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Laboratory Studies of Stratospheric Aerosol Chemistry

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INTRODUCTION

In this report we summarize the results of the two sets of projects funded by the NASA grant NAG2-632, namely investigations of various thermodynamic and nucleation properties of the aqueous acid system which makes up stratospheric aerosols, and measurements of reaction probabilities directly on ice aerosols with sizes corresponding to those of polar stratospheric cloud particles. The results of these investigations are of importance for the assessment of the potential stratospheric effects of future fleets of supersonic aircraft. In particular, the results permit to better estimate the effects of increased amounts of water vapor and nitric acid (which forms from nitrogen oxides) on polar stratospheric clouds and on the chemistry induced by these clouds.

PHASE TRANSFORMATIONS IN THE $H_2SO_4/HNO_3/H_2O$ SYSTEM

Heterogeneous reactions play an important role in the conversion of inactive chlorine to active chlorine in the stratosphere. Cold temperatures at high latitudes in the winter and spring months allow efficient formation of polar stratospheric clouds (PSCs), some of which are composed of ice aerosol, forming only at temperatures below the ice frost point, while others form at somewhat higher temperatures and consist of either liquid or solid mixtures of water and sulfuric and nitric acids.

We have carried out a variety of laboratory investigations to elucidate the nature and chemical identity of PSC particles. We have investigated thermodynamic (i.e. equilibrium) properties for the $H_2SO_4/HNO_3/H_2O$ system such as vapor pressures, and crystallization enthalpies, as well as nucleation properties such as freezing probabilities.

The PSC formation mechanism which had been most commonly accepted involves freezing of the background supercooled sulfuric acid aerosol (SSA) liquid dropletsto form solid sulfuric acid tetrahydrate (SAT) followed by condensation of nitric acid and water vapors to form nitric acid trihydrate (NAT). However, our own laboratory investigations, together with the results of field measurements and other laboratory studies, lead us to conclude that the most likely PSC formation mechanism involves instead incorporation of significant amounts of water and nitric acid vapors into the liquid SSA droplets, thus forming liquid solutions which do not freeze readily. It appears that freezing requires reaching – even if only for brief periods -- the ice frost point; ice crystals then promote the nucleation of NAT and possibly SAT as well. In fact, a careful analysis of stratospheric aerosol observations indicates that PSCs are sometimes solid and sometimes liquid, in agreement with expectations based on the more recent laboratory results.

The results of our laboratory investigations supported by this grant related to PSC formation mechanisms have appeared in several literature publications, which describe and discuss the experiments in some detail. Hence, we provide these publications as appendices to this report (some of them were also partially supported by other grants). The list is as follows:

R. Zhang, P.J. Wooldridge, J.P.D. Abbatt and M.J. Molina. Physical chemistry of the H_2SO_4/H_2O binary system at low temperatures: Stratospheric implications. *J. Phys. Chem.*, **97**, 7351 (1993).

R. Zhang, P.J. Wooldridge, J.R. McMahon, J.E. Kim, H.Y. Chang, K.D. Beyer and M.J. Molina. Physical chemistry of the $H_2SO_4/HNO_3/H_2O$ system: Implications for polar stratospheric clouds. *Science*, **261**, 1418 (1993).

R. Zhang, J.T. Jayne and M.J. Molina. Heterogeneous interactions of $ClONO_2$ and HCl with sulfuric acid tetrahydrate: Implications for the stratosphere. *J. Phys. Chem.*, **98**, 867 (1994).

K.D. Beyer, S.W. Seago, H.Y. Chang and M.J. Molina. Composition and freezing of aqueous H_2SO_4/HNO_3 solutions under polar stratospheric conditions. *Geophys. Res. Lett.*, **21**, 871 (1994).

P. J. Wooldridge, R. Zhang and M.J. Molina. Phase equilibria of H_2SO_4, HNO_3, and HCl hydrates and the composition of polar stratospheric clouds. *J. Geophys. Res.*, **100**, 1389 (1995).

M.J. Elrod, R.E. Koch, J.E. Kim and M.J. Molina. HCl vapor pressures and reaction probabilities for $ClONO_2$ + HCl on liquid H_2SO_4-HNO_3-HCl-H_2O solutions. *Faraday Discuss.*, **100**, 269 (1995).

