2. The decomposition is strictly unimolecular in all cases. The specific decomposition rate decreases in the order given above. In nitrogen tetroxide it is about twice as large as in the gas phase.

3. The critical increment, E, calculated from the temperature coefficient of reaction rate is 24,700 calories within the limit of experimental error in every case.

4. The specific decomposition rate is somewhat greater in concentrated than in dilute solutions and yet the unimolecularity is maintained throughout the whole course of the reaction. Apparently N_2O_4 and N_2O_5 are equally effective in accelerating the decomposition.

5. Moisture does not affect the decomposition rate.

6. In a mixed solvent the effects of the solvents are proportional to their mole fractions.

7. The decomposition rate was determined in saturated solutions. The results are of interest in the study of activities.

8. The stability of crystalline nitrogen pentoxide is discussed.

9. The constancy of E in different solvents and the universal constancy of the temperature effect are interpreted on the basis of the Arrhenius equation, $k = se^{-E/RT}$ using the experimental data for nitrogen pentoxide.

10. The factor, s, in the Arrhenius equation was found to be constant when the temperature coefficient of reaction rate was determined with great accuracy. It is predicted that s will approach an approximate constant in nearly all unimolecular reactions as experimental measurements become more accurate. The quantity, s, may be identified with the infrared oscillation frequency at the valence bond which is about to break.

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THE DECOMPOSITION OF NITROGEN PENTOXIDE IN CHEMICALLY ACTIVE SOLVENTS

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Received December 26, 1929 Published April 7, 1930

In the preceding communication[1] it was shown that the normal decomposition rate of nitrogen pentoxide is not appreciably affected by inert solvents. It was found that the specific decomposition rate might vary from the normal rate in the gas phase to twice the normal rate but that the temperature effect and the critical energy of activation, E, remained the same within the limits of experimental error.

Another group of solvents is described here in which the decomposition rates and their temperature coefficients are quite abnormal. The distinction between "inert" and "chemically active" solvents is a matter only of

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[1] Eyring and Daniels, This Journal, **52**, 1472 (1930).

degree and the small variations among the inert solvents described before may be due to some slight combination with the solvent. Solvation is quite marked in some of the solvents recorded here and it is shown for example that nitric acid reduces the decomposition to one-twentieth of its normal value and yet the decomposition follows the unimolecular law.

Experiments on saturated solutions in the preceding communication were interpreted to indicate that the solvated molecules studied there decomposed slightly faster than the normal molecules. In the present communication other types will be presented, those in which the solvated molecules do not decompose, those in which the solvated molecules decompose at once into new products and those in which the normal decomposition rate is accelerated.

The experimental technique and the method of calculation were the same as those described in the preceding report. Nitrogen pentoxide in solution was sealed off in a small bulb of 5 cc. and shaken violently in a thermostat. The rate of evolution of oxygen was measured with the help of a gas buret connected through a flexible glass spiral.

Experimental Results

Nitric Acid.—Nitrogen pentoxide was dissolved in 3 cc. of 96% nitric acid so that the final concentration was about 0.003 mole of N_2O_5 in 0.07 mole of HNO_3, assuming that the total gas evolved is a measure of the nitrogen pentoxide content.

DATA AT 45°

Time, sec.	0	687	1069	2474	6896	7551	23,876	∞
O_2, cc.	0	0.61	0.96	1.85	4.96	5.33	13.71	37.48
$k \times 10^5$		2.36	2.08	1.76	2.05	1.75	1.83	

In a second experiment the rate of oxygen evolution was determined at 15 and 35° and the critical energy of activation, E, was found to be 28,300 calories.

As the ratio of N_2O_5 to HNO_3 increased the specific decomposition rate increased, and when the HNO_3 was present only in small amounts it was without noticeable effect. The nitric acid itself showed no appreciable decomposition. The experiments were in agreement with the observation that the addition of a little water to a solvent has no effect on the specific decomposition rate in solution except in special cases (as with carbon disulfide). Rice and Getz,[2] using a titration method, found that nitrogen pentoxide decomposed about one-tenth as fast in the nitric acid as in the gas phase under their conditions, but they did not obtain data for calculating E.

The large value of E and the large temperature coefficient of decomposition rate have the effect of making the nitrogen pentoxide dissolved in nitric

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[2] Rice and Getz, *J. Phys. Chem.*, **31**, 1572 (1927).

acid appear quite stable at 15° even though at 45° it decomposes rather rapidly.

