type which were studied. A possible explanation might be the inability of the perchlorate ion to function as a coördinating anion or even to approach the cation closely in forming an electrostatic ion pair. The cation would then be left free to exert a maximum influence in orienting solvent molecules.

This explanation is in accord with the fact that very high activity coefficients are encountered in concentrated aqueous solutions of perchlorate salts. Since the cation would be effectively masked by solvent from specific interactions with the anion, this might also explain the lack of individualistic behavior of perchlorates in comparison with the corresponding chlorides.

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The Thermal Decomposition of Nitrous Oxide[1]

BY LEWIS FRIEDMAN AND JACOB BIGELEISEN

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A study of the isotopic composition of the nitrogen from the thermal decomposition of a sample of N_2O enriched in $N^{15}N^{14}O$ shows that no equilibration of the nitrogen atoms takes place during the decomposition reaction. It is shown that NO neither exchanges with N_2O nor catalyzes the equilibration of nitrogen during the decomposition of N_2O. These results support the unimolecular decomposition mechanism and add restrictions to the chain mechanism.

Introduction

The homogeneous decomposition of nitrous oxide is classical in gas kinetics. No completely satisfactory description of the order of the reaction was available until Pease[2] proposed a 3/2 order reaction instead of the second order rate law of Hinshelwood and Burk[3] and the combinations of unimolecular reactions suggested by Volmer,[4] Musgrave and Hinshelwood,[5a] and Hunter.[5b] Pease's rate law is in good agreement with the experimental data over the wide ranges of temperature and pressure investigated. Another feature of the 3/2 power rate law is that it leads to an activation energy independent of pressure, whereas the first order rate constants lead to activation energies which rise by about 30% in the pressure interval 0–40 atmospheres. Pease proposed a mechanism consistent with the 3/2 order rate law involving chains which include nitrogen atoms and nitric oxide.

Subsequent to the completion of the work described in this paper, Johnston[6] reported the results of an analysis of all the published data on the rates of the decomposition. His analysis is consistent with the assumption that the decomposition may in part be heterogeneous. After one corrects for the heterogeneous portion of the reaction, the kinetics follow those expected for a unimolecular reaction. The second order rate constants for activation in the Rice–Ramsperger–Kassel theories now lead to a single activation energy. The reaction mechanism can be pictured as

$$N_2O + N_2O \longrightarrow N_2O^* + N_2O \qquad (1)$$

$$N_2O^* + N_2O \longrightarrow 2N_2O \qquad (2)$$

$$N_2O^* \longrightarrow N_2 + O \qquad (3)$$

$$O + O + M \longrightarrow O_2 + M \qquad (4)$$

$$O + N_2O \longrightarrow N_2 + O_2 \qquad (5)$$

$$O + N_2O \longrightarrow 2NO \qquad (6)$$

We have carried out some experiments on the decomposition of mixtures of $N^{15}N^{14}O$ and $N^{14}N^{14}O$ and looked for possible equilibration of N^{14} and N^{15} in the nitrogen product. It is known that the homogeneous equilibration of nitrogen gas is slow at 750°.[7] Some additional experiments were carried out to look for exchange between $N^{14}O$ and each of the isomers $N^{15}N^{14}O$ and $N^{14}N^{15}O$. The results of these studies are in agreement with predictions from the unimolecular decomposition mechanism. The nitrogen atom–nitric oxide chain mechanism of Pease is ruled out.

Experimental

Samples of N_2O enriched in either $N^{15}N^{14}O$ or $N^{14}N^{15}O$ were prepared by methods described previously[8,9] from the thermal decomposition of $N^{15}H_4N^{14}O_3$ and $N^{14}H_4N^{15}O_3$, respectively. Enriched $N^{15}H_4NO_3$ and $HN^{15}O_3$ were obtained from Eastman Kodak Co.

The N_2O decomposition reactions were carried out in sealed cylindrical quartz vessels 3 × 20 cm. filled to a pressure of about 80 mm. at room temperature. The decomposition and exchange reaction temperatures were about 750°.

