

DISCUSSION

LABORATORY STUDY OF NO2 REACTION WITH DISPERSED AND BULK LIQUID WATER*

Recently Novakov and his colleagues (Bambauer et al., 1994) have reexamined the rate of the reactive uptake of nitrogen dioxide (NO₂) by water under laboratory conditions. Two types of gas-liquid contactor were employed, a bubbler, similar to that employed in our earlier work (Lee and Schwartz, 1981a), and a cloud chamber, in order to examine the applicability of kinetic information determined in bulk liquids to a dispersed system such as a cloud. We commend Bambauer et al. (1994) for undertaking this study and recognize the difficulty of the experiment, especially in maintaining constant conditions in the cloud chamber for the rather long periods (typically an hour) required to collect sufficient amounts of cloudwater to permit chemical analysis. We nonetheless appreciate the advantage afforded by direct comparison between reaction rate measured in the cloudchamber reactor with that measured in the bubbler in confirming the applicability of "bulk" rate laws to reactions in dispersed clouds. The expectation of course is that the rates would be equal. In fact the reaction rate was found to be substantially greater in the cloud-chamber reactor, leading Bambauer et al. (1994), to conclude that different mechanisms govern the reaction rate in the bulk reactor vs in the dispersed system. Here we suggest that the rate measured in the cloud-chamber reactor may have been enhanced artificially because of nonuniform concentration distribution of the reagent gas NO2 together with the second-order dependence of the rate on NO₂ concentration. Consequently the conclusion by Bambauer et al. (1994) that the rate expression determined using a bulk reactor is inapplicable to evaluation of the rate of this reaction in clouds in the ambient atmosphere may not be warranted.

By way of background, we note that the reactive dissolution of NO₂ into liquid water is a process of a major industrial importance in the manufacture of nitric acid. At NO₂ concentrations characteristic of this process NO₂ and/or its dimer N₂O₄ dissolve in water and rapidly react to form nitrous and nitric acids:

$$2NO_2(N_2O_4) + H_2O \rightarrow HNO_2 + HNO_3.$$
(1)

In view of the strong thermodynamic driving force for reaction (1) and the commonly observed rapid rate of reaction, this reaction had long been presumed to proceed rapidly also in liquid water clouds in the atmosphere.

In order to determine the solubility and rate constants necessary to evaluate the rate of reaction (1) in the ambient atmosphere, we conducted a laboratory study of the rate of this reaction at low partial pressures, $p_{NO_2} = 0.1-800 \ \mu atm$ (Lee and Schwartz, 1981a). That study consisted of passing NO₂ (in nitrogen or in air) through water as finely dispersed bubbles produced by passing the gas stream through a glass frit that comprised the bottom surface of a vessel containing the liquid. The small bubble size together with the vigorous mixing induced by the bubble swarm promoted efficient

phase mixing, the rate of which could be independently characterized in terms of a stochastic rate coefficient k_m . The rate of reaction was measured continuously by monitoring the rate of increase of electrical conductivity of the solution, and the reaction stoichiometry was confirmed by analysis of the final solution composition.

From the dependence of the reaction rate on NO₂ partial pressure and $k_{\rm m}$, it was possible to infer separately Henry's law coefficient for physical dissolution of NO₂ in water $H_{\rm NO_2}$, and the rate law of reaction (1), which was found to be second order in NO₂. The values of $H_{\rm NO_2}$ and of the reaction rate coefficient are consistent with values of these quantities inferred from a review of the literature on thermodynamics and kinetics of the nitrogen oxide-oxyacid system (Schwartz and White, 1981, 1983). Subsequent studies by others have borne out the rate expression obtained in our study (e.g. Cape *et al.*, 1993).