Propylene Chloride.—The propylene chloride, obtained from the Eastman Kodak Company, was distilled and dried with phosphorus pentoxide. The data are as follows and the calculated value of E is 27,000 calories.

Data at 20°

Time, sec.	0	807	1390	1832	2097	2653	2917	∞
O_2, cc.	0	0.38	0.62	0.81	0.92	1.14	1.24	18.22
$k \times 10^5$		0.261	0.231	0.246	0.238	0.230	0.222	...

Data at 35°

Time, sec.	3140	3225	3511	3620	4309	
O_2, cc.	4.00	4.34	5.34	5.73	7.82	
$k \times 10^5$	.....	2.32	2.11	2.26	2.08	
Time, sec.	5470	6077	6577	6730	13.64	∞
O_2, cc.	10.72	12.16	13.04	13.31	19.50	21.40
$k \times 10^5$	2.07	2.39	2.00	2.14	2.10	

The oxygen evolved was free from carbon dioxide. Another less consistent experiment over the same temperature interval gave 28,200 calories for E, and it may be concluded that the critical energy of activation is considerably larger than the 24,700 obtained for the gas phase and for the decomposition in inert solvents. Other data gave 4.13×10^{-5} at 40° and 7.35×10^{-5} at 45° but these data are not suitable for calculating E, as explained in the preceding communication, because the concentrations were not the same in the two experiments.

Carbon Disulfide.—The decomposition of nitrogen pentoxide in carbon disulfide solution is complicated by the oxidation of the solvent and the oxygen evolved contains carbon dioxide and sulfur dioxide. The rate of oxidation is greatly affected by traces of water. In one experiment at 15° when gas was being evolved very slowly, the addition of a small drop of water produced 5 cc. of gas in five minutes and then the reaction slowed down. Three more drops of water caused the evolution of an additional 10 cc. of gas in about two minutes and 5 drops gave a still more violent action, the reaction in each case lasting only for a short time until the nitric acid was used up. The gas consisted chiefly of carbon dioxide and sulfur dioxide and it is evident that carbon disulfide is oxidized rapidly by nitric acid and very slowly by nitrogen pentoxide. Pure nitric acid and carbon disulfide react instantly with great violence.[3]

It was found also that carbon disulfide vapor added to gaseous nitrogen pentoxide gives an abnormal increase in pressure,[4] probably on account of oxidation of the carbon disulfide.

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[3] A. C. Andrews, B.S. Thesis, University of Wisconsin, **1924**.

[4] Busse and Daniels, This Journal, **49**, 1259 (1927).

In spite of the complications introduced by the oxidation of the solvent, the data with *dry* carbon disulfide gave satisfactory constants when calculated by the unimolecular formula, but the results obtained did not check with those obtained several years before and no confidence can be placed in the absolute values of k nor of E.

Iodine.—Iodine in carbon tetrachloride is quickly oxidized by nitrogen pentoxide giving a precipitate of iodine pentoxide. The rate of the reaction has been studied colorimetrically[5] and the reaction is much faster than the normal decomposition rate of nitrogen pentoxide. The reaction at 0° is practically finished in a few minutes. At higher temperatures some oxygen is liberated.

Acetone.—When nitrogen pentoxide is dissolved in acetone, gas is evolved very slowly. It is not oxygen, however, and a unimolecular reaction constant cannot be calculated from the rate of gas evolution.

One typical analysis of the gas gave 25.0 cc. of CO_2, 24.0 cc. of N_2O and 1.0 cc. of oxygen. Carbon dioxide and oxygen were determined in an Orsat apparatus and the density of the residual gas was determined by expelling the gas into a toy rubber balloon tied to the apparatus. The neck of the balloon was then carefully tied off and the balloon was weighed. The 24 cc. at 740-mm. pressure and 25° weighed 0.014 g. in air, giving a molecular weight 14.6 greater than air ($28.9 + 14.6 = 43.5$). In a second experiment 24.2 cc. of gas weighed 0.0141 in air, giving again a molecular weight of 43.5. The chemical inactivity and the density showed that the residual gas was nitrous oxide. The chief product in the liquid phase was acetic acid together with a small amount of an unidentified white crystalline solid moderately soluble in water and alcohol.

