The Heat of Formation of Nitric Oxide and Phosphorus Trioxide

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radical recombination gives maximum rates almost exactly the same as the collision treatment, both for methyl radicals and for these addition reactions,[26,27] we feel confident that the order of magnitude of the maximum possible rate is $2-3 \times 10^{14}$ cm³/mole sec leaving room for at most 1–3 Kcal activation energy.

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[26] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw Hill, Book Company, Inc., New York, 1941), p. 131, 220, 260.
[27] T. L. Hill, J. Chem. Phys. **17**, 503 (1949).

This negligible activation energy leads to the conclusion that the transition state must be relatively loose, i.e., the B−N distance must be large enough so that steric repulsions of substituent groups are still unimportant. It would appear that the type of steric effects suggested by Brown[5] comes into play only at shorter distances and controls the depth of the potential energy minimum of the stable adduct rather than produce an activation energy hump in the reaction coordinate.

The Heat of Formation of Nitric Oxide and Phosphorus Trioxide*

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The heat of formation of nitric oxide has been redetermined by burning samples of red phosphorus in nitric oxide and in an equimolecular mixture of nitrogen and oxygen. A varying fraction of the phosphorus consumed by reaction with nitric oxide was converted to phosphorus trioxide; the remainder being converted to the pentoxide. A value of 21.8 kcal per mole was obtained for the heat of formation of nitric oxide at 25°C. A value of −270 kcal per mole was chosen as the best value for the heat of formation of phosphorus trioxide at 25°C.

INTRODUCTION

THE heat of dissociation of nitrogen, oxygen, and nitric oxide molecules into neutral atoms of oxygen and nitrogen can be studied using band spectroscopy, electron impact, and photochemical methods. The set of values chosen for the three molecules, NO, N_2, and O_2, is subject to the restriction that the sum of the heats of dissociation of nitrogen and oxygen minus twice the value for the heat of dissociation nitric oxide must give the experimentally determined heat of reaction for the reaction:

$$N_2 + O_2 \rightarrow 2NO.$$
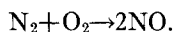
The presently accepted value of ΔH for this reaction is Berthelot's value of 43.2 kcal at 25°C,[1] giving a value for the heat of formation of nitric oxide of 21.6 kcal per mole. His value was obtained by burning samples of either cyanogen or ethylene in nitric oxide and in oxygen. This value is also supported by equilibrium constant measurements at different temperatures.[2]

Schmid and Gero,[3] according to Zeise,[4] have suggested

a value of 35.1 kcal. This conflicting value and the present controversy about the heats of dissociation of nitrogen and nitric oxide[5-13] into neutral atoms made it desirable to check Berthelot's value for the reaction.

In the present investigation red phosphorus was burned in a 50–50 mixture of pure oxygen and nitrogen and also in nitric oxide. When the same amount of phosphorus is burned and the products are the same, the difference between the heat evolved in oxygen and the larger amount evolved in nitric oxide is a measure of the heat released by the decomposing nitric oxide.

EXPERIMENTAL PROCEDURE

A flow calorimeter utilizing the combustion chamber illustrated in Fig. 1 was used for all experiments. The chamber and attached spiral heat exchanger were made of Pyrex glass, and the sample dish was made of fused quartz. The brass calorimeter held about 1400 g of water. An electrical resistance heater was used to measure the heat capacity of the calorimeter which was found to be 239 cal/°C.

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* More complete details may be obtained from a part of a Ph.D. thesis of William E. Koerner filed in the library of the University of Wisconsin in August, 1949.

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[1] M. Berthelot, Ann. chim. et phys. (5) **6**, 178 (1875); (5) **20**, 255 (1880).

[2] G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill Book Company, Inc., New York, 1923).

[3] R. Schmid and L. Gero, Math. naturwiss. Anz. ungar Akad. Wiss. **62**, 408 (1942) (Chem. Abstracts **41**, 7262 (1947)).

[4] H. Zeise, Physik. Z. **45**, 53 (1944).

[5] A. G. Gaydon, Nature **153**, 407 (1944).

[6] A. G. Gaydon and W. G. Penney, Proc. Roy. Soc. (London) **A183**, 374 (1945).

[7] P. J. Flory and H. L. Johnston, J. Chem. Phys. **14**, 212 (1946).

[8] J. G. Valatin, J. Chem. Phys. **14**, 568 (1946).

[9] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947).

[10] G. Glockler, J. Chem. Phys. **16**, 602, 604 (1948).

[11] H. D. Hagstrum, J. Chem. Phys. **16**, 848 (1948).