Knowledge of the values of H_{NO_2} and k_1 determined in this way allowed evaluation of the rate of reaction (1) in liquid water clouds in the ambient atmosphere as

$$R_1 = k_1 [NO_2(aq)]^2 = k_1 H_{NO_2}^2 p_{NO_2}^2$$
(2)

where the second equality holds under phase mixed conditions. The requirements for satisfaction of the phase mixed condition can be evaluated and shown to be met under representative atmospheric conditions. Evaluations of R_1 for representative conditions indicate that this reaction is quite slow, owing to the second-order kinetics and the low Henry's law solubility of the gas (half life of gas-phase NO₂~1 month at $p_{NO_2} = 1 \mu$ atm to ~100 yr at 1 natm, for cloud liquid-water content 1 cm³ m⁻³; Lee and Schwartz (1981b)). The expectation of slow reaction in clouds based on this laboratory study is consistent with the common field observation of NO₂ present in persistent liquid-water clouds (e.g. Daum *et al.*, 1984; Fuzzi *et al.*, 1994; Colvile *et al.*, 1994).

In the study of Bambauer et al. (1994), NO₂ was first introduced into a cloud chamber and exposed to a suspension of droplets produced when a humidified air stream was mixed with a cold dilution air stream. The rate of reaction was determined from the concentration of dissolved NO₃ and/or NO₂⁻ in collected liquid water and the contact time, ca. 3 min. A second independent measurement of the rate was achieved by passing the gas exiting the cloud chamber first through a filter (to remove any suspended particles) and then into a bubbler reactor, evidently similar to that used in our study, with determination of reaction rate from analysis of the composition of the solution after a given contact time. With the bubbler reactor Bambauer reported, rates that they indicated were consistent with those reported in our earlier study, taking into account plausible differences in the mass-transport properties of the two reactors, since the mixing rate coefficient characterizing their reactor was not determined. In contrast, with the cloud-chamber reactor, Bambauer et al. (1994) found aqueous concentrations that corresponded to reaction rates much greater than were observed in the bubbler reactor (500- to 1700-fold) or than would be expected based on equation (2) (30- to 400-fold, Table 1). Based on an approximate linear dependence of measured rate on NO2 partial pressure in the cloud chamber, Bambauer et al. ascribed this rate to a first-order reaction, which they attributed either to mass-transport limitation reducing the reaction order (from the expected second order to first order), or to a different mechanism for reaction in or on cloud droplets than in the bulk.

^{*}Bambauer A., Brantner B., Paige M. and Novakov T. (1994) Atmospheric Environment 28, 3225–3232.

Discussion

Table 1. Comparison of reaction rates (column 5) derived from data of Bambauer *et al.* (1994) for cloud-chamber reactor (columns 1-3) with rates (column 6) calculated according to second-order reaction [equation (2)] with $H_{NO_2} = 7 \times 10^{-3} \text{ M atm}^{-1}$ and $k_1 = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Lee and Schwartz, 1981a)

Average p_{NO_2} (µatm)	LWC (cm ³ m ⁻³)	${NO_3^-} \\ (\mu mol m^{-3})$	$[NO_3^-] (\mu mol \ell^{-1})$	R _{meas} (nM s ⁻¹)	R_{calc} (nMs ⁻¹)	C_1/C_{avg}	$R_{\rm meas}/R_{\rm calc}$
3.16	1.89	0.51	270	1910	48.9	158	39
3.06	1.81	0.66	365	2580	45.9	163	56
2.76	1.36	0.34	250	1770	37.3	181	47
2.56	2.39	0.44	184	1300	32.1	195	41
1.55	2.27	0.3	132	935	11.8	323	79
1.51	1.29	0.24	186	1316	11.2	331	118
0.86	0.75	0.11	147	1037	3.62	581	286
0.75	1.54	0.14	91	643	2.76	667	233
0.52	3.14	0.17	54	383	1.32	962	289
0.48	1.2	0.08	67	472	1.13	1040	418
0.46	2.94	0.11	37	265	1.04	1090	255

Note: R_{meas} is evaluated as the concentration of aqueous nitrate $[NO_3^-]$ divided by the contact time, here taken as 141 s, evaluated from the reactor volume 30.2 ℓ and the flow rate 12.8 ℓ min⁻¹. The concentration ratio C_1/C_{svg} is taken as the ratio of the inlet partial pressure of NO₂, 500 μ atm, to the average NO₂ partial pressure in column 1.