CHLORINE ACTIVATION REACTIONS ON ICE AEROSOLS

Reactions (1) and (2) have been shown in the laboratory to occur efficiently on ice and to be a major contributor to active chlorine production in the polar stratosphere.

$$ClONO_2 + HCl\,(ice) \Rightarrow Cl_2 + HNO_3 \qquad (1)$$

$$ClONO_2 + H_2O\,(ice) \Rightarrow HOCl + HNO_3 \qquad (2)$$

Previous laboratory investigations of these reactions have primarily been carried out with bulk solid films. In contrast, we have studied reactions directly on ice aerosol, which is more representative of the stratosphere. By performing the reaction directly on small particles entrained in a gas flow, some uncertainties associated with film studies are avoided. In particular, ice films can be extremely porous and rough, and these features might affect reaction probability measurements carried out at low pressures. In principle, the surface area should be determined and should remain constant over the course of an experiment. Furthermore, films of ice often contain many grain boundaries. Some previous studies suggest that HCl molecules collect at grain boundaries of ice, enhancing the amount of uptake per unit area on a bulk film. Therefore, reaction probabilities measured on polycrystalline ice could misrepresent stratospheric ice, which is thought to have near single-crystal structure with few grain boundaries. Carrying out relevant reactions on monocrystalline ice particles will provide mechanistic information and minimize uncertainties in the application of film studies to the atmosphere.

Experimental

An experimental study of reactions (1) and (2) on ice particles was performed using a high pressure turbulent flow system. The apparatus used for both the kinetic studies and the uptake experiments is shown in Figure 1. The system consists of four stages: an aerosol generation chamber, a particle analyzer, a turbulent flow reactor, and a chemical ionization mass spectrometer. Solid ice particles were created through homogeneous nucleation by injecting supersaturated nitrogen into a cold chamber held at 200-210 K. The ice aerosol size and total surface area were analyzed with a laser light-scattering method. Typical values for the particle surface area per unit volume and for the number density in the flow reactor were 0.01 cm^2/cm^3 and 1×10^6 particles/cm^3. Also, ice particles were examined with a microscope to investigate their structure, which appeared to be near monocrystalline (*i.e.*, few, if any, grain boundaries).

Ice particles of size 1-5 microns were entrained in the flow, and the reactive uptake was determined by measuring the decay of chlorine nitrate as a function of moveable injector position. Typically, the flow tube temperature and pressure were 208 K and 770 torr respectively. Reactant concentrations were roughly 1×10^{11} molecule/cm^3 $ClONO_2$ and 5×10^{11} molecules/cm^3 HCl. Chemical ionization mass spectrometry (CIMS) techniques were used to monitor gas concentrations. The reagent ion, SF_6^-, reacts with hydrogen chloride and chlorine nitrate in the following ion-molecule schemes:

$$HCl + SF_6^- \Rightarrow SF_5Cl^- \ (m/z = -162) + HF \qquad (3)$$

$$ClONO_2 + SF_6^- \Rightarrow ClONO_2{\cdot}F^- \ (m/z = -116) + SF_5 \qquad (4)$$

Results

First, the coverage of hydrogen chloride was determined on the aerosol ice particles. Experimental HCl partial pressures ranged from 10^{-4} to 10^{-7} torr. The HCl concentration in the gas phase was measured in the presence and in the absence of flowing ice aerosol. The decrease in HCl signal provided the coverage concentration for a given surface area of ice. Uptake experiments were performed at total pressures of 770 torr and 200 torr. Table 1 shows the results of these measurements indicating a coverage of $\sim 10^{13}$ molecule/cm^2 for stratospheric HCl concentrations. This coverage is comparable with results reported by us and by others on ice films, which rules out serious effects from grain boundaries.