The exchange experiments between N_2O and $N^{14}O$ were similarly carried out in quartz reactors. Matheson tank NO was used without further purification. Semi-quantitative tests on the purity of the tank NO indicate possible errors from this source of the order of 1% in the 29/28 and 31/30 ratios in the exchange experiments. NO_2 was observed as a reaction product after the vessel was cooled to room temperature for analysis. It was separated from the N_2, NO and O_2 by passing the mixture through a trap cooled to −80°.

All samples were analyzed mass spectrometrically after the reaction mixture cooled to room temperature. In all cases the decomposition of N_2O was complete.

Results and Discussion

The results of a typical mass spectrometric analysis of the N_2 and NO formed from the thermal

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(1) Research carried out under the auspices of the Atomic Energy Commission. Presented at the 118th meeting of the American Chemical Society, September 3-8, 1950, Chicago, Ill.

(2) R. N. Pease, *J. Chem. Phys.*, **7**, 749 (1939).

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decomposition of a mixture of predominantly $N^{15}N^{14}O$ and $N^{14}N^{14}O$ are given in Table I.

TABLE I

ISOTOPIC ANALYSIS OF N_2 AND NO FROM THE THERMAL DECOMPOSITION OF $N^{15}N^{14}O$ AND $N^{14}N^{14}O^a$ AT 750°

Mass	28	29	30	31
Species	$N^{14}N^{14}$	$N^{14}N^{15}$	$N^{15}N^{15}$ + $N^{14}O^{16}$	$N^{15}O^{16}$
Measured peak height (arbitrary units)	37.8	61.5	0.44	0.15
Calcd. peak height (neglecting formation of NO and assuming no equilibration of N atoms)	37.8	61.9	0.23	
Calcd. peak height (neglecting formation of NO and assuming equilibration of N atoms)	47.3	42.9	9.73	

[a] The N_2O was prepared from NH_4NO_3 containing 62.0% $N^{15}H_4^+$. The composition of the N_2O is therefore $N^{15}N^{14}O$, 61.8%; $N^{14}N^{15}O$, 0.14%; $N^{14}N^{14}O$, 37.8%; $N^{15}N^{15}O$, 0.23%. The natural abundance of N^{15} is assumed to be 0.37% (A. O. Nier, *Phys. Rev.*, **77**, 789 (1950)).

The data in Table I show conclusively that there is no equilibration of nitrogen atoms in the decomposition. The slight excess at mass 30 over that calculated, 0.44 *vs.* 0.23, can be reasonably attributed to $N^{14}O^{16}$ which would be expected to occur to the extent of 0.2%. The large abundance of $N^{15}O^{16}$ above the natural abundance of $NN^{15}O^{16}$ indicates that the main source of NO is from the reaction

$$O^{16} + N^{15}N^{14}O^{16} \longrightarrow N^{15}O^{16} + N^{14}O^{16}$$

This reaction has been suggested by Noyes[10] to account for the NO formation in the photolysis of N_2O. Small amounts of NO may arise from the reaction

$$X + NNO \longrightarrow NX + NO$$

where NX is neither NO nor does it react to form it.

The results of the exchange experiments between $N^{14}O$ and $N^{15}N^{14}O$ and $N^{14}N^{15}O$, respectively, are given in Table II. The only conclusion consistent with the experimental data is that there is no exchange of either of the nitrogen atoms of the N_2O with NO during the decomposition of the former and that NO does not catalyze the isotopic equilibration of the nitrogen atoms in N_2O during the decomposition. The observed 29/28 ratio from the $N^{15}N^{14}O$ experiment is 7% low from that calculated for no exchange or equilibration. This is larger than what would be anticipated solely from the precision of the measurements. The source of this discrepancy is unknown, but the other three columns of the table suffice to establish the conclusion stated above.