In our opinion neither of these explanations seems plausible. The mass-transport explanation seems ruled out by the fact that the rate is in fact much greater than would be calculated based on assumed Henry's law saturation, not less, as would be the case for mass-transport limitation. In any event, the rather fine dispersion would promote mass transport, not inhibit it. Likewise, it is difficult to postulate a chemical mechanism that would be first order in NO₂, especially given the roughly comparable concentrations of NO_2^- and NO_3^- observed by Bambauer et al. in the collected cloudwater samples. (The depletion of NO₂ noted by Bambauer et al. at higher acidities seems reasonably ascribed to volatility of HNO2.) We are thus motivated to explore alternative explanations that might account for the observations of Bambauer et al. that are consistent with present understanding of the mechanism and kinetics of this reaction.

A possible explanation for the anomalously high rates observed with the cloud chamber, is suggested by an observation of Bambauer et al. with reference of their Fig. 1, that "determination of the rate for the reaction between NO₂ and cloud droplets ... is difficult because of the unknown NO₂ concentration gradient resulting from the manner in which the NO₂ is introduced into the chamber". Reference to that figure shows that rather than the NO₂ being introduced into the cloud chamber at the partial pressure desired for a given run (0.5 to 3 μ atm), it was introduced at the partial pressure of the NO₂ source (500 μ atm), with dilution occurring within the chamber itself. Since according to equation (2) the rate of reaction (1) is second order in NO₂, the rather high inlet partial pressures could lead to quite rapid reaction prior to dilution to the final partial pressure. We thus tried to assess the effect on the observed average rate due to reaction occurring near the region of the NO2 inlet prior to complete dilution of NO₂ to its final partial pressure. If substantial reaction occurs in the inlet region, then this might trivially account for the observed apparent high reaction rates obtained with the cloud-chamber reactor.

In order to assess the magnitude of this effect we formulated a model in which the reactor volume is conceptually divided into two regions of unequal volume, each containing a fixed fraction of the reagent. Here the volume fraction f_1 , representing the region in the vicinity of the NO₂ inlet, is much smaller than the remainder of the reactor volume $f_2 (= 1 - f_1)$ and contains a much higher reagent concentration. Because of the second-order nature of the reaction, the rate of reaction averaged over the entire reactor volume is considerably greater than would be the case if the reagent



Fig. 1. Ratio of rate of second-order reaction for a nonuniform reagent concentration averaged over a reactor volume to that evaluated for the average reagent concentration. Curve denotes results of two-box model calculation as described in the text plotted as a function of the ratio of the reagent concentration in the small, high concentration box to the average concentration. Points denote ratio of the average reaction rate, as evaluated from the measurements presented by Bambauer *et al.* (1991), to rate calculated according to equation (2) with H_{NO_2} and k_1 determined by Lee and Schwartz (1981a), plotted as a function of the ratio of the inlet partial pressure to the average reagent partial pressure in their cloud-chamber reactor.

were uniformly distributed. The enhancement of mean reaction rate is displayed in Fig. 1 as a function of the ratio of the concentration in the smaller, higher concentration subregion C_1 to the mean concentration C_{avg} . Variation of the ratio of the inlet concentration to the mean concentration (corresponding to changing the inlet flow rate and hence the mean partial pressure of the NO₂ reagent in the experiment) is achieved in the model by varying the volume fraction f_1 , which here ranges from 2×10^{-6} at $C_1/C_{avg} = 200$ to 4×10^{-7} at $C_1/C_{avg} = 1000$. There is only a single adjustable parameter in the calculation, namely the fraction of reagent

in the volume f_1 , here taken as 0.04%. As anticipated, the ratio $R_{\text{meas}}/R_{\text{calc}}$ is substantially greater than unity and increases with increasing C_1/C_{avg} , corresponding to decreasing the flow rate of NO₂ at the inlet to achieve lower average NO₂ partial pressures in the reactor. Also shown in the figure are values of $R_{\text{meas}}/R_{\text{cale}}$ from Table 1 plotted against the corresponding values of C_1/C_{avg} . Despite the simplicity of the model, namely, representing the continuous distribution of NO2 partial pressures between the inlet region and the bulk of the reactor by only two regions, it is seen that the model quite accurately reproduces both the magnitude of the departure of the observed reaction rate from that calculated with equation (2) for the average NO_2 partial pressure and the sense of the dependence of this departure on NO₂ partial pressure. It is thus felt that this model lends credence to present suggestion that the high spatial gradient of reagent partial pressure within the reactor volume is responsible for the departure between measured and calculated rates. We conclude that the results obtained by Bambauer et al. with the cloud-chamber reactor should not be viewed as inconsistent with the rate expression for reactive dissolution of NO₂ determined using bulk solutions.

