not intended to carry implications regarding structure.

Chromyl isocyanate, $CrO_2(NCO)_2$, appeared to be quite stable as a deep red solution in carbon tetrachloride. Upon evaporation to dryness under atmospheric pressure an explosion occurred.

Chromyl thiocyanate, $CrO_2(SCN)_2$, seemed to be present for a few minutes as a dark purple solution in cold carbon tetrachloride which shortly decomposed in the cold, and explosively at higher temperatures.
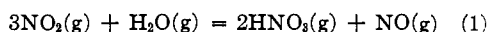
CAMBRIDGE, MASS.   RECEIVED MAY 11, 1943

Equilibrium Measurements by Infrared Absorption for the Formation of Nitric Acid from Oxygen, Water Vapor and Nitrogen Dioxide
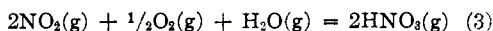
BY ERNEST J. JONES

Several workers[1] have studied the reaction

$$3NO_2(g) + H_2O(g) = 2HNO_3(g) + NO(g) \quad (1)$$

while others[2] have studied the reaction

$$NO(g) + \tfrac{1}{2}O_2(g) = NO_2(g) \quad (2)$$

These two equations combine to give the equation of the reaction

$$2NO_2(g) + \tfrac{1}{2}O_2(g) + H_2O(g) = 2HNO_3(g) \quad (3)$$

In line with the interest of this Laboratory in problems concerning the chemistry of nitrogen it was felt that a direct determination of the equilibrium constant of reaction (3) would be helpful.

During the course of some absorption studies on nitrogen oxides in the infrared it was noted that nitric acid in the vapor phase possessed a characteristic absorption, due presumably to the first overtone of the O·H vibration, in a region (1.4μ) which was sufficiently clear from the interfering absorption of nitrogen dioxide, water vapor and nitric oxide to permit measurement. This suggested that the direct study of the equilibrium could be made using the infrared absorption of nitric acid as a measure of its concentration, while the concentrations of nitrogen dioxide and water could be calculated from a knowledge of the initial concentration of nitric acid.

The experimental work reported here was terminated due to the dismantling of the apparatus preparatory to moving the laboratory to Beltsville, Maryland. During the period of preparing this material for publication a paper by Forsythe and Giauque[3] on the thermodynamic study of nitric acid appeared. These authors give in addition to their own experimental results a complete review of the work on the thermodynamics of nitric acid and some of the reactions leading to its formation. One of these is reaction (3) the direct determination of the equilibrium constant of which is the purpose of the present paper.

Apparatus and Method

The large infrared recording spectrograph which has previously been described by Brackett and Liddel[4] was used in making the measurements. An electric oven equipped with double windows housed the absorption cells and this assembly was mounted on an optical bench in front of the slit of the spectrograph. Measurement and control of the cell temperature (to within 1°) was made outside the spectrograph room to avoid interference with the automatic operation of the spectrograph itself. Pyrex glass tubing 5 cm. in diameter and 50 cm. in length with ground and polished windows fused to each end constituted the cells. These cells were sealed by means of side tubes to an all-glass vacuum system.

Construction of a working curve that would allow one to determine the concentration of nitric acid in the vapor phase as a function of its infrared absorption in the 1.4μ region was the first step in the work. To do this a number of cells were filled with known amounts of nitric acid vapor. Nitric acid was prepared by pumping excess nitrogen dioxide off fuming nitric acid at room temperature until the liquid was colorless, the time required being about thirty minutes. The liquid was then immediately frozen under continued pumping and after a short time introduced into the evacuated cell (10^{-3} mm.) by allowing the solid nitric acid to warm up by adjusting the position of the cooling bath surrounding it until the vapor pressure had attained the desired value as determined roughly by a "nujol" manometer. Temperatures of the liquid nitric acid never exceeded 30°. At this point the tube containing the nitric acid was closed and the cell and three sampling bulbs which had been connected in parallel through a manifold were each sealed off. Titration of the contents of each bulb gave values, the average of which was taken as the concentration of the nitric acid vapor for the cell. The nitric acid vapor remained colorless, a sensitive test for the absence of nitrogen dioxide, throughout the period of measurement.