The unimolecular mechanism of the reaction discussed in equations 1–6 is consistent with the decomposition studies of enriched $N^{15}N^{14}O$, the isotopic composition of the NO formed in the decomposition of the latter, and the exchange studies with NO.

A principal difficulty with Pease's mechanism is the chain initiating reaction of N_2O to give nitrogen atoms and NO. The standard free energy change for this reaction is some +50 kcal. mole^{-1}. Kassel[11] has previously objected to this mechanism on thermochemical and kinetic grounds. In addition to Kassel's objections, it is significant that the N–O bond in N_2O is definitely weaker than the N–N bond.[9] These are the most serious criticisms of Pease's mechanism.

We shall now examine Pease's mechanism in the light of the present experiments. According to this mechanism

$$N_2O \longrightarrow N + NO \quad (7)$$

$$N + N_2O \longrightarrow N_2 + NO \quad (8)$$

$$NO + N_2O \longrightarrow N_2 + N + O_2 \quad (9)$$

$$N + NO \longrightarrow N_2O \quad (10)$$

In order to avoid equilibration of the nitrogen atoms of the N_2O and exchange with NO one must postulate that reactions (8) and (9) proceed without rupture of the N–N bond in N_2O (*e.g.*)

$$N^{15} + N^{15}N^{14}O \longrightarrow N^{15}O + N^{15}N^{14} \quad (11)$$

$$N^{14} + N^{15}N^{14}O \longrightarrow N^{14}O + N^{15}N^{14} \quad (12)$$

$$N^{14}O + N^{14}N^{15}O \longrightarrow N^{15}N^{14} + N^{14} + O_2 \quad (13)$$

TABLE II

EXCHANGE EXPERIMENTS BETWEEN N_2O AND NO IN THE DECOMPOSITION OF N_2O

	$N^{15}N^{14}O$ + $N^{14}O$ at 750°				$N^{14}N^{15}O$ + NO			
Species	Initial compn., %	NO/N_2O (init.)	29/28 (final)	31/30 (final)	Initial compn., %	NO/N_2O (init.)	29/28 (final)	31/30 (final)
$N^{15}N^{14}O$	7.49	2.02	0.0796	0.0038	0.25	0.939	0.455	0.0040
$N^{14}N^{15}O$	0.35				31.3			
$N^{15}N^{15}O$	0.029				0.12			
$N^{14}N^{14}O$	92.1				68.3			
$N^{15}O$	0.37				0.37			
$N^{14}O$	99.6				99.6			
Calculated 29/28 and 31/30 ratios								
1 Exchange with N*N*O								
a Isotopic equil. of N_2			0.0820	0.0037			0.183	0.195
b No equil. of N_2			.0853	.0037			.197	.196
2 Exchange with *NN*O			.0440	.0220			.244	.123
3 Exchange with *N*NO								
a Isotopic equil. of N_2			.0319	.0281			.378	.0036
b No equil. of N_2			.0319	.0281			.461	.0037
4 No exchange								
a Isotopic equil. of N_2			.0820	.0037			.378	.0036
b No equil. of N_2			.0853	.0037			.461	.0037

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(10) W. A. Noyes, Jr., *J. Chem. Phys.*, **5**, 807 (1937).

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The chain-ending step, reaction (10), would serve as a mechanism for equilibration of the N_2 and exchange with NO when the decomposition is carried out in the presence of the latter. From the experimental data one therefore would conclude that the chain length in the presence of NO must be of the order of 50–500. If there were chains of this length, then NO, when present in large concentrations such as our exchange experiment, would produce a sufficient concentration of nitrogen atoms by reaction (9) to lead to the production of N_2 by the recombination of the former. This nitrogen would necessarily come from NO, have the isotopic composition $N^{14}N^{14}$, and act as a diluent of the N_2 from the decomposition of N_2O. Since no dilution of the nitrogen product over the original N_2O is observed, this would argue for short chains. The apparent paradox argues against the above chain mechanism.[12]

[12] We are grateful to the referee of this paper for emphasizing the role of NO as a diluent for the nitrogen product.