We also report values for the reaction probability, γ, of reactions (1) and (2) on ice aerosol. Measurement of the decrease in $ClONO_2$ concentration vs. reaction time in the presence of ice particles gives a first order decay with loss rate coefficient, k':

$$[ClONO_2]/[ClONO_2]_o = \exp(-k't_{rxn}) \qquad (5)$$

Loss of reactant is directly dependent on the particle surface area per unit volume, Θ; therefore, we define $k' = k''\Theta$. Figure 2 shows a plot of k' vs. surface area for a given experiment. The slope is k" in units of cm/s. In addition, the surface area of the particles was often measured at each injector position, and the data was fit to the following equation, which accounts for small changes in surface area during the course of an experiment:

$$f = C \exp(-k''\{\Theta t - \Theta_0 t_0\}) \qquad (6)$$

and

$$\ln f = D - k''\Theta t \qquad (7)$$

Values of k" determined by both analysis methods are in good agreement.

Control experiments were performed often with the aerosol input bypassing the flow tube. In some of these experiments, significant amounts of ice particles had built up on the walls. Very small decays for these wall reaction studies serve as a validation for the near "wall-less" nature of turbulent flow apparatus employed for these kinetic studies. A typical plot of reactant signal vs. injector position with and without ice particles is shown in Figure 3.

From the measured decay rate constant, the reaction probability was calculated based on the resistive uptake model. It can be shown that for a gas reacting on a solid particle surface the following equation applies:

$$1/k'' = a/D_g + 4/v\gamma \qquad (8)$$

where k'' = measured rate constant (cm/s)

a = mean particle radius (cm)

D_g = gas diffusion coefficient (cm^2/s)

v = mean molecular speed (cm/s)

γ = reaction probability

The first and second terms in equation 8 are contributions due to gas diffusion and reactant molecule surface collision rate, respectively. The binary diffusion coefficient for chlorine nitrate in nitrogen under our experimental conditions was calculated to be 0.062 cm^2/s for $ClONO_2$ in N_2. The mean speed of the gaseous reactant molecules, v, was calculated to be 4×10^4 cm/s. From a measured decay rate, one can solve for the value of the reaction probability. Typical values for γ for reactions (1) and (2) are shown in Table 2. Within experimental error, no significant size dependence is observed.

Summary

HCl uptake experiments and kinetic studies of reactions (1) and (2) on ice aerosols were completed for a particle size range of 1-5 microns. In addition, $ClONO_2$ decays were measured in the absence of aerosol at the beginning and at the end of each set of kinetic experiments to determine wall effects. HCl coverage on ice aerosol was experimentally determined to be near monolayer for typical stratospheric gas concentrations, and within experimental error shows no significant size dependence. A preliminary lower limit for the reaction probability, γ, of $ClONO_2$ + HCl on ice is reported as ~ 0.1 and for $ClONO_2 + H_2O$ on ice as ~ 0.05. Again, within experimental error, no size dependence is noted. These results are consistent with previous ice film experiments carried out in our laboratory as well as in other laboratories. The agreement serves to rule out large errors due to bulk film morphology as a consequence of effects such as accumulation of HCl on grain boundaries. A manuscript, entitled "Chlorine Activation Reactions on Ice Aerosols" and co-authored by D. Leard, D. Dai, L.T. Molina and M.J. Molina, is being prepared and will be submitted to the Journal of Physical Chemistry for publication.

Table 1: HCl Uptake Results.