The spectral absorption of each cell was then measured throughout the 1.4μ region by recording the galvanometer trace on a photographic plate. By reading the height of this trace above an arbitrary base line at regular intervals along the frequency scale the area under the absorption peak could be determined.[5] Each area so obtained was plotted against the corresponding concentration and

(1) Burdick and Freed, THIS JOURNAL, **43**, 526 (1921); Chambers and Sherwood, **59**, 316 (1937); Abel, Schmid and Stein. Z. Elektrochem., **36**, 692 (1930).

(2) Giauque and Kemp, J. Chem. Phys., **6**, 40 (1938).

(3) Forsythe and Giauque. THIS JOURNAL. **64**, 48 (1942).

(4) Brackett and Liddell. Smithsonian Miscel. Collections, **85**, No. 5 (1931).

(5) An approximate calculation of the absorption coefficient yields a value of

$$k = 150 \; \frac{\text{liters}}{\text{mole cm.}^2}$$

which is close to the values of other OH containing molecules for the same type of vibration: cf. Wulf and Liddel, THIS JOURNAL, **57**, 1464 (1935).

yielded a linear relationship which formed the working curve for the equilibrium study.

The equilibrium study was made by filling a cell with a known amount of nitric acid vapor and then adding oxygen to give a total pressure close to one atmosphere. The one factor evident from the beginning was the slowness of reaction (3) in the gas phase. For example, at a temperature of 70° it was necessary to hold a cell for over two months at this temperature in order to attain equilibrium; at 90 and 120°, the other two temperatures used, shorter time sufficed. The method used for all temperatures was to approach the equilibrium from both sides. This was done by taking records of the absorption at frequent intervals and plotting the concentration of nitric acid, as measured by its absorption, *versus* time. The two sets of values thus obtained could be extrapolated to a common asymptote and it was this value which was used as the equilibrium value of the nitric acid concentration. This is illustrated in Fig. 1.
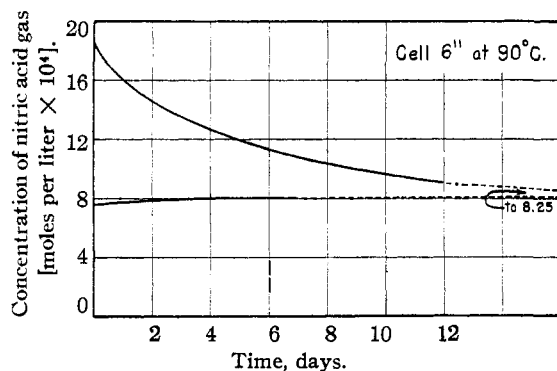

Fig. 1.

Results and Discussion

Table I shows the results obtained. Values of K_p, for reaction (3), in this table were obtained from the following expressions

$$K_c = \frac{[HNO_3]^2}{(H_2O)(NO_2)^2(O_2)^{1/2}} = \frac{C^2}{\frac{X}{2}X^2q^{1/2}}$$

$$K_p = K_c/(RT)^{3/2}$$

TABLE I

EQUILIBRIUM CONSTANT FOR THE REACTION
$2NO_2(g) + {}^1/_2O_2(g) + H_2O(g) = 2HNO_3(g)$

Cell	T, °K.	$n \times 10^4$, moles/ liter	$C \times 10^4$, moles/ liter	$X \times 10^4$, moles/ liter	q, moles/ liter	Ln K_p
6–11	363	21.60	8.25	13.35	0.0377	2.90 ± 0.3 est.
6–11	393	21.60	3.50	18.1	0.0377	0.15 ± 0.1 est.
9–13	343	24.15	13.40	10.75	.0371	4.6 ± 0.4 est.
	363	24.15	8.55	15.60	.0371	2.5 ± 0.3 est.
	391	24.15	4.20	19.95	.0371	0.25 ± 0.1 est.

