F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938.

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

(5) H. L. Johnston and W. F. Giauque, ibid., 51, 3194 (1929).

(6) H. S. Johnston and D. M. Yost, J. Chem. Phys., 17, 386 (1949).