# THE KINETICS AND PRODUCT YIELD OF THE REACTION OF HO WITH $HNO_3$

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Room temperature rate constants for the reaction HO + $HNO_3$ were obtained by laser flash photolysis, HO was observed by resonance fluorescence [$k \pm 2\sigma = (8.2 \pm 1.8) \times 10^{-14}$ cm$^3$ s$^{-1}$]; and the product $NO_3$ was measured by laser absorption [$(10.6 \pm 3.4) \times 10^{-14}$ cm$^3$ s$^{-1}$]. The nitrate free radical $NO_3$ was a major product of the reaction.

## 1. Introduction

The rate constant for the reaction of hydroxyl radicals with nitric acid

$$HO + HNO_3 \rightarrow H_2O + NO_3 \qquad (1)$$

was recently remeasured by Wine et al. [1] and found in their study to be faster than previously accepted at room temperature and to have a negative temperature dependence. The unusually low *A* factor that was measured has led to speculation about a long-lived intermediate complex which may not decompose to $NO_3$ and $H_2O$. Because of the potential importance of these recent results to an understanding of atmospheric chemistry, we have studied this reaction in both the reactant and product channels.

## 2. Experimental

The techniques of flash photolysis/resonance fluorescence (FP/RF) and flash photolysis/laser absorption (FP/LA) were used to obtain kinetic information by following the time evolution of HO and $NO_3$ respectively.

The flash photolysis/resonance fluorescence studies were conducted in an apparatus of conventional design [2]. Hydroxyl radicals were produced by photodissociation of $HNO_3$ with the output of a Lumonics 860-01 excimer laser operating at 249 nm (KrF). Repetition rates were typically 30 Hz and the output energy was 10–20 mJ. Fluorescence from the 0–0 band of the HO $A\,^2\Sigma$–$X\,^2\Pi$ system was excited by the output of a microwave driven resonance lamp operating on a 3% $H_2O$/Ar mixture at a total pressure of 1 Torr. A Vycor resonance lamp window was used to block VUV atomic lines and some NO emission which contribute to the background signal. The fluorescence signal was monitored at right angles to the laser beam and resonance lamp with a detection system that included a $CaF_2$ window and three baffled, Suprasil-1, *f*/1 lenses which focus the fluorescence through a 307.2 nm interference filter (20% peak transmission, 10 nm fwhm) onto the cooled cathode of a PMT (RCA C31034) operated in photon counting mode. The time evolution of the fluorescence signal was obtained by recording the photon counting output with an instrument computer operating in the multichannel scaling mode. Typically, the decay following 4096 laser flashes was averaged to obtain a pseudo-first-order rate constant.

All experiments were performed in the "slow flow" regime. Nitric acid was entrained in a stream of Ar flowing through a four-pass, non-bubbling, Pyrex saturator. This stream then passed through a 1 m UV absorption cell where the $HNO_3$ concentration was continuously measured at 200 nm. The output of a deuterium lamp was chopped, focused through the absorption cell, wavelength selected by a McPherson (model 218) 0.3 m monochromator operating with a 0.3 nm bandpass, and detected by a PMT (S-5 response), the output of which was amplified and sent to a lock-in detector. Before and after each decay, pure Ar was flowed through the cell and $I_0$ measured. The absorption cross section of $HNO_3$ was measured by titration of the gas stream with NaOH solutions and found to be $6.5 \times 10^{-18}$ cm$^2$ under our conditions at 200 nm in agreement with the literature values [3,4]. The $HNO_3$ cross sections were also measured in a static, 10 cm cell with a Cary 118 spectrometer in the region 180–210 nm. The result obtained at 185 nm is $1.63 \times 10^{-17}$ cm$^2$ which agrees well with the determinations of Wine et al. [1] and Biaume [5].

After exciting the UV absorption cell, the gas stream entered the 10 cm long photolysis cell equipped with $CaF_2$ windows The total pressure in this cell was measured by an MKS Baratron capacitance manometer. Checks were made to ensure that the total pressure and $HNO_3$ concentration were the same in the photolysis and the UV absorption cell under the flow conditions used.

