proceed as was suggested by Krebs, Weitz, and Worms[5] for the white.

Summary

A vitreous phosphorus has been prepared from white phosphorus by two totally dissimilar methods. The properties of this form are different from all other known forms of phosphorus.

Acknowledgments.—The author gratefully acknowledges the extensive help from Dr. D. M. Warschauer and the stimulating discussions with Professors W. C. Schumb, J. W. Irvine, and C. C. Stevenson of M.I.T.

Contribution from Rohm and Haas Company,
Redstone Arsenal Research Division, Huntsville, Alabama

Nitrosodifluoramine. II. The Gas Phase Equilibrium

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Received July 16, 1962

The gas phase equilibrium: $2NO + N_2F_4 \rightleftarrows 2NF_2NO \rightleftarrows 2NO + 2NF_2$ has been investigated. The heat of formation of NF_2NO at 295° was found to be +20.4 kcal./mole ± 1.4 kcal. and the N–N bond dissociation energy in F_2N–NO was observed to be 10.1 ± 1.4 kcal.

The low temperature synthesis of nitrosodifluoramine (F_2NNO) and its partial characterization have recently been reported by Colburn and Johnson.[1] These investigators found this substance to possess a blue-purple color in both the liquid and gas phase. The intensity of the color of the material in the gas phase was a function of temperature and pressure. This observation suggested the existence of a gas phase equilibrium

$$2NO + N_2F_4 \rightleftarrows 2NF_2NO \rightleftarrows 2NO + 2NF_2$$

The present investigation is a quantitative study of this equilibrium.

Experimental

Materials.—Nitric oxide (Matheson) was purified by double passage through a trap at −160° (isopentane slush). Nitrogen dioxide was essentially removed by this treatment, and nitrous oxide was reduced to approximately 0.2%.

Tetrafluorohydrazine[2] of high purity was available. The principal impurity in the N_2F_4 was approximately 0.5% N_2O; other impurities were 0.1% NO and 0.1% SiF_4. The purity of the starting materials was determined by mass spectrometric analysis.

Apparatus.—A Beckman DU quartz spectrophotometer was used for the absorbance measurements. The optical cell was a Perkin-Elmer high pressure infrared cell with calcium fluoride windows; the path length was 6.15 ± 0.05 cm. Absorbance readings were taken against air as a standard, since the cell absorbance was relatively small and constant in the region of interest.

Temperature control was achieved by circulation of water through the coils of the Beckman thermospacers. The optical cell fit snugly against the metal faces of the two spacers after removal of the rubber buffer rings from the spacers, and thus gave good thermal contact. The temperature was measured to 0.1° by a two-junction copper–constantan thermocouple read to 0.01 mv. on a Leeds and Northrup potentiometer. The thermocouple junctions were attached to the body of the cell and protected with an asbestos shield.

The remainder of the pressure apparatus consisted of 0.25 in. copper tubing, a vacuum pump, and a 1-l. steel bomb with a pressure gage reading to 2 p.s.i. Materials were charged by condensing the starting materials into the bomb with liquid nitrogen after P–V measurements had been made in a calibrated glass bulb. Expansions and pressure operations were carried out remotely and the optical cell shielded by 3/8 in. Plexiglas sheet (see cautionary note).

The difference in the volatilities of NO and N_2F_4 made it necessary to allow several hours for complete mixing to occur in the gas phase following the volatilization of the condensed reactants. The usual practice was to permit at least 15 hr. mixing time although no detectable change occurred after 2 to 3 hr. The rates of the reactions involved in this equilibrium are not slow since the expected absorbances were established in a very short time when pressures were reduced rapidly by venting.

Results

Stoichiometry.—A series of spectra obtained at 25° by adding various incremental amounts of nitric oxide to a constant concentration of tetrafluorohydrazine is shown in Fig. 1. The absorption peak at 550 mμ is similar to the 570 mμ band assigned[1] to NF_2NO in low temperature solutions. The absorption appears to be due to a single species and is in the approximate position expected from the qualitative observation that the gas possesses a blue color.

The much weaker absorption at approximately 1750 mμ was shown to be characteristic of the nitric oxide used, since it was present when NO was examined in the absence of N_2F_4. It has not been established whether this absorption is an overtone of the N–O stretching vibration or a minor impurity in the NO.