n = initial concn. of nitric acid vapor (by titration)
C = final concn. of nitric acid vapor (by infrared absorption)
X = $(n - c)$ = concn. of nitric acid dissociated
$X/2$ = concn. of H_2O formed in the reaction
X = concn. of NO_2 formed in the reaction
q = concn. of O_2 added
$X/4$ = concn. of O_2 formed in the reaction (neglected in comparison with q)

Values of ln K_p are plotted as a function of $1/T$ in Fig. 2. The straight line shown in this figure is given by the results listed in Table XIX of Forsythe and Giauque, while the circled points are

the experimental values of the present paper. Agreement of the experimental values with those of Forsythe and Giauque is within the limits of the estimated error.
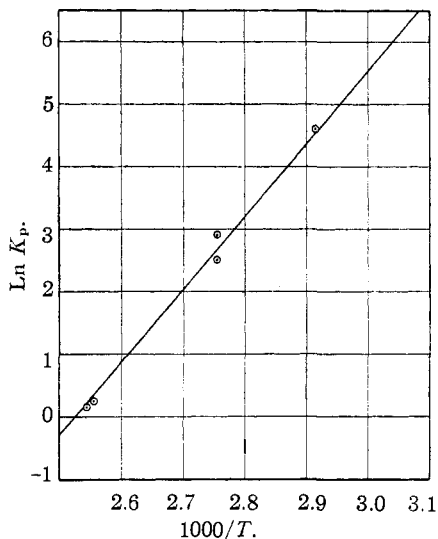

Fig. 2.

Forsythe and Giauque have reviewed previous experimental work from which equilibrium constants were determined for reaction (1). They point out that the measurements in the literature are not trustworthy due to failure of correctly measuring the vapor pressure of nitric acid, for which satisfactory values are not yet available. Experimental results listed in Table I, of course, do not depend upon the vapor pressure of nitric acid. They lead rather to a direct measurement of the equilibrium constant for reaction (3).

It was found in the course of this work that nitrous acid also possesses an absorption in the region near 1.4μ as seen in Fig. 3. Presumably this is due to the same type of vibration as that of nitric acid, namely, the 1st overtone of the O–H frequency. Here, however, we see that the peak has a doublet structure as would be expected from two isomeric forms of nitrous acid. These forms could result from different orientations of the OH group, a possibility not present in nitric acid.
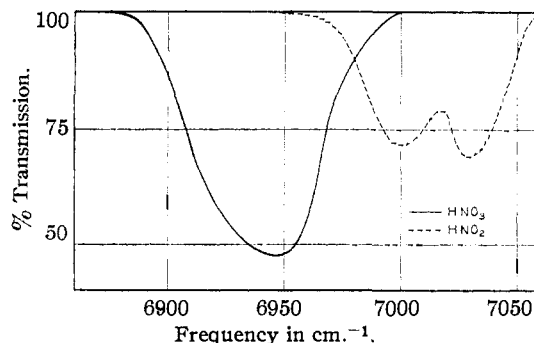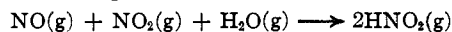

Fig. 3.

Some preliminary experiments were made to measure the equilibrium in the reaction

$$NO(g) + NO_2(g) + H_2O(g) \longrightarrow 2HNO_2(g)$$

without first determining the absorption coefficient of nitrous acid gas. An attempt to solve for the absorption coefficient and the equilibrium constant simultaneously was not successful. Results obtained indicated that considerably more work would have to be done in order to select the proper range of concentrations and that the absorption coefficient of nitrous acid gas would have to be measured directly. However, it is worth noting that the absorptions of the two compounds, nitrous and nitric acid, are sufficiently differentiated in the 1.4μ region to make feasible the measurements of the concentrations of each in the presence of the other.

