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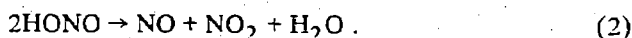
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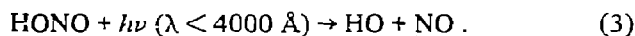
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A kinetic study of the nitrous acid decay reaction, $2\text{HONO} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$ (2), and the formation reaction, $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO}$ (1), has been made using essentially continuous FT-IR monitoring of the reactants and products in mixtures at the ppm level. The data suggest that the reactions are homogeneous for the conditions employed in this study. The results give: $k_1 = (2.2 \pm 0.7) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$ and $k_2 = (1.4 \pm 0.4) \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$ at 23°C. It is concluded that the homogeneous generation of HONO may be important in power plant plumes and in auto exhaust gases during the early stages of the dilution of these NO_x-H₂O-rich mixtures. Reactions (1) and (2) are a negligible source and sink of HONO in the atmosphere once the usual low ambient levels of NO and NO₂ are achieved. These reactions may influence smog formation in urban atmospheres during the early morning hours when nitrous acid formation by alternative pathways is slow. For these conditions the sunlight photolysis of HONO may be the major source of HO-radicals which, in combination with hydrocarbons and their oxidation products, lead to NO → NO₂ conversion, O₃ development, and other manifestations of photochemical smog.

Many aspects of the mechanism of photochemical smog formation are reasonably well understood today [1-3]. The chemical transformation of the atmospheric mixture of hydrocarbons, carbon monoxide, and the oxides of nitrogen to the notorious blend of irritants present in photochemical smog, ozone, peroxyacylnitrates, acids, aldehydes, and other oxidation products of the hydrocarbons, is believed to occur by way of a series of chain reactions which involve various active free radical species as chain carriers. One of the most important of these active species is the HO-radical, and the nitrous acid molecule is one of several potential primary sources of this radical in a sunlight-irradiated, polluted atmosphere. Nitrous acid molecules may build up in the atmosphere through the occurrence of the reactions



In turn the photolysis of HONO in sunlight may generate HO-radicals:



The importance of reactions (1) and (2) in controlling the nitrous acid levels in the atmosphere is uncertain at present. There are no kinetic data on reaction (2), and the existing information on reaction (1) does not appear to apply to the homogeneous reaction. Thus Graham and Tyler [4] measured a rate constant $k_1 = (1.2 \pm 0.6) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$, a value about 1/500th of that first observed by Wayne and Yost [5]. Furthermore, as in the Wayne and Yost results, the kinetics at high water concentration showed a rate dependence on a power of the water concentration which was greater than one. The large difference between these rate constants was attributed to the large difference in surface to volume ratio of the reaction vessels used (factor of 40). Hence the observed reaction was thought to be controlled by heterogeneous wall reactions [4]. Recently England and Corcoran [6] have invoked the occurrence of reactions (1) and (2) to rationalize their observed kinetic effects of water vapor on the rate of oxidation of NO to NO₂ in the NO, NO₂, O₂, H₂O system.

From very indirect evidence they concluded that $k_1 \approx 1.5 \times 10^{-8} \text{ ppm}^{-2} \text{ min}^{-1}$ at temperatures above 40°C ; there was indication of reaction heterogeneity for experiments near room temperature.

Although reaction (2) has not been measured directly in kinetic studies, published qualitative observations suggest that it is very slow. Asquith and Tyler [7], Nash [8], and Cox and co-workers [9-11] observed that HONO vapor is seemingly quite stable at concentrations well above its equilibrium value.

All present evidence points to the conclusion that the rate constants for the homogeneous reactions (1) and (2) are small, and there is even some question as to whether these reactions occur measurably at all in the gas phase.

In the previous kinetic studies of the nitrous acid system no direct measurement of nitrous acid itself was made. Indirect information was obtained either from the determination of changes in visible light absorption due to the reactant NO_2 alone, or from chemiluminescence detection of NO and NO_x coupled with the "selective" chemical removal of HONO vapors. Obviously rate information based on the direct measurement of HONO vapor is necessary to test the hypotheses formulated from indirect experiments

and to derive meaningful values of k_1 and k_2 . In the work reported here a Digilab FTS 20 infrared spectrometer was employed to study the NO, NO_2 , H_2O , HONO system. The allowed essentially continuous monitoring of all the reactants and products. The relatively large reaction vessel, a tank of 21 m length and 76 cm in internal diameter, gave a surface-to-volume ratio which was 0.052 times that used by Graham and Tyler [4]. The multiple pass, White optical system allowed the use of path lengths from 82 m to 1.5 km and unambiguous measurements could be made of very low reactant and product concentrations in the ppm range of major interest in atmospheric reactions. This work provides the first direct measurement of the rate constants of the homogeneous reactions (1) and (2). In terms of these results reasonable speculation can be made about the potential role of these reactions in the atmosphere.