The equilibrium formation of nitrosodifluoramine can be represented by the equation

$$2NO + N_2F_4 \rightleftarrows 2NF_2NO \qquad (1)$$

For this reaction the equilibrium constant expression is

$$K_c = \frac{[NF_2NO]^2}{[NO]^2[N_2F_4]} \qquad (2)$$

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[1] C. B. Colburn and F. A. Johnson, *Inorg. Chem.*, **1**, 715 (1962).

[2] C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

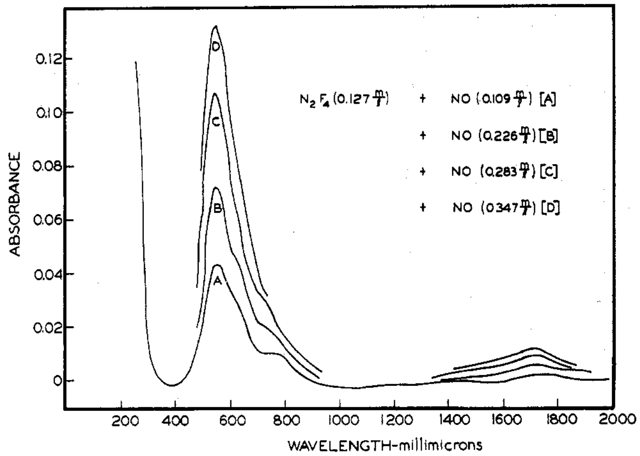

Fig. 1.—Gas spectra of NF_2NO.

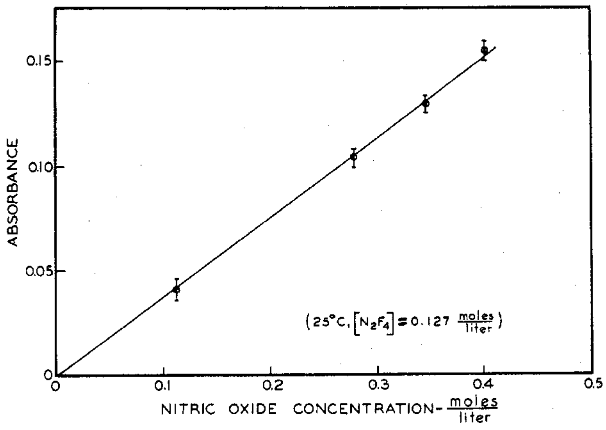

Fig. 2.—Absorbance at 550 mμ as a function of nitric oxide concentration.

If NF_2NO is the absorbing species at 550 mμ, the NF_2NO concentration can be replaced by its Beer's law equivalent $[(NF_2NO) = A/\epsilon l]$. ($A$ is absorbance at 550 mμ, ϵ is the molar absorptivity in l. mole^{-1} cm.$^{-1}$, and l is the path length in cm.). Substitution in and rearrangement of eq. 2 gives

$$A = \epsilon l K_c^{1/2}[NO][N_2F_4]^{1/2} \quad (3)$$

Equation 3 predicts that the absorbance should depend directly upon the nitric oxide concentration when the concentration of tetrafluorohydrazine is maintained at a constant level. Figure 2 shows the linear variation of absorbance with [NO] at constant $[N_2F_4]$.

Equation 3 also predicts that absorbance should increase with increasing N_2F_4 concentration. Figure 3 illustrates the linear variation of absorbance with $[N_2F_4]^{1/2}$ at constant [NO].

If the ratio between NO and N_2F_4 is held constant, the mole fractions X_{NO} and $X_{N_2F_4}$ can be used with the total concentration C to give

$$A = \epsilon l K_c^{1/2} X_{NO} X_{N_2F_4}^{1/2} C^{3/2} \quad (4)$$

As predicted by this equation Fig. 4 illustrates the linear relationship between $C^{3/2}$ and absorbance for two widely different NO : N_2F_4 ratios.

From the slopes of the curves in Fig. 2, 3, and 4 the numerical value for the product $\epsilon K_c^{1/2}$ can be obtained.