The flash photolysis/laser absorption experiments were conducted in a single-pass, jacketed, 1.9 m absorption cell Nitric acid, entrained in a slow flow (≈280 standard cm$^3$ min$^{-1}$) of $N_2$ passed through a saturator at 250 K, flowed through the cell at 10 Torr total pressure, and was photolyzed by output of the excimer laser operating at 249 nm. Approximately 0.04% of the $HNO_3$ in the beam was photolyzed per 10–20 mJ shot at repetition rates of 1–2 Hz. The energy of each photolysis pulse was measured using an energy meter located at the cell exit, and a suitable model of photolysis-laser-beam divergence was used to calculate an averaged fluence. Typical $HNO_3$ concentrations ranged from $\approx 8 \times 10^{15}$–$4 \times 10^{16}$ molecules cm$^{-3}$ and were determined by continuously monitoring the exhaust from the photolysis cell at 215 nm in a 1 m UV absorption cell similar to the one previously described. The absorption cross section used at 215 nm was that of Molina and Molina [3] ($3.56 \times 10^{-18}$ cm$^2$ molecule$^{-1}$) which is in good agreement with Johnston and Graham [4]. A pressure drop was found to exist between the photolysis and monitoring cells; its magnitude was determined by flowing a standard mixture of $NO_2$ in $N_2$ through both cells under experimental conditions and obtaining the relative $NO_2$ concentrations via absorption of the 488 nm output of an Ar ion laser. The results are adjusted to reflect this factor.

The $NO_3$ produced from the reaction of HO with $HNO_3$ was monitored by observing the absorption of the cw output from a Spectra-Physics model 375 dye laser propagated coaxially to the photolysis beam and operating on R6G dye at 623.5 nm, the $NO_3$ A–X $\nu_1$ (1–0) transition. The bandwidth of the laser was ≈0.29 nm. The dye laser output was monitored by an EG&G SGD-100A silicon photodiode coupled to a preamplifier of in-house design having a total system bandwidth of 1 MHz. The output from the preamplifier was recorded by a 9 bit A–D converter interfaced to a multichannel scaler. A typical experiment was the sum of 256 shots.

The Ar used in this study had a stated purity of >99.999% and the $N_2$ 99.998%, both were used without further purification The $HNO_3$ was distilled from mixtures of $NaNO_3$ or $KNO_3$ in 96% $H_2SO_4$ under vacuum. The product was collected at 250 K with only the middle portion saved. The nitric acid invariably contained 0.1–0.2% $NO_2$ impurity as measured by its 350 nm absorption; storage at 196 K had no effect on the purity.

## 3. Results and discussion

All experiments in the flash photolysis/resonance fluorescence study were performed under pseudo-first-order conditions with $[HNO_3] > 1000$ [HO]. A typical semilogarithmic HO decay plot is shown in fig. 1. The decay is linear over 2–3 1/e times.

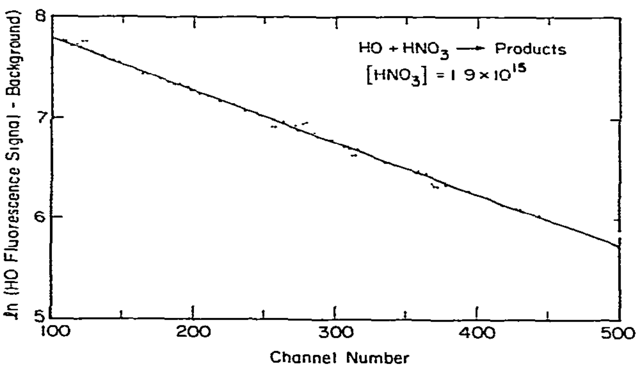

Fig. 1. A typical semilogarithmic HO decay plot from the flash photolysis/resonance fluorescence experiments with the line fit to the data by linear least-squares methods.

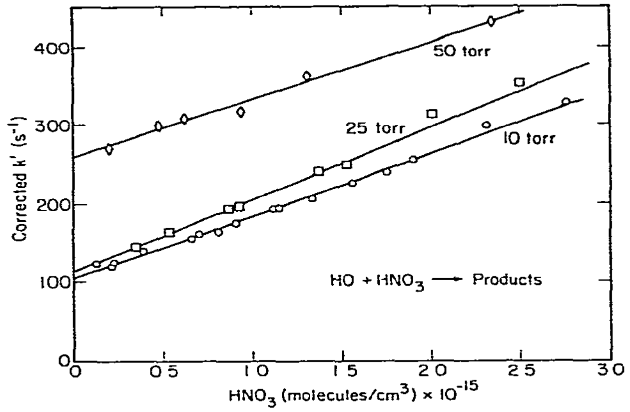

Fig. 2. Pseudo-first-order rate constant $k'$ plotted against the concentration of nitric acid obtained in the flash photolysis/resonance fluorescence experiments at 10, 25, and 50 Torr total pressure. A linear least-squares fit to each data set results in the lines shown.

