The Journal of Physical Chemistry, Vol. 83, No. 7, 1979

# Gas Phase Reaction of Nitric Oxide with Nitric Acid

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The reaction between nitric acid and nitric oxide forming nitrogen dioxide and water occurs in the gas phase and forms nitrous acid as an intermediate. The rate constant for the reaction $NO + HONO_2 \rightarrow HONO + NO_2$ at 298 K is 8.4 L mol$^{-1}$ s$^{-1}$.

We report a reexamination of the gas phase reaction between nitric acid and nitric oxide to form nitrogen dioxide and water (1). Previous experimental results[1-4]

$$2HONO_2 + NO \rightarrow H_2O + 3NO_2 \qquad (1)$$

were most easily interpreted with the assumption that the reaction is heterogeneous. The clearest evidence was the fact that Johnston et al.[4] failed to observe reaction of nitric acid at 343 K in their reactor of lowest surface/volume ratio, while other studies[1-3] at lower temperatures, in which the addition of nitric oxide caused substantial amounts of reaction 1, involved experiments designed more to achieve temperature stability than low (surface/volume) ratio.

In the present work we have used cylindrical flow reactors at atmospheric pressure and 293–298 K, with nitrogen as the major component. These experiments confirmed the previous observation that substantial decomposition of nitric acid occurred (within reaction times of 2–10 s) but only when NO was present, and that the stoichiometry of the reaction was adequately described by eq 1. In addition, it was found that the extent of this decomposition was not significantly altered by coating the borosilicate reactor walls with phosphoric acid or by using a poly(tetrafluoroethane) reactor in place of a borosilicate reactor.

Typical values of the variation of extent of reaction with initial composition and time are listed in Table I. These results can be interpreted in terms of eq 2–5, in which nitrous acid is the intermediate species.

$$NO + HONO_2 \xrightarrow{k_2} HONO + NO_2 \qquad (2)$$

$$HONO + NO_2 \xrightarrow{k_3} NO + HONO_2 \qquad (3)$$

$$HONO + HONO_2 \xrightarrow{k_4} H_2O + 2NO_2 \qquad (4)$$

$$2NO_2 + H_2O \xrightarrow{k_5} HONO + HONO_2 \qquad (5)$$

Reaction 4 has been studied recently[5] and its rate coefficient ($k_4$) is reported to be $9.3 \times 10^3$ L mol$^{-1}$ s$^{-1}$. In the same study reaction 2 also appeared. It was reported to be heterogeneous and to have $k_2 = 9$ L mol$^{-1}$ s$^{-1}$. Computer simulation of our experiments in terms of reactions 2–5 leads to satisfactory agreement of the observed and calculated extents of reaction with $k_2 = 8.4$ L mol$^{-1}$ s$^{-1}$ and $k_4 = 9.3 \times 10^3$ L mol$^{-1}$ s$^{-1}$. The values of the ratios $k_2/k_3$ (12.24) and $k_4/k_5$ (0.75 L mol$^{-1}$) were calculated from the values[6] of the standard free energies of formation of the substances. In the case of nitrous acid, the value of $\Delta G_f°$ (−44.87 kJ mol$^{-1}$) was the value appropriate to an equilibrium mixture of the cis and trans isomers and was corrected[7] for the entropy of mixing of the isomers. The equilibrium amounts of $N_2O_4$ were assumed to be present throughout reaction.

TABLE I: Compositions and Extent of Reaction of Nitric Acid-Nitric Oxide Mixtures

| | $10^2$ (mole fraction) | | | |
|---|---|---|---|---|
| residence time, s | initial NO | initial $HONO_2$ | final $NO_2$ | rate coeff, L mol$^{-1}$ s$^{-1}$ |
| 7.8 | 6.4 | 0.198 | 0.069 | 7.4 |
| 11.5 | 9.3 | 0.291 | 0.210 | 7.9 |
| 14.5 | 12.6 | 0.435 | 0.460 | 8.4 |
| 10.6 | 9.1 | 0.312 | 0.225 | 9.1 |
| 9.1 | 7.7 | 0.268 | 0.147 | 8.9 |
| 8.6 | 7.3 | 0.253 | 0.117 | 7.9 |
| 8.8 | 4.04 | 0.268 | 0.077 | 8.1 |
| 8.8 | 2.04 | 0.259 | 0.045 | 9.1 |
| 14.0 | 7.9 | 0.127 | 0.064 | 5.2 |
| 13.1 | 7.4 | 0.227 | 0.184 | 10.8 |
| 16.4 | 9.4 | 0.287 | 0.30 | 10.3 |
| | | | av | 8.4 |

Our proposal for the mechanism of this reaction is thus in agreement with that advanced by Kaiser and Wu,[5] except that we believe that reactions 4 and 5 are predominantly homogeneous under our conditions. It is improbable that heterogeneous reaction would lead to such similar (apparent) rate constants. The values of the rate coefficients are such that the failure to observe reaction in Johnston et al.'s[4] large reactor would be expected.

## Experimental Section

*Reagents. Nitric acid* (100 ± 0.5%) was prepared by distillation at 16 kPa from mixtures of analytical reagent grade potassium nitrate (Ajax Chemicals) and sulfuric acid (May and Baker). It was colorless when prepared and used, and its concentration was confirmed by chemical analysis and by measurement of the vapor pressure at 273 K. *Nitric oxide* and *nitrogen* were the purest grades available. Water and other condensible impurities were removed by passage through traps packed with "molecular sieves" (5 Å) and cooled to 200 K.