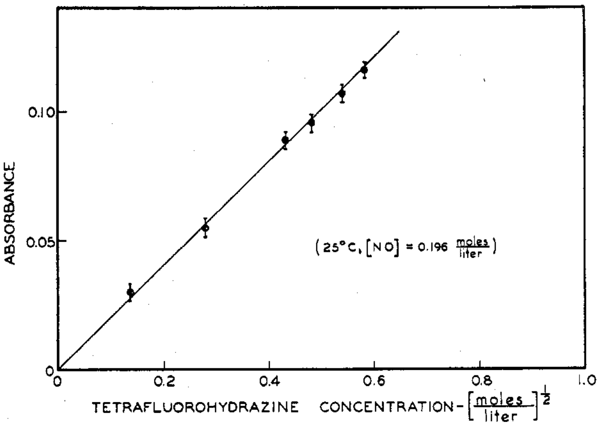

Fig. 3.—Absorbance at 550 mμ as a function of the one-half power of tetrafluorohydrazine concentration.

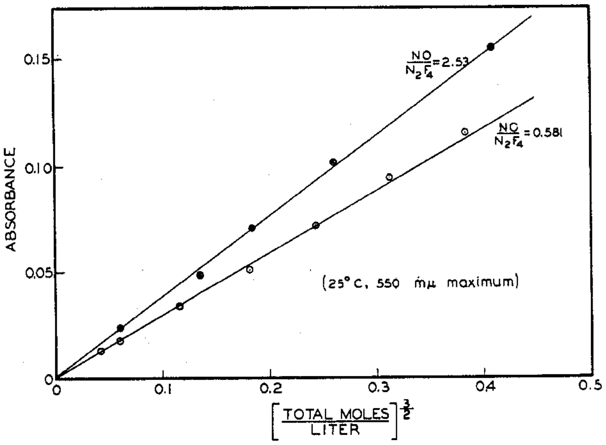

Fig. 4.—Absorbance at 550 mμ as a function of the three-halves power of the total concentration.

These values are given in Table I. It should be noted that in Fig. 2, 3, and 4 the abscissa values are approximate in that the NO or N_2F_4 added to the cell is used as the concentration of each species. This simply is the assumption that $[NO] \simeq [N_2F_4] >> [NF_2NO]$. The fact that there is no systematic deviation from linearity in Fig. 2, 3, and 4 is in agreement with this approximation. Estimates of K_c to be derived later also are in agreement with this approximation. Little error is introduced into the $\epsilon K_c^{1/2}$ values from this source.

Temperature Variation.—The combination of eq. 2 with Beer's law and the integrated van't Hoff equation leads to

$$\log K_c = \frac{-\Delta E^0}{4.576T} + \frac{\Delta S^0}{4.576} = 2 \log A - \log \epsilon^2 l^2 [NO]^2 [N_2F_4] \quad (5)$$

ΔE may be obtained from a plot of 2 log A against $1/T$. The internal energy changes resulting from a least

TABLE I

Plot	$\epsilon K_c^{1/2}$
A *vs.* [NO]	0.174
A *vs.* $[N_2F_4]^{1/2}$	.166
A *vs.* $C^{3/2}$ $\left(\frac{[NO]}{[N_2F_4]} = 0.5\right)$	.164
A *vs.* $C^{3/2}$ $\left(\frac{[NO]}{[N_2F_4]} = 2.4\right)$	.164
Av.	.167

squares fitting of four such experiments are given in Table II. The enthalpy changes in this table are calculated from $\Delta H = \Delta E + \Delta nRT$ where $\Delta n = -1$, the change in the number of molecules in reaction 1.

TABLE II

Run	ΔE, kcal.	ΔH (calcd.), kcal.	σ, kcal.
1	+0.22	−0.4	0.13
2	+ .31	− .3	.12
3	+ .16	− .4	.18
4	+ .13	− .5	.10
Av.	+ .2	− .4	± .2

An alternate approach is to run the thermal experiment at constant pressure. Under these circumstances the enthalpy change is related to the temperature and absorbance by

$$\frac{-\Delta H^0}{4.576T} + \frac{\Delta S^0}{4.576} = 2 \log A + 2 \log T + \text{constant} \quad (6)$$

The values given in Table III were found by a least squares procedure from the slope of the plot of $2 \log A + 2 \log T$ *vs.* $1/T$.