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AUTHOR'S REPLY

In our paper (Bambauer et al., 1994), we reported results of a cloud-chamber study of the reaction of NO, with water droplets. One of the main conclusions of this study is that the NO₃ and NO₂ concentrations produced in our laboratory cloud during approximately constant contact time, under phase mixed regime, are linearly dependent on the NO₂ concentrations measured in the cloud chamber. This observation led us to suggest that the reaction between NO2 and cloud droplets appears to be first order with respect to gaseous NO₂ concentrations. This finding is in disagreement with the results of Lee and Schwartz (1981a, b), who concluded that the reaction is second order with respect to NO₂ in the phase mixed regime. In their comments on our paper, Schwartz and Lee (henceforth referred to as S&L) present a hypothesis, according to which our observations can be readily explained by the second-order reaction and therefore our results should not be viewed as inconsistent with their previous conclusions. In the following, we show that the S&L hypothesis fails to explain the apparent linear dependence of the reaction products on NO₂ concentrations, as observed in our experiments.

In their discussion S&L suggest that the rate measured in our cloud-chamber experiments may have been enhanced artificially because of a nonuniform concentration distribution of the reagent gas NO2. As we pointed out in our paper, because of the unknown NO_2 concentration gradient in the chamber, we have not attempted to derive the reaction rate. Accounting for this gradient is difficult because of the intense turbulence around the NO₂ inlet into the chamber. Because of this difficulty, we limited our analysis to the estimation of the reaction order. We have concluded that our results suggest a first-order reaction based on the linear dependence of mass and aqueous concentrations of NO_3^- (or NO_2^-) on NO₂ concentrations measured after dilution in the chamber (Fig. 2 and Tables 1 and 2, in Bambauer et al. (1994)). Therefore, more pertinent to this discussion is an examination of the S&L assertion that the observed apparent firstorder reaction can be explained by the second-order rate expression [S&L, equation (2)], if it is assumed that the reaction occurs near the region of the NO2 inlet prior to dilution of NO₂ to its final partial pressure.

In their model calculations, S&L compared the calculated reaction rate for a nonuniform reagent concentration averaged over a reactor volume R_{avg} , to the rate $R(C_{avg})$ evaluated for the average reagent concentration. S&L do not explicitly show the dependence of the predicted rate R_{avg} , assumed to be comparable to the apparent reaction rate derived from cloud-chamber measurements, on average (diluted) NO₂ concentration in the chamber. This information, however, is implicit in their Fig. 1, where the values of $R_{avg}/R(C_{avg})$ are plotted against the C_1/C_{avg} . C_1/C_{avg} denotes the ratios of the constant NO₂ concentrations at the chamber inlet to variable NO₂ concentrations measured at the top of the chamber. Because R_{avg} should correspond to the apparent rate expected in the chamber, and because $R(C_{avg})$ is equivalent to the rate R_{calc} [calculated from S&L, equation (2)] for uniform NO_2 concentrations, the expected dependence of the apparent rate can be obtained by multiplying the $R_{avg}/R(C_{avg})$ values by R_{calc} (S&L do not give numerical values, therefore these were read from Fig. 1). The values of R_{avg} derived in this manner for several NO₂ partial pressures are shown in Table 1. The values of R_{avg} are practically constant and independent of NO2 concentrations after dilution. Thus, the S&L hypothesis does not reproduce the experimentally observed linear relationship between cloud water NO_3^- (or NO_2^-) concentrations and NO_2 measured in the chamber.

It is of interest to note that the $R_{avg}/R(C_{avg})$ values derived by S&L are essentially the same as the ratios of a constant