The reaction between acetone and nitric acid (95% HNO_3) gave the same gaseous products in the same proportions as the reaction with nitrogen pentoxide. McIntosh[6] showed the existence at low temperatures of an equimolecular compound of nitric acid and acetone.

When nitric acid (95% HNO_3) at room temperature is added rapidly to acetone, the latter bursts into flame, but if it is added slowly at 0° no visible reaction occurs. The results may be explained by assuming that the molecular compound between acetone and nitric acid evolves sufficient heat to start the oxidation reaction, which is violently exothermal. The temperature is raised and the reaction is accelerated, whereupon the heat is generated faster and the process continues until the reaction is so fast as to simulate an explosion. The oxidation reaction proceeds normally at 35° provided there is sufficiently rapid shaking to dissipate the heat evolved in the reaction. In one case when the shaking of a bulb containing approximately 2 cc. of nitric acid (95%) and 2 cc. of acetone was discontinued for a

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[5] T. Nash, B.S. Thesis, University of Wisconsin, **1925**.

[6] McIntosh, This Journal, **27**, 1013 (1905).

few minutes a violent explosion occurred although previously the reaction had been proceeding slowly and smoothly. Explosions occurred also when a considerable quantity of nitrogen pentoxide was dissolved in acetone at room temperature but small quantities dissolved without apparent reaction.

The chief reactions appear to be

$$CH_3COCH_3 + HNO_3 = CH_3COCH_3{\cdot}HNO_3$$
$$CH_3COCH_3{\cdot}HNO_3 + HNO_3 = CH_3COOH + CO_2 + N_2O + H_2O$$

This equation gives carbon dioxide and nitrous oxide in equal quantities and acetic acid as the product in solution and it suggests that the reaction is bimolecular.

To determine whether the reaction is bimolecular, as indicated, 2.06 cc. of 95% nitric acid was added to 2.06 cc. of dry redistilled acetone. The solution evolved gas at the rate of 0.00143 cc. per second or at the rate of 3.43×10^{-4} cc. per sec. per cc. To this volume of nitric acid and acetone was added 4.12 cc. of nitromethane as an inert solvent. Gas was then evolved at the rate of 0.00054 cc. per 8.24 cc. of solution. The two measurements were made at 20° with ample shaking and in immediate succession so that no appreciable amount of material decomposed between measurements. Since the concentration of the reacting constituents was half as much in the diluted solution as in the original solution, the rates should be in the ratio of 4 to 1 if the reaction is bimolecular. Actually they are in the ratio of 3.43/0.655 or 5.2 and this agreement is sufficiently close, considering the nature of the assumptions, to conclude that the reaction is bimolecular.

Theoretical Discussion

The experiments described in these two communications illustrate various ways in which the decomposition of nitrogen pentoxide may be affected by solvents. An extreme case of chemical reaction with the solvent might be illustrated by the solution in nitrobenzene. Stable products, dinitrobenzene and nitric acid, are formed at once and no further change occurs. At the other extreme are the inert solvents described in the preceding communication, which have very little effect on the decomposition rate. Probably there is slight solvation, however, in some of these "inert" solvents and the solvated molecules of nitrogen pentoxide decompose at a different rate. In propylene chloride this solvation appears to be carried to a considerable extent so that the critical energy of activation, E, is considerably larger than in the inert solvents.

Solvation can lead to an increased decomposition rate as already shown or it can lead to a decreased decomposition rate as in the case of nitric acid. Part of the molecules of nitrogen pentoxide are apparently locked up in stable complex molecules of the form $N_2O_5{\cdot}n HNO_3$. Although the specific decomposition rate is only about one-twentieth as large, it still follows the unimolecular law because the number of simple molecules which decompose is always proportional to the total concentration of nitrogen pentoxide at any time and this is the criterion of a unimolecular reaction.

The nitric acid solution may be treated mathematically on the assumption that the slow rate is due to the existence of an equilibrium number of stable complex molecules. The energy of activation, 28,300 calories, is 3600 calories greater than the energy of activation in the gas phase or in inert solvents as shown below, and the following reaction may be written.

$$N_2O_5 \cdot nHNO_3 = N_2O_5 + nHNO_3;\ \Delta H = 3600$$

The equilibrium constants for this reaction may be written

$$K = \frac{C^n_{HNO_3}\, C_{N_2O_5}}{C_{N_2O_5 \cdot nHNO_3}}$$

and since $\Delta F = -RT \ln K$ and $\Delta F = \Delta H - T\Delta S$

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

where F is free energy, H is heat content, S is entropy and T is absolute temperature.