TABLE III

Run	ΔH, kcal.	σ, kcal.
1	−1.14	±0.27
2	−1.02	± .31
Av.	−1.1	± .3

Discussion

Heat of Reaction.—As seen from the relationship $\Delta H = \Delta E + \Delta nRT$, where $\Delta n = -1$, the values of ΔH and ΔE for reaction 1 must be 0.6 kcal. apart. The experimental values of these quantities are 1.3 ± 0.4 kcal. apart, the errors stated being due solely to the variance of the data obtained. The most probable explanation of this difference is offered by the effect of non-ideality of N_2F_4 on the constant pressure experiment. Here, heating the N_2F_4 causes less mass of N_2F_4 to remain in the optical path than the assumed ideal gas law predicts; therefore the measured absorbance is less at higher temperatures, resulting in a more negative value of ΔH than is correct. Consequently the −0.4 ± 0.2 kcal. value calculated from the constant volume determination of ΔE is to be preferred, since here the increase in ideality due to higher temperature and the decrease in ideality due to higher pressure must partially compensate.

Heat of Formation of Nitrosodifluoramine.—The heats of formation of tetrafluorohydrazine and nitric oxide are known to be −2 ± 2.5 kcal./mole[3] and 21.6 kcal./mole,[4] respectively. The heat of formation of nitrosodifluoramine at 298° is found to be +20.4 kcal./mole with an approximate error of ±1.4 kcal.

N–N Bond Dissociation Energy.—The heat of reaction for $NF_2NO \rightarrow NO + NF_2$ corresponds to the N–N bond dissociation energy. Using known heats of formation[5] [$\Delta H_f(NF_2) = 8.9 \pm 1.8$ kcal.], the value of $D^{298}(ON{-}NF_2)$ is 10.1 ± 1.5 kcal. Sufficient data to calculate $D_0^0(ON{-}NF_2)$ are lacking. For the replacement of three excited vibrational degrees of freedom by three degrees of translational freedom, the assumption of $\Delta H^{298} - \Delta E_0^0 = 0.9$ kcal. found for N_2O_4 by Giauque and Kemp[6] appears reasonable. A D_0 of 9.2 ± 1.5 kcal. is thereby estimated. This is not an unreasonably low value in view of $D(ON{-}NF_2)$ of 10 kcal. and $D(O_2N{-}NO_2)$ of 12.9 kcal.[7]

Entropy, K_p, K_c, and ϵ.—Sufficient experimental data are not available to calculate exact numerical values for the above quantities. However, several approximations can be made. If more than 1% of the N_2F_4 in the experiments illustrated in Fig. 1 was converted to NF_2NO, the points at high NO concentration should fall below the line. Since $[NF_2NO]$ is less than 1% of $[N_2F_4]$, an upper limit of 10^{-4} can be set on K_c as shown on the first line of Table IV. A second approach is to estimate the entropy change in reaction 1. The approximate method of Wenner[8] was used to obtain a value of 45.4 e.u. Values calculated with this entropy are given in the second line of Table IV. Finally, an independent value of ϵ is available from spectrophotometric work[1] in the condensed phase. Some distortion of the absorption peak is to be expected on going from solution at −160° to gas at 25°, but the 110 l. mole^{-1} cm.$^{-1}$ value should still be a reasonable estimate, since temperature and vapor–solution effects will partially compensate.

TABLE IV

ΔS^{298}, e.u.	K_c	K_p	ϵ
>35	$<1 \times 10^{-4a}$	$<2 \times 10^{-7}$	>13
45.4^a	1×10^{-7}	2×10^{-10}	480
40.5	2.7×10^{-6}	4.5×10^{-9}	110^a

^{a} Values assumed.

Of this set of constants those on the last line appear to be by far the most reliable, although no great accuracy can be claimed. Both the estimated entropy and absorptivity confirm the observation of linear composition plots in Fig. 2, 3, and 4. Indeed they predict that the conversion of NO and N_2F_4 to NF_2NO never exceeds 0.1% in any of the experiments described herein, and reconfirm the validity of the assumption that under the experimental conditions used in this work $[NF_2NO] << [NO] \simeq [N_2F_4]$.

Caution.—The mixture of N_2F_4 and NO is thermodynamically unstable with respect to a variety of products such as O_2, N_2, NF_3, NOF, etc. Accordingly this potentially dangerous combination should be treated with care, although no difficulty was experienced in this study.

Acknowledgment.—This work was carried out under Contract No. DA-01-021 ORD-11878.

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