This research was initiated under the supervision of Dr. Oliver R. Wulf and it is a pleasure to acknowledge his assistance in the earlier stages of this work. To Lola S. Deming the author is indebted for most of the calculations involved.

Summary

A direct determination was made of the equilibrium constant for the reaction $H_2O(g) + NO_2(g) + \frac{1}{2}O_2(g) \rightarrow 2HNO_3(g)$, using the infrared absorption at 1.4μ of nitric acid vapor as a method of analysis. Agreement with the calculations of Forsythe and Giauque is within limits of error. Transmission values of nitric acid and nitrous acid in the 1.4μ region are given.

The Catalytic Isomerization of Paraffin Hydrocarbons. I. Butanes[1]

BY PHILIP A. LEIGHTON AND JULIUS D. HELDMAN[2]

The catalyzed isomerization of n-butane has been a subject of considerable interest and application in recent years. The rearrangement is achieved at relatively low temperatures with the aid of a Friedel–Crafts type catalyst, usually aluminum chloride, plus a "promoter" such as hydrogen chloride.[3]

Montgomery, McAteer and Franke[4] have shown that aluminum bromide, which is soluble in the lower paraffin hydrocarbons, will catalyze the isomerization of liquid n-butane at room temperature.

Very little is known regarding the actual mechanism of the catalyzed isomerization. It warrants careful study from a fundamental standpoint because of its importance, because of its chemically clean-cut character, and because it offers a good starting point for the general understanding of halide catalysis.

The first possibility considered was that of a homogeneous gas phase isomerization. When aluminum chloride, hydrogen chloride and n-butane were mixed as vapors at 130° or above, no isomerization of the alkane could be observed, although extensive carbonization occurred in one experiment. Because of the difficulty of handling aluminum chloride as a vapor, boron trifluoride was substituted for it. In nine experiments, over

widely varying temperatures (up to the threshold of pyrolysis of the butanes) and with substantial amounts of boron trifluoride and hydrogen chloride present, no detectable reaction occurred.

Kinetic studies of the liquid phase isomerization, which was briefly checked for homogeneity in Pyrex tubes, were then undertaken. It was found in earlier "qualitative" experiments that extremely small traces of water or hydrogen bromide exert a promoter effect on the catalyst. For quantitative rate experiments it was necessary to devise a technique for the introduction of pure, dry aluminum bromide and hydrogen bromide in known amounts into the reaction bomb tubes.

Experimental

All work was done on the vacuum bench with a pumping system capable of producing a vacuum of 10^{-5} mm. or better.

Hydrogen bromide was made either by the addition of water to phosphorus tribromide or the dehydration of a 48% solution of the acid by excess phosphorus pentoxide. The product in each case was purified by several distillations from dry-ice to liquid air with subsequent pumping off of the residue. There was apparently no difference between the products made by the two methods.

Aluminum Bromide.—The anhydrous catalyst was prepared by direct combination of the elements, using an excess of aluminum. The product was distilled three times in vacuum. It was a heavy crystalline mass with a faint pink tinge. In the qualitative experiments it was quickly transferred in air into the reaction tubes. After several runs, it became obvious that some hydrogen bromide was always produced by reaction of the catalyst with air moisture and that it was impossible to reproduce rate measurements with aluminum bromide handled in air. The further purification and handling of the catalyst is described under the procedure in quantitative experiments.

Butanes.—The hydrocarbons were the gift of the Shell Development Company. The stated analyses were as

(1) Original manuscript received October 19, 1942.

(2) Present address: University of California, Berkeley, California.

(3) For a review of work in this field, see Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, N. Y., 1942.

(4) Montgomery, McAteer and Franke, (a) THIS JOURNAL, **59**, 1768 (1937); (b) papers presented before the Petroleum Division of the American Chemical Society. Part I, Baltimore Meeting, April 3–7, 1939, p. M-1.