$$\frac{C^n_{HNO_3}\, C_{N_2O_5}}{C_{N_2O_5 \cdot nHNO_3}} = e^{\Delta S/R}\, e^{-\Delta H/RT}$$

The rate of decomposition is given by the expression

$$\frac{-\mathrm{d}\, C_{N_2O_5}}{\mathrm{d}t} = kC_{N_2O_5} = \frac{kC_{N_2O_5 \cdot nHNO_3}}{C^n_{HNO_3}}\, e^{[(\Delta S/R) - (\Delta H/RT)]}$$

k is the fraction of the nitrogen pentoxide molecules decomposing per second and by the Arrhenius equation

$$k = se^{-E/RT}$$

where s is a constant and E is the critical energy of activation. Then

$$\frac{-\mathrm{d}\, C_{N_2O_5}}{\mathrm{d}t} = \left(s\, \frac{C_{N_2O_5 \cdot nHNO_3}}{C^n_{HNO_3}}\, e^{\Delta S/R}\right) e^{-(E + \Delta H)/RT}$$

In solutions containing a large excess of nitric acid solvent, the quantity in the parentheses is nearly proportional to $C_{N_2O_5}$ and since ΔS changes but slightly with temperature, the quantity is nearly independent of temperature. The value of $E + \Delta H$ may then be calculated with fair accuracy from the experimentally determined temperature coefficient of the reaction rate in the usual manner.

$E + \Delta H$ was found to be 28,300 and E for simple nitrogen pentoxide molecules has been found repeatedly to have the value 24,700. The heat of formation of the solvated molecules is then 3600 calories.

The three additional solvents described here were studied because they involve definite chemical interaction with the solvent to give new products. In all cases the apparent reaction is more rapid than the normal decomposition. Carbon disulfide is oxidized rather slowly, while iodine in solution is oxidized rapidly to iodine pentoxide. In both cases some of the nitrogen pentoxide decomposes spontaneously in the normal way to liberate oxygen.

The decomposition in acetone is interesting although seriously complicated by the formation of a solvated molecule which reacts to give an entirely different set of products. The reaction is probably typical of many organic reactions. It is further complicated by the fact that water is produced as one of the products and, it in turn, forms nitric acid, which reacts faster with the acetone. The reaction between nitrogen pentoxide and any substance containing hydrogen which is oxidized should be considered also as a reaction with nitric acid, and, in fact, the latter may be the predominating reaction on account of its greater speed.

These studies are of interest in connection with the use of activities in reaction rate calculations. Concentration measurements give both solvated and unsolvated molecules while activities may give the concentration of the unsolvated molecules alone. If the solvated molecules do not decompose (as in this case of solution in nitric acid), the rate of decomposition should be proportional to the activities of the unsolvated molecules. If concentrations are used in the calculations, the reaction rate will still follow the unimolecular formula in dilute solutions because the concentration of unsolvated molecules is always proportional to the total concentration, but the specific decomposition rate calculated in this way will be abnormally low.

If the solvated molecules decompose faster than the unsolvated molecules, as in the case of solvents described in the preceding communication, the specific decomposition rate will be too high, and the substitution of activities for total concentrations will not help.

Summary

1. Nitrogen pentoxide dissolved in nitric acid decomposes very slowly and follows the unimolecular formula. The results can be explained on the assumption of stable solvated molecules in equilibrium with the nitrogen pentoxide. The decomposition rate has a very high temperature coefficient. $E = 28{,}300$ and $k_{45^\circ} = 1.97 \times 10^{-5}$.

2. In propylene chloride, nitrogen pentoxide decomposes without apparent action on the solvent. The temperature coefficient is abnormally high, giving E a value of 28,000. At 35° $k = 2.3 \times 10^{-5}$.

3. Carbon disulfide is oxidized by dissolved nitrogen pentoxide but the latter also decomposes with the liberation of oxygen. A little water produces nitric acid and gives a much more rapid oxidation.

4. Iodine in solution is rapidly oxidized by nitrogen pentoxide but some nitrogen pentoxide decomposes independently.

5. With acetone nitrogen pentoxide or nitric acid forms an addition product which reacts further to give nitrous oxide, carbon dioxide and acetic acid.

6. The concept of activities is discussed in connection with the decomposition rate in the various cases of solution.

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