[12] J. Kaplan, Phys. Rev. **78**, 93 (1950).

[13] A. E. Douglas and G. Herzberg, Can. J. Research **29**, 294 (1951).

Pellets made from Eimer and Amend special "micro" amorphous phosphorus were ignited by the spark from a 4000-volt transformer. Matheson nitric oxide ($\sim$93 percent NO $-$7 percent N_2) was used. A calibrated Beckman thermometer having divisions of 0.01°C was used to measure the temperature rise. A small Cottrell precipitator in the exit line from the calorimeter was used to remove the last traces of finely divided phosphorus pentoxide smoke.

The determination of the amount of red phosphorus burned was straightforward in the experiments in which the nitrogen-oxygen mixture was used. The red phosphorus pellet was weighed before ignition, and the residue was collected and weighed on a tared Gooch crucible. To check this result the phosphorus pentoxide produced was dissolved in water and either titrated with sodium hydroxide or determined gravimetrically as magnesium pyrophosphate.

Combustion of red phosphorus in nitric oxide is analogous to combustion in a limited supply of oxygen, and a mixture of phosphorus trioxide and phosphorus pentoxide is obtained. Solution of the mixed oxides was effected by carefully hydrating the solids, using nitrogen gas saturated with water vapor. The mixture of phosphoric and phosphorous acids was titrated with sodium hydroxide solution to determine the total phosphorus consumed. The phosphite ion was determined iodometrically using the method of Wolf and Jung.[14] The small amount of nearly pure phosphorus pentoxide recovered from the Cottrell precipitator and other parts of the exit line was determined by precipitation and weighing as ammonium phosphomolybdate.

RUBBER
COVERED
WIRE

TUNGSTEN
SEALS

SOLDERED JOINT
SHOWN WITH
RUBBER TAPE
REMOVED

TUNGSTEN
IGNITION
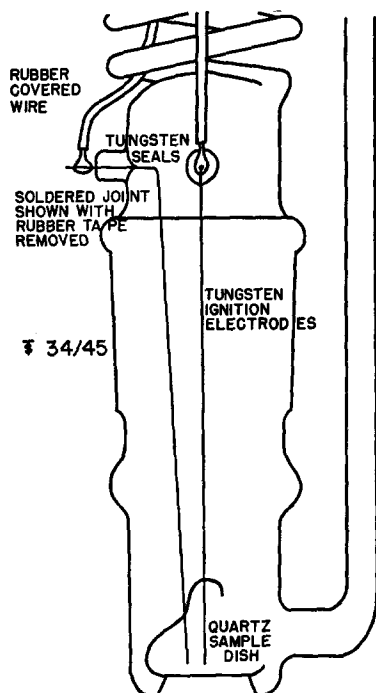ELECTRODES

$\mathbf{T}$ 34/45

QUARTZ
SAMPLE
DISH

FIG. 1. Lower portion of calorimeter combustion chamber.

In all of the nitric oxide experiments a small amount of the oxygen, produced from the nitric oxide by the high temperature flame, failed to combine with the phosphorus. Instead, nitrogen dioxide was produced by combination with the excess of nitric oxide. The magnitude of this heating effect, 14 kcal per mole of nitric oxide, was determined by absorbing the nitrogen dioxide in a 0.1N solution of sodium hydroxide and titrating the resulting nitrite ions with a solution of 0.02N potassium permanganate according to the method of Laird and Simpson.[15]

Appropriate corrections were made in the calculations for the heat produced by the ignition arc, the stirrer, and formation of nitrogen dioxide and the heat lost by radiation and convection.

RESULTS

Eight experiments were made in which red phosphorus samples were burned in an equimolecular mixture of nitrogen and oxygen. The product of combustion was pure phosphorus pentoxide. An average value of -355 kcal per mole was obtained for the heat of formation of phosphorus pentoxide with a mean deviation of ±2 kcal per mole. The heat of formation of phosphorus pentoxide from red phosphorus is -351.6 kcal per mole for the macrocrystalline form and -358.6 kcal per mole for the amorphous form according to Bichowsky and Rossini.[16] Thus it appears that a mixture of the two forms of phosphorus pentoxide was obtained in the experiments described here and that the calorimeter had been correctly calibrated.

Because no reliable data for the heat of formation of phosphorus trioxide were available, a different method of calculation was used for the experiments in which red phosphorus was burned in nitric oxide. An arbitrary value for the heat of formation of phosphorus trioxide, -180 kcal per mole, was used to calculate an apparent heat of formation of nitric oxide from each of seven experiments. These results together with the mole fraction of phosphorus converted to phosphorus trioxide are shown in Table I. A sample calculation for the last experiment follows.