The bimolecular rate constant was determined at 3 total pressures and for a 21 fold range of $HNO_3$ concentration. The observed HO decay times were corrected for the contribution of the HO + $NO_2$ recombination reaction

$$HO + NO_2 + M \rightarrow HNO_3 + M, \qquad (2)$$

using recommended values of the reaction rate constant as a function of pressure [6]. These data are shown plotted versus $HNO_3$ concentration in fig. 2. The rate constants calculated are $(8.0 \pm 0.3) \times 10^{-14}$, $(9.2 \pm 0.56) \times 10^{-14}$, and $(7.5 \pm 0.89) \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 10, 25, and 50 Torr total pressure respectively. The uncertainties are twice the standard deviation and do not include systematic errors. The non-zero intercepts are a result of HO diffusion from the product viewing zone and reaction with impurities in the Ar carrier gas.

To calibrate this experimental system of resonance fluorescence, it was used to study the reaction of hydroxyl radicals with hydrogen peroxide (HO + $H_2O_2$ $\rightarrow$ $H_2O$ + HOO), where $H_2O_2$ was monitored by absorption at 200 nm ($4.67 \times 10^{-19}$ cm$^2$), at concentrations between $3.1 \times 10^{14}$ and $2.1 \times 10^{15}$ cm$^{-3}$, with 10 Torr Ar total pressure, and at 295 K. The second-order rate constant ($\pm 2\sigma$) was found to be $(1.57 \pm 0.1) \times 10^{-12}$ cm$^3$ s$^{-1}$, in agreement with recent literature values [7,8].

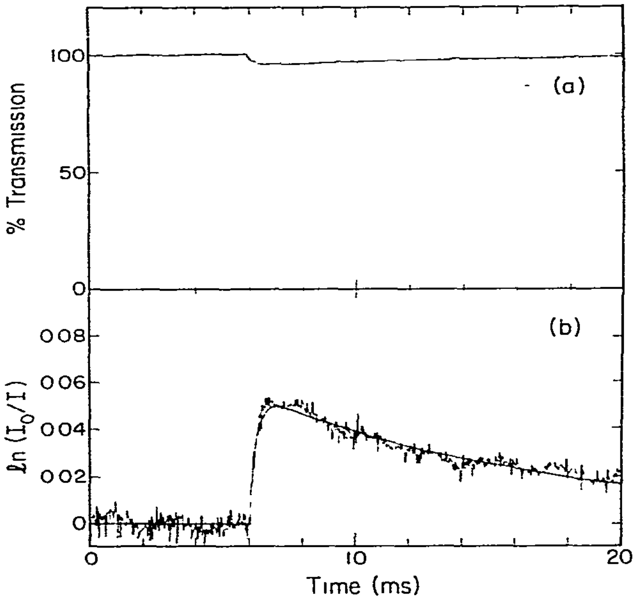

Fig. 3. (a) Data as recorded in transmission mode for $NO_3$ laser absorption. (b) Data converted to optical density [ln $(I_0/I)$] and computer fit to expression (3).

The data in the $NO_3$ absorption experiments were recorded in transmission mode (fig. 3a) and converted to optical density [$D = \ln(I_0/I)$] by using the transmission during the pretrigger period as $I_0$ (fig. 3b). Experimental runs were performed with 20 ms sweep times, however longer sweep times were explored to ensure that the signal returned to baseline between flashes. The time evolution of the $NO_3$ optical density was analyzed by fitting it to the expression

$$D(t) = D_A\,[\exp(-k_r t) - \exp(-k' t)]\,, \qquad (3)$$

where $k'$ is the pseudo-first-order rate constant for reaction (1), $k_r$ is the first-order rate constant for removal of $NO_3$ (diffusion from the viewing area, reaction with trace amounts of $NO_2$, NO, or other species) and $D_A$ would be the asymptotic optical density of $NO_3$ if the removal processes $k_r$ had negligible rates. A non-linear least-squares iteration method was used to fit $D_A$, $k_r$, and $k'$ to the experimental data and that fit is included in fig. 3b. These fits converged to a unique solution for a wide range (10×) of initial inputs for the fitting parameters. For each experiment $i$ the second-order rate constant $k_1$ for reaction (1) is related to the pseudo-first-order rate constant by

$$k_{1i} = k_i'/[\mathrm{HNO_3}]_i . \qquad (4)$$

The values of $k_1$ are plotted against nitric acid to show the lack of trend with nitric acid concentration, fig. 4. The average of these results (± 2$\sigma$) is (10.6 ± 3.4) × $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

