

Comment on “Possible Role of NO₃ in the Nighttime Chemistry of a Cloud” by William L. Chameides

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Recently, Chameides [1986] presented the results of calculations on the rate of uptake of NO₃ by cloud droplets and discussed the consequences of solution phase free radical chemistry initiated by this species. However, this calculation may be in error due to the neglect of reevaporation of NO₃ from the drops. It has been shown [Schwartz, 1984] that reevaporation is significant for HO₂ radicals. Since NO₃ should be much less soluble, the effect of reevaporation is likely to be much larger.

Berdnikov and Bazhin [1970] have estimated the solubilities of a series of free radicals. Their method is based on a correlation between the polarizabilities and solubilities of stable gases. Uncertainties in the estimated heats of formation range from 1 to 2 kcal mol⁻¹, implying that the Henry's law constants are uncertain by a factor of 5–30. As shown in Table 1, their estimates for several free radicals have since proven to be within these uncertainties. I will use their estimated NO₃ Henry's law constant of 0.03 M atm⁻¹ for the following calculations. In an earlier paper, Chameides [1984] assumed a value of 1 × 10⁵ M atm⁻¹ for this constant. If the solubility is this large, reevaporation would be negligible. However, such large solubilities are usually only observed for highly polar species, such as H₂O₂ and HNO₃.

From Chameides stated mass transport rate (1.5 × 10⁻⁹ M s⁻¹), mass accommodation coefficient (0.01), and cloud parameters (120 drops cm⁻³, 10 μm radius), the steady state gas phase NO₃ concentration would appear to be 4 × 10⁶ molecules cm⁻³. This yields a saturated solution concentration of 5 × 10⁻¹⁵ M, compared to a calculated concentration of 10⁻¹² M. Thus, if the estimated Henry's law constant is reasonably accurate, reevaporation will be important in this system.

To calculate the rate of uptake, we must consider gas phase diffusion, transport across the gas-liquid interface, liquid phase diffusion, and the rate of liquid phase chemical reaction. This problem has been discussed in detail by Schwartz and Freiberg [1981]; an alternate, but equivalent, form is used here. At steady state the solution may be expressed as

$$\tau_{\text{loss}} = \left\{ \tau_{g,D} + \tau_I + \tau_{L,D} \left[\left[\frac{3\tau_{L,D}}{\tau_R} \right]^{1/2} \coth \left[\frac{3\tau_{L,D}}{\tau_R} \right]^{1/2} - 1 \right]^{-1} \right\} / F_L$$

where F_L is fraction of the volume which is liquid water and the various time constants, which are defined slightly differently than Schwartz and Freiberg's, are

- τ_{loss} disappearance of the gas phase species;
- $\tau_{g,D}$ gas phase diffusion, equal to $a^2/3D_g$, where a is the drop radius and D_g is the gas phase diffusion coefficient;
- τ_I transport across the interface, equal to $4a/3\alpha c$, where α is the mass accommodation coefficient and c is the mean molecular speed;
- τ_R liquid phase reaction, equal to $1/kHRT$, where k is the pseudo first-order rate constant, H is the Henry's law constant, R is the ideal gas constant, and T is absolute temperature;
- $\tau_{L,D}$ liquid phase diffusion, equal to $a^2/3HRTD_L$, where D_L is the liquid phase diffusion coefficient.

Chameides implicitly assumes that $\tau_{L,D}$ and τ_R are zero.

Using the above Henry's law constant, reasonable NO₃ diffusion coefficients of 0.1 cm² s⁻¹ (gas phase) and 2 × 10⁻⁵ cm² s⁻¹ (liquid phase), and $\alpha = 0.01$, $k = 10^3$ s⁻¹, and cloud parameters from Chameides [1986] we have $\tau_{g,D} = 3 \times 10^{-6}$ s, $\tau_I = 4 \times 10^{-6}$ s, $\tau_{L,D} = 2 \times 10^{-2}$ s, $\tau_R = 1 \times 10^{-3}$ s, $F_L = 5 \times 10^{-7}$, and $\tau_{\text{loss}} = 6000$ s. With these parameters the uptake of NO₃ is limited by condensed phase diffusion and reaction and is a factor of 600 slower than calculated by Chameides. If the actual Henry's law constant is larger than the estimate used here, then the time constant for loss of NO₃ to drops will decrease in proportion.

The time constant for NO₃ reaction with NO₂ is about 15 s under the conditions used by Chameides. Thus most NO₃ formed should lead to production of N₂O₅. N₂O₅ loss to droplets is likely to be efficient since it may react with liquid water to form nitric acid. However, it should not initiate condensed phase free radical chemistry. Thus we should expect that heterogeneous reactions of NO_x would contribute significantly to the formation of condensed phase nitrate but have little effect on sulphur oxidation. The actual role of NO₃ solution chemistry cannot be settled until the Henry's law constant has been determined by experiment.

TABLE 1. Comparison of Estimated and Experimental Henry's Law Constants

Species	Estimated,* M atm ⁻¹	Experimental, M atm ⁻¹	Measured by
OH	30	32	Klaning et al. [1985]
HO ₂	4700	2700	Schwartz [1984]
NO ₂	0.03	0.007	Lee and Schwartz [1981]
Cl ²	0.015	0.2	Schwarz and Dodson [1984]
Br	0.03	1.2	Schwarz and Dodson [1984]
I	0.006	0.08	Schwarz and Bielski [1984]

*From Berdnikov and Bazhin [1970].

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