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Low Temperature Heat Capacities of Inorganic Solids. XV. The Heat Capacity and Entropy of Red Mercuric Oxide[1]

BY THOMAS W. BAUER AND HERRICK L. JOHNSTON

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The heat capacity of red mercuric oxide was measured over the temperature range from 15°K. to room temperature. Thermodynamic functions were obtained from these values for the heat capacity, the molal entropy at 298.16°K. being 16.77 ± 0.05 e.u. Calculations were also made which confirmed the applicability of the Third Law to the entropy of red mercuric oxide.

Introduction

The question as to whether the red and yellow modifications of mercuric oxide differ only in particle size, or whether they are allotropic modifications is still undecided. The heat capacity of the red modification has been measured between 25 and 75° by Guenther,[2] and between 85 and 300°K. by Garrett.[3] The heat capacity of the yellow modification has been measured between 85° and room temperature by McDowell[4] and the results agree to within the limits of error.

Garrett and Hirschler[5] deduced from differential solubility measurements that the free energy of the yellow form was 31 cal./mole larger than that of the red form, but they were unable to decide whether this increase was due to an increase in surface energy or to a free energy of transition. Calorimetric heat of formation values for the two modifications are so inaccurate as to provide no means of ascertaining whether the two forms have different heats of formation. Even free energy of formation values calculated from cell measurements do not decide the dilemma, since the values of different investigators vary widely, and some neglected to state which modification was used in their cells, while others neglected to state the concentration of the electrolyte and failed to correct for this concentration. It was therefore decided to measure the heat capacity of red mercuric oxide over the range from 15°K. to room temperature, to get a reliable value for the entropy.

Apparatus and Material.—The mercuric oxide used was the red modification, commercial Baker Analyzed Reagent, containing the following percentage impurities: insoluble in HCl, 0.020; non-volatile matter, 0.010; Cl, 0.001; Fe, 0.004; SO_4, 0.005; total N, 0.003.

The calorimetric data were obtained with Calorimeter No. 3, whose construction and operation have been described previously.[6] Measurements were made with the calorimeter filled with 189.981 g. (0.87787 mole) of red HgO. The experimental values of the molal heat capacity in defined thermochemical calories are given in Table I. The smoothed curve through these points is believed to be accurate to within 0.2% above 45°K., but may be in error by as much as 0.5% at 20°K.

Smoothed values of the thermodynamic functions obtained from the heat capacity by graphical means are entered in Table II. The molal entropy at 298.16°K. is 16.77 ± 0.05 e.u.; of this amount 0.31 e.u. was contributed by a Debye extrapolation below 16°K., with θ equal to 126.8.

Third Law Check.—The dissociation pressures of red and yellow HgO have been measured by Taylor and Hulett,[7] who found them to be the same at all temperatures measured, and from their data Randall[8] has calculated the free energy and heat of formation of HgO (red or yellow):

$$\text{Hg (liq)} + {}^1/_2\text{O}_2\ \text{(g)} = \text{HgO (crystalline, red or yellow)}$$
$$\Delta F^\circ_{25} = -13{,}950\ \text{cal.};\quad \Delta H^\circ_{25} = -21{,}600\ \text{cal.};\quad \Delta S^\circ_{25} = -25.66\ \text{e.u.}$$

without giving an indication of the method of calculation or of the accuracy of the data.

Calorimetric values for the heat of formation of HgO vary widely: thus Berthelot[9] gives $\Delta H = -21{,}300$ cal., Thomsen[10] gives $-22{,}000$ cal., Nernst[11] reports $-20{,}700$ cal., and Varet[12] found $-21{,}500$ cal. The cell

$$\text{H}_2,\ \text{Pt}\ |\ \text{alkali}\ |\ \text{HgO(c), Hg}$$
$$\text{HgO(c)} + \text{H}_2\text{(g)} = \text{Hg(liq)} + \text{H}_2\text{O(liq)}$$

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

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