Several unambiguous absorption peaks were used to follow the reactants and products of the NO, NO_2 , H_2O , HONO interactions [spectral resolution, 0.5 cm^{-1} ; temperature, 23°C ; total pressure, 700 torr (N_2 gas)]: NO_2 , ν_2 band, Q-branch transition at 823 cm^{-1} ($c = [\ln(I_0/I)]/pl = 0.0807 \pm 0.0012 \text{ torr}^{-1} \text{ m}^{-1}$); NO, fundamental Q-branch at 1876 cm^{-1} ,

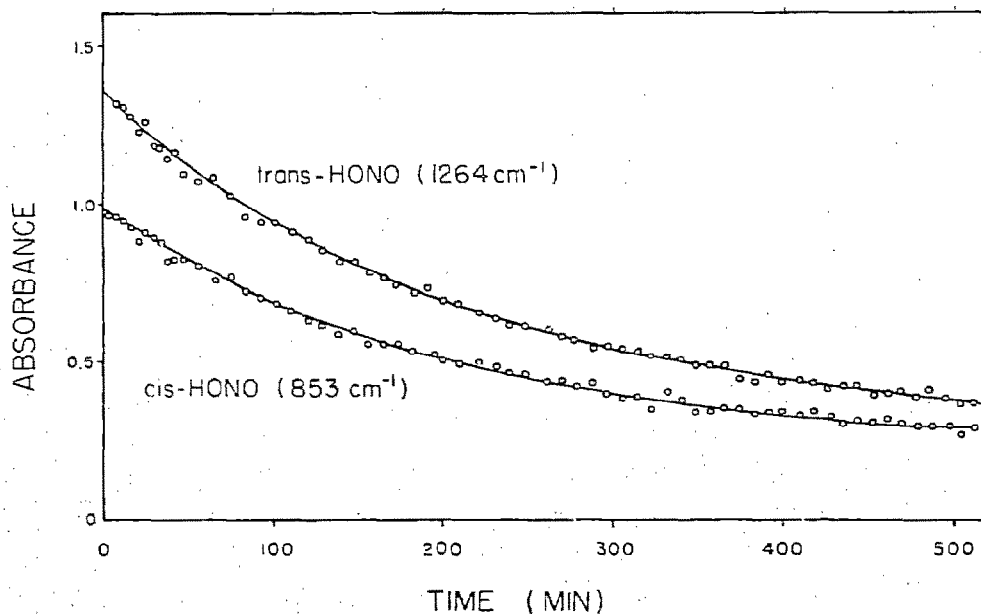


Fig. 1. Absorbance versus time plot for the *trans*-HONO (1264 cm^{-1}) and *cis*-HONO (853 cm^{-1}) in a HONO, NO, NO_2 , H_2O mixture originally rich in HONO.

$\epsilon = 0.513 \pm 0.006 \text{ torr}^{-1} \text{ m}^{-1}$; *cis*-HONO, ν_4 band, Q-transition at 853 cm^{-1} , $\epsilon = 9.36 \pm 0.94 \text{ torr}^{-1} \text{ m}^{-1}$; *trans*-HONO, ν_3 band, Q-branch transition at 1264 cm^{-1} , $\epsilon = 5.20 \pm 0.52 \text{ torr}^{-1} \text{ m}^{-1}$. Water vapor was introduced to the desired level (190–4200 ppm) by evaporating into the cell weighed samples of liquid water; this quantity was in large excess of the amount reacted, so that the H_2O concentration was essentially constant in a given kinetic run. Nitrous acid was introduced to the cell much in excess of the equilibrium pressure by following a procedure based on the studies of Nash [8] and Cox and co-workers [9–11]. In all calibration and kinetic runs the reaction cell was pressurized to 700 torr with added high purity nitrogen gas.