*Reactor.* The reactors were borosilicate or poly(tetrafluoroethane) cylinders (4 cm i.d.) along which one set of reactants flowed. The second set of reactants was introduced from 20 radial holes in a bulb blown on the end of an inner (coaxial) tube. The effective length of the reactor was altered by sliding the inner tube relative to the outer, with an O-ring seal. Silver chloride windows permitted IR spectrophotometric measurements on the cell contents. Nitric acid at known mole fraction was introduced to the reactor in a nitrogen gas stream via two saturators in series. In the first, nitrogen bubbled through 100% nitric acid maintained at ca. 12 °C. The second saturator, moistened with 100% nitric acid, was carefully maintained at 0 °C. Analysis of the exit gases showed that the saturation vapor pressure of nitric acid (1.92 kPa at 0 °C)[8] was attained by this two-stage procedure. Variation of gas composition was achieved by blending variable amounts of nitrogen with the stream containing nitric acid using a gas mixer similar to that in the reactor. The performance of these mixers was checked by observation

0022-3654/79/2083-0779$01.00/0

TABLE II: Analytical IR Frequencies and Cross Sections

| substance | freq, $cm^{-1}$ | $10^{19}$ cross section/$cm^2$ molecule$^{-1}$ (base *e*) |
|---|---|---|
| $HONO_2$ | 1325 | 12.4,[a] 25.1,[b,c] |
| $NO_2$ | 1629 | 17.3[a,d] |
| $H_2O$ | 3855 | 1.08[a] |
| NO | 1875 | 1.06[b] |

[a] Spectrometer resolution 2 $cm^{-1}$. Pressure $10^5$ Pa. [b] Resolution 0.2 $cm^{-1}$. Pressure $10^5$ Pa. [c] Prior value $9.3 \times 10^{-19}$ at 2 $cm^{-1}$ (ref 9). [d] Prior value $13 \times 10^{-19}$ at 4 $cm^{-1}$ (ref 10).

of the flow patterns when they were used to mix nitrogen dioxide with nitrogen. Capillary flowmeters with a pressure transducer (National Semiconductor Type LX1601D) as measuring element were calibrated by volumetric measurement of gas flow. Spectrophotometric measurements were made on a Perkin-Elmer Model 180 spectrometer operated at 2-$cm^{-1}$ resolution in the linear absorbance mode. At the frequencies used, careful calibration established linear dependence of absorbance on mole fraction of the substance measured. The frequencies and approximate cross sections are given in Table II. They are in approximate agreement with other available values.

*Data Treatment.* The experiments were simulated using the values of $k_2/k_3$, $k_3$, and $k_4/k_5$ indicated earlier. It was assumed that the gases entered the reactor with a uniform composition and maintained uniform composition over the cross section of the reactor. The value of $k_2$ was varied until the computed composition of nitrogen dioxide at the position of measurement equaled that obtained experimentally.

*Acknowledgment.* We gratefully acknowledge financial support of this work by the Australian Research Grants Commission. M. J. McEwen and L. G. Phillips, University of Canterbury, N.Z., gave us the principle of the mixers and sliding seal in the reactors. H. S. Johnston (University of California, Berkeley) gave hospitable comment.

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# Hydroxyl Radical-Induced Oxidation of 2-Methyl-2-propanol in Oxygenated Aqueous Solution. A Product and Pulse Radiolysis Study[†]

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*(Received October 6, 1978)*

*Publication costs assisted by the Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung*

The reactions of the 2-methyl-2-hydroxypropylperoxyl radical were investigated by $\gamma$ and pulse radiolysis of aqueous oxygenated solutions of 2-methyl-2-propanol. The products and their *G* values [in brackets] on $\gamma$ radiolysis of a $N_2O/O_2$ (80/20 v/v) saturated solution at 20 °C are formaldehyde (I [1.3]), acetone (II [1.6]), 2-methyl-2-hydroxypropionaldehyde (III [2.0]), 2-methyl-2,3-propanediol (IV [0.5]), an organic peroxide, very likely di(2-methyl-2-hydroxypropyl) peroxide (V [0.7]), and hydrogen peroxide (VI [2.0]). Two major decay processes for the 2-methyl-2-hydroxypropylperoxyl radical are proposed: (i) formation of $O_2$ and two 2-methyl-2-hydroxypropyloxyl radicals which either combine (product V), disproportionate (products III and IV), or fragment (products I and 2-hydroxypropyl-(2) radicals), and (ii) formation of VI and III. The 2-hydroxypropyl-(2) radicals add oxygen to give the corresponding peroxyl radicals which rapidly eliminate $HO_2\cdot$ (product II). The $HO_2\cdot$ radicals largely disproportionate (products VI and $O_2$). At pH 9.4 the rate of the formation of $O_2^-\cdot$ ($pK_a(HO_2\cdot) = 4.75$) is determined by the bimolecular decay of the primary peroxyl radicals. The rate constant of the latter reaction was obtained pulse conductometrically as $2k = (8 \pm 2) \times 10^8\ M^{-1}\ s^{-1}$. Competition among the different modes of reaction is evident from the effect of deuterium substitution and temperature on the distribution of products yields.

## Introduction

The radiolysis of dilute aqueous 2-methyl-2-propanol solutions in the presence of oxygen provides a unique and convenient way to study the behavior of $\beta$-hydroxyalkylperoxyl radicals. Here the radiation energy is absorbed by the solvent water. The primary reactive species are OH radicals, solvated electrons, and H atoms. OH radicals attack 2-methyl-2-propanol by preferentially abstracting carbon-bound hydrogen atoms,[1] generating the 2-hydroxy-2-methylpropyl radical (reaction 1). The latter

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[†] Radiation Chemistry of Alcohols XXII. For part XXI see R. Ford, H.-P. Schuchmann, and C. v. Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 1338 (1975).

0022-3654/79/2083-0780$01.00/0