Duration of experiment = 520 sec. Corrected temperature rise = 1.716°.
Calories evolved = 2824.
Arc heating = 12 cal.
Heat loss from gas flow = 2 cal.
Heat of chemical reactions = 2824 + 2 − 12 = 2814 cal.
Phosphorus titrated as H_3PO_4 and H_3PO_3: 0.4037 g.
Phosphorus titrated as phosphite ion: 0.1407 g.
NO_2 produced in side reaction: 6.2×10^{-4} mole.
Calories from P_2O_5 formation = 0.00444 × 355,000 = 1575.
Calories from P_2O_3 = 0.00227 × 180,000 (assumed) = 409.
Calories from $2NO + O_2 \rightarrow 2NO_2$ = 0.00062 × 14,000 = 9.
Calories from NO dissociation = 2814 − (1575 + 409 + 9) = 821 cal.

[14] L. Wolf and W. Jung, Z. anorg. u allgem. Chem. **201**, 337 (1931).

[15] J. S. Laird and T. C. Simpson, J. Am. Chem. Soc. **41**, 524 (1919).
[16] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

Moles of NO dissociated in forming $P_2O_5 = 0.00444 \times 5 = 0.0222$.
Moles of NO dissociated in forming $P_2O_3 = 0.00227 \times 3 = 0.0068$.
Moles of NO dissociated into O_2 which combined with excess NO: 0.0006.
Moles of NO dissociated $= 0.0222 + 0.0068 + 0.0006 = 0.0296$.
Kcal apparently released when one mole of NO dissociates into N_2 and O_2 at 25°C assuming the heat of formation of P_2O_3 is -180 kcal/mole $= 0.821/0.0296 = 27.7$.

When the value of ΔH_{NO} is plotted against the mole fraction of phosphorus burned to phosphorus trioxide as given in Table I and the best straight line is drawn through the points, this straight line extrapolates out to about 21.6 for a value of ΔH_{NO} at zero mole fraction of phosphorus burned to phosphorus trioxide. In other words, a rather unsatisfactory extrapolation gives 21.6 as the value for the heat of formation under conditions where all the phosphorus is burned to phosphorus pentoxide and there is no correction for incomplete combustion to phosphorus trioxide.

By using the method of least squares to determine the best straight line for the extrapolation, a value of 21.8 kcal per mole was obtained. If a different arbitrary value for the heat of formation of phosphorus trioxide is used, the value for the heat of formation of nitric oxide will vary by at most 0.3 kcal per mole.

By using the value of 21.6 kcal per mole for the heat of formation of nitric oxide a value for the heat of formation of phosphorus trioxide was calculated from each experiment. The mean of these seven values was -262 kcal per mole with a mean deviation of ± 4 kcal per mole.

DISCUSSION

The value of -262 kcal per mole for the heat of formation of phosphorus trioxide from red phosphorus becomes -270 kcal per mole for white phosphorus. Ogier[17] reported -244 kcal in fair agreement with the

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[17] J. Ogier, Compt. rend. **87**, 210 (1878).

TABLE I. The relationship between the apparent heat of formation of nitric oxide and the mole fraction of phosphorus burned to phosphorus trioxide.

Mole fraction P_2O_3	0.221	0.225	0.268	0.268	0.299	0.303	0.338
ΔH_{NO} (apparent)	25.6	25.5	26.5	26.8	26.7	27.2	27.7

present value but Berthelot[16] reports a value of only -78 kcal. Accurate measurements on these products of incomplete combustion are very difficult.

The value obtained for the heat of formation of nitric oxide in this research is 21.8 ± 0.3 kcal per mole. It is more reliable than the values for the phosphorus oxides since the conditions after suitable corrections are the same for the nitric oxide as for the equimolecular mixture of nitrogen and oxygen. Under these conditions the only difference lies in the heat of dissociation of the nitric oxide.

This value of 21.8 kcal is in excellent agreement with old, accepted value of Berthelot, 21.6 kcal. Whatever the values that are accepted for the heat of dissociation of nitric oxide, oxygen and nitrogen gases into atoms the present investigation indicates that they should meet the requirement that the sum of the heat required to dissociate the nitrogen molecule into atoms plus the heat required to dissociate the oxygen molecule into atoms should be 43.6 kcal greater than the heat required to dissociate two molecules of nitric oxide into oxygen and nitrogen atoms.

ACKNOWLEDGMENTS