In most of the kinetic experiments we have observed the decay of HONO isomers as the NO, NO_2 , H_2O , and HONO gaseous system returned to equilibrium. The data in fig. 1 show the time dependence of the absorbance measured for *trans*-HONO (1264 cm^{-1}) and *cis*-HONO (853 cm^{-1}) in the early stages of the decomposition reaction. The two isomers decayed essentially in tandem at a very slow rate. A clue as to the nature of the kinetics of the decay of nitrous acid can be obtained from the plot of the reciprocal of the absorbance of the isomers versus time; see fig. 2. Note that the data follow well a second order decay for these conditions, a result consistent with that expected if reaction (2) is the elementary rate determining step in the decomposition. As the reaction proceeded to much longer times the rate of nitrous acid loss decreased until constant equilibrium levels of HONO, NO_2 , NO, and H_2O were achieved. This can be seen in fig. 3 for an experiment of over 28 hours duration. Obviously a nitrous acid forming reaction becomes important at long times. It is reasonable to assume this to be the result of the occurrence of reaction (1).

If reactions (1) and (2) are the only reactions involving HONO in our system, then the rate law which describes the HONO decay is:

$$-dP_{\text{HONO}}/dt = 2(P_{\text{HONO}})^2 k_2 - 2P_{\text{NO}} P_{\text{NO}_2} P_{\text{H}_2\text{O}} k_1. \quad (4)$$

The integrated form of relation (4) describes well the experimental variation of P_{HONO} over the entire time period. We varied the value of k_2 chosen for the cal-

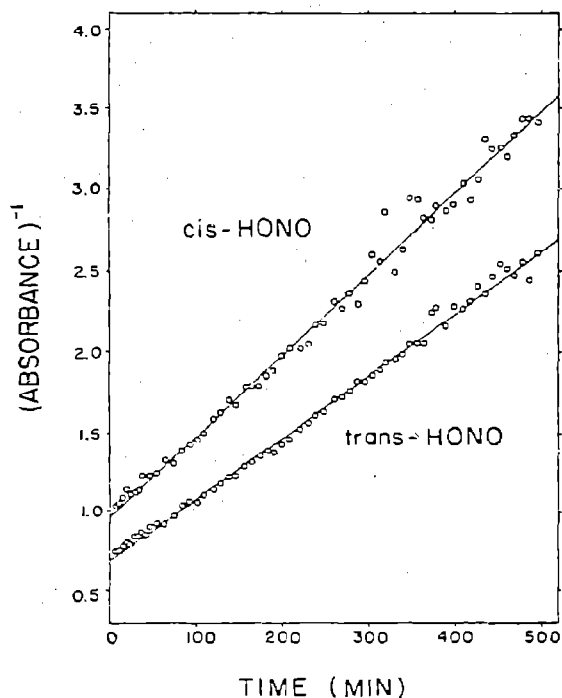


Fig. 2. Plot of the reciprocal of the absorbance of *trans*-HONO and *cis*-HONO versus time for a HONO, NO, NO_2 , H_2O mixture originally rich in HONO.

culation, but then the choice of k_1 was fixed through the average value of the published equilibrium constant for 23°C and its relation to k_1 and k_2 ; $k_1 = k_2 K_1$; $K_1 = (P_{\text{HONO}})^2 / P_{\text{NO}} P_{\text{NO}_2} P_{\text{H}_2\text{O}}$. The sensitivity of the fit of the data on the choice of k_2 is seen in the fig. 3. For the particular conditions employed in this run choices of $k_2 = 1.4 \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$, and hence $k_1 = (1.51 \times 10^{-6}) (1.4 \times 10^{-3}) = 2.1 \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$, fit the data well. Initial rate data such as those in fig. 2 also yield similar results; thus those in fig. 2 give $k_2 = (1.3 \pm 0.1) \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$.

Kinetic experiments involving HONO decay were carried out for several initial reactant and product pressures. Also experiments were attempted by starting with NO– NO_2 -rich mixtures and watching the HONO formation rate as the reaction drifted toward equilibrium. The results of all of these experiments are summarized in table 1. The average values of the rate constants derived from all the studies at 23°C gave: $k_1 = (2.2 \pm 0.7) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$ and $k_2 = (1.4 \pm 0.4) \times 10^{-3} \text{ ppm}^{-1} \text{ min}^{-1}$.