The $NO_3$ product yield ($\phi$) from reaction (1) relative to the number of photons absorbed by nitric acid is given by

$$\phi = \frac{D_\mathrm{A}}{\sigma_{\mathrm{NO_3}} L} \frac{1}{E[\mathrm{HNO_3}]\sigma_{\mathrm{HNO_3}}} . \qquad (5)$$

where $L$ is the optical pathlength (193 cm), $\sigma_{HNO_3}$ is the absorption cross section of Molina and Molina [3] at 250 nm (2.0 × $10^{-20}$ cm$^2$), $E$ is the laser fluence in photons/cm$^2$, and $\sigma_{NO_3}$ is the $NO_3$ cross section at 623.5 nm, the probe wavelength used in these experiments. For 15 determinations the average $NO_3$ quantum yield (± 2$\sigma$) is 1.34 ± 0.18 using $\sigma_{NO_3}$ from Graham and Johnston [9] (1.2 × $10^{-17}$ cm$^2$), 1.53 ± 0.21 using $\sigma_{NO_3}$ from Mitchell et al. [10] (1.05 × $10^{-17}$ cm$^2$), or 0.92 ± 0.12 using the change proposed by Magnotta [11] for the results of Graham and Johnston [9]. Since there are no known chain mechanisms that would result in a quantum yield greater than one; it must be assumed that there is some systematic error. The two most likely quantities to be questioned here are the intensity of the laser pulse and the value of $\sigma_{NO_3}$ under our experimental conditions. The divergence of the excimer laser in the 193 cm absorption cell is difficult to model and some additional $HNO_3$ photolysis due to window or other internal reflections cannot be entirely discounted. The range of values reported for $\sigma_{NO_3}$ under varying experimental conditions of bandwidth, pressure, and optical density also contribute to the uncertainty of this result. While the $NO_3$ quantum yield cannot be precisely determined from these results, it is clear that $NO_3$ was produced at a rate comparable to that of HO loss [(10.6 ± 3.4) × $10^{-14}$ relative to (8.2 ± 1.8) × $10^{-14}$] and with a product quantum yield comparable to one. Thus the major product channel of reaction (1) is confirmed to be formation of $H_2O$ and $NO_3$.

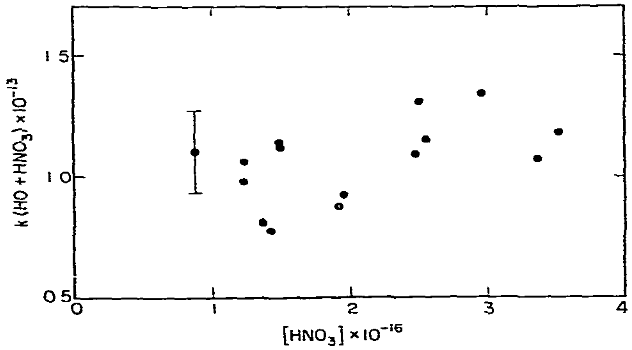

Fig. 4. Second-order rate constants for HO + $HNO_3$ → $H_2O$ + $NO_3$ as determined in flash photolysis/laser absorption experiments.

The room-temperature rate constants for the reaction of HO with $HNO_3$ determined in this work are (8.2 ± 1.8) × $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (FP/RF) and (10.6 ± 3.4) × $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (FP/LA). Given some of the experimental difficulties encountered in the FP/LA experiments, we feel that the FP/RF experiments are more accurate as well as more precise. The rate constant measured in the FP/RF experiment is in agreement with Smith and Zellner [12] (8.0 × $10^{-14}$) and Margitan et al. [13] (8.9 × $10^{-14}$), but it disagrees with the results of Wine et al. [1] (12.5 × $10^{-14}$). However the value of $k_1$ determined by Wine et al. does fall within the upper error limit of the FP/LA result. Measurement of the temperature dependence of this reaction is currently being carried out in this laboratory.

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