There are no previous measurements of k_2 with

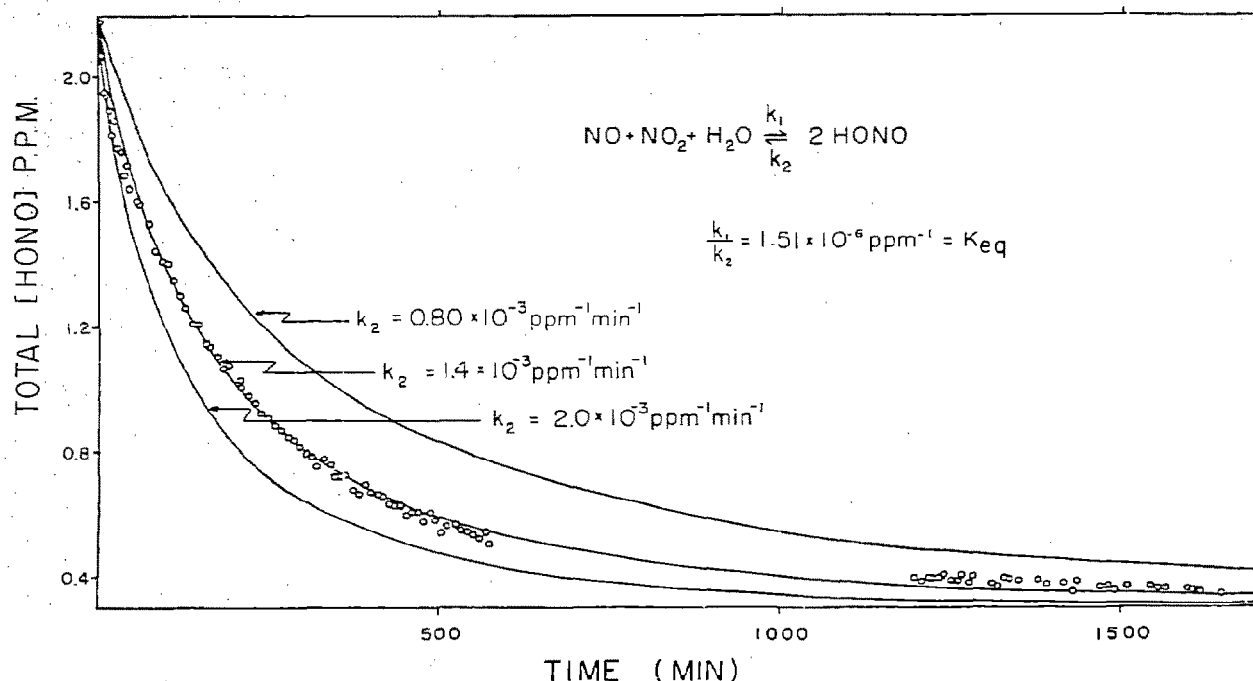


Fig. 3. Plot of total HONO concentration versus time for an extended run of 1648 min duration using an initially HONO-rich mixture; initial concentrations, ppm: HONO, 2.14; NO, 2.37; NO₂ 3.53; H₂O, 4200; temperature, 23°C; curves shown have been calculated using the integrated form of relation (4) and the rate constants indicated on the figure.

which we can compare our results. However reaction (1) has been investigated by Graham and Tyler [4] who obtained kinetic data from experiments over a wide range of reactant concentrations: $P_{\text{NO}} = 4.3\text{--}200$ torr; $P_{\text{NO}_2} = 1.7\text{--}7.5$ torr; $P_{\text{H}_2\text{O}} = 4.7\text{--}14$ torr. Although these results seem to show an enhanced rate of reaction for runs at $P_{\text{H}_2\text{O}} > 9$ torr, which suggests an order for H₂O which is higher than one, the calculated third order rate constants k_1 for $P_{\text{H}_2\text{O}} < 9$ torr appear to be reasonably constant; they show only random variation over the wide range of reactant concentrations employed. Indeed it is important to note that the average value of k_1 derived from Graham and Tyler's data, $k_1 = (1.2 \pm 0.6) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$, is equal within the experimental uncertainties of the measurements to that observed here: $k_1 = (2.2 \pm 0.7) \times 10^{-9} \text{ ppm}^{-2} \text{ min}^{-1}$. In view of the low surface to volume ratio (0.052 cm^{-1}) of the reaction vessel in our study compared with that of Graham and Tyler (1 cm^{-1}), and the fact that the concentration ranges of all of the reactants were several orders of magnitude lower (10^{-3} to 10^{-5})

in our work, the agreement between the two very different systems provides strong evidence that the rate constant observed here is that for a homogeneous reaction. Indeed the data of Graham and Tyler may apply also to the homogeneous system, at least in their experiments for which water pressures less than 9 torr were employed.

The present estimates for k_1 and k_2 provide a new basis for the evaluation of the significance of these reactions in the atmosphere. It can be shown that the rate of HONO formation will be important for high levels of NO, NO₂ and H₂O which are typical of those encountered near pollution sources. Thus in a mixture containing initially $P_{\text{NO}} = 500$ ppm, $P_{\text{NO}_2} = 50$ ppm, with the relative humidity of 100% (25°C), 1.70 ppm of HONO will be generated in only 30 s elapsed time, assuming no dilution of the mixture during this period. When account is taken of the typical dilution rates within the plume of power plant or an auto exhaust, the HONO developed during the early stages of the dilution is still very significant. However once the NO_x-H₂O mixture has

Table 1
Summary of the rate constant estimates^{a)} for reactions (1) and (2)

Initial concentrations, ppm ^{b)}						
[NO]	[NO ₂]	[H ₂ O]	[HONO]	P _{N₂} , torr	k ₂ , ppm ⁻¹ min ⁻¹	k ₁ , ppm ⁻² min ⁻¹
(a) 2HONO → NO + NO ₂ + H ₂ O experiments						
5.42	7.81	560	6.73	700	1.6 × 10 ⁻³	2.4 × 10 ⁻⁹
5.65	7.01	1120	6.04	700	1.6 × 10 ⁻³	2.4 × 10 ⁻⁹
4.64	5.60	2240	5.21	700	1.4 × 10 ⁻³	2.1 × 10 ⁻⁹
5.18	4.89	2800	3.95	700	0.90 × 10 ⁻³	1.4 × 10 ⁻⁹
2.37	3.53	4200	2.14	700	1.4 × 10 ⁻³	2.1 × 10 ⁻⁹
4.23	8.50	190	9.01	300	1.5 × 10 ⁻³ c)	2.3 × 10 ⁻⁹ c)
1.91	10.7	190	4.77	20	2.3 × 10 ⁻³ c)	3.5 × 10 ⁻⁹ c)
(b) NO + NO ₂ + H ₂ O → 2HONO experiments						
15.8	8.16	1400	0.130	700	0.80 × 10 ⁻³	1.2 × 10 ⁻⁹
10.6	9.72	2240	0.141	700	1.4 × 10 ⁻³	2.1 × 10 ⁻⁹
best estimates:					(1.4 ± 0.4) × 10 ⁻³	(2.2 ± 0.7) × 10 ⁻⁹

^{a)} Temperature in all runs, 23 ± 1°C.

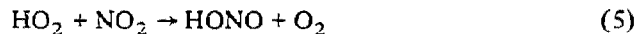
^{b)} The unit ppm used here is defined as [pressure(torr)/760] × 10⁶ at 23°C.

^{c)} Calculated assuming there is no pressure dependence in the extinction coefficient of the Q-branch of the vibrational bands used for concentration estimation; this appears to be a good approximation from a limited study of the effect of pressure on the absorbance of the species involved here.

been diluted to ambient levels, HONO generation is very slow. Thus P_{HONO} will reach only 4.2% of its equilibrium value after 60 hours for an NO_x-H₂O mixture at commonly encountered ambient levels of NO_x ($P_{\text{NO}} = 0.05$, $P_{\text{NO}_2} = 0.0125$ ppm, 50% relative humidity, 25°C).

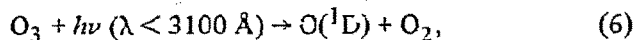
In view of the rate of HONO generation near pollution sources, we would predict that the P_{HONO} in the early morning hours may be a significant fraction of the HONO equilibrium pressures expected from the ambient NO, NO₂, and H₂O present in the NO_x-polluted atmospheres. Thus it appears likely to us that the photolysis of HONO can enhance the rate of primary HO-radical formation which in consort with CO and hydrocarbon reactions generates the products of photochemical smog. It has been noted previously that if HONO is present in a polluted atmosphere near its value for equilibrium with NO, NO₂, and H₂O present in the early morning hours, then the predicted rate of conversion of NO to NO₂ would be enhanced by a factor of two over that expected in the absence of HONO initially [1]. Once the initial burst of HO formation starts the chain

sequences involving the HO, HO₂, and RO₂ radicals, the generation of HONO through the reaction



will also be a major source of this species, and the combination of (1), (2), and (5) will maintain a significant level of HONO as the smog development continues.

In view of this work it is recommended that those atmospheric scientists concerned with the chemistry within stack plumes, include reactions (1) and (2) in their considerations and simulations; they appear to be important steps in the triggering of the chemical changes which occur. The present theory offers a more reasonable mechanism for HO-radical generation in power plant plumes than the sunlight photolysis of ozone:



Ozone levels must remain quite low until considerable conversion of NO to NO₂ has occurred; [O₃]

≈ 0.02 $[\text{NO}_2]/[\text{NO}]$ ppm for a solar zenith angle of 40° . Our simulations suggest that the rates of $\text{O}(^1\text{D})$ and HO-radical formation from the sequence (6) and (7) will be very much lower than the HO-radical formation rate from HONO photolysis even at $[\text{NO}_2]/[\text{NO}]$ ratios near unity.

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