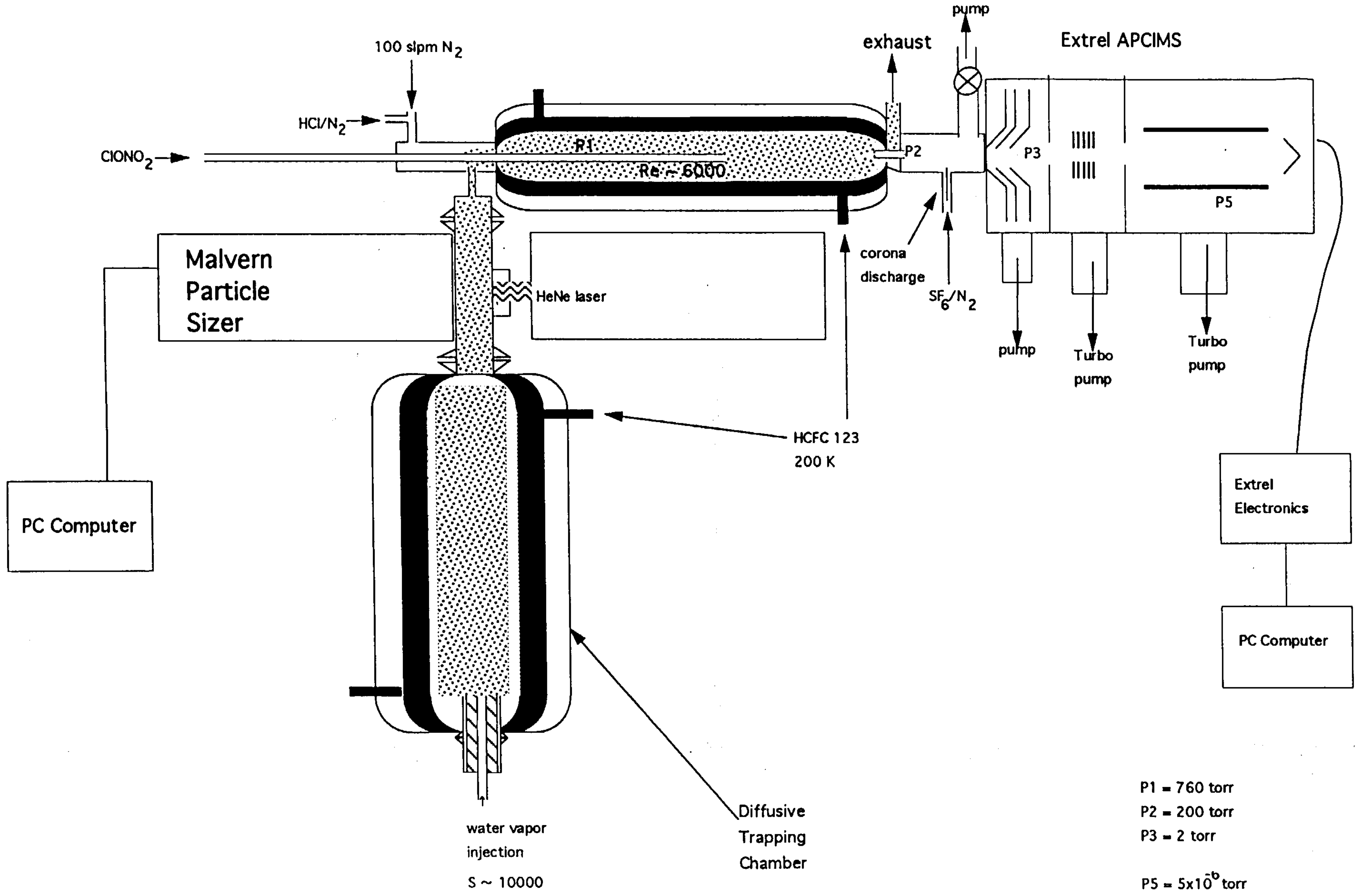
Experiment Number	Total P (torr)	P(HCl) x10^{-6} (torr)	Average Radius (microns)	Coverage x10^{13} (cm^2/cm^3)
1	770	1.5	2.0	0.4
2	770	1.5	3.1	0.7
3	770	2.3	1.8	0.5
4	770	2.3	2.4	0.7
5	770	2.3	3.2	1.1
6	200	3.0	2.3	3.6
7	200	3.0	4.1	2.4
8	200	3.0	4.9	2.4
9	770	4.6	2.2	1.5
10	770	4.6	2.9	1.6
11	770	5.4	1.2	1.1
12	770	5.4	2.1	2.2
13	770	5.4	3.0	1.8
14	770	5.4	3.9	2.6
15	770	6.2	2.1	1.8
16	770	6.9	3.9	3.7
17	770	7.7	2.1	2.2
18	770	7.7	2.4	8.6
19	770	7.7	3.0	2.8
20	770	7.7	3.5	4.1
21	770	7.7	4.2	3.6
22	770	11.6	2.0	2.4
23	770	11.6	3.1	3.4
24	770	11.6	4.0	3.6
25	770	11.6	5.1	5.2
26	770	15.4	2.5	5.8
27	770	15.4	3.8	5.5
28	770	19.3	1.7	4.4
29	770	23.1	2.3	4.5
30	770	30.8	2.5	6.8
31	770	38.5	1.7	4.6
32	770	38.5	2.6	4.7
33	770	77.0	2.9	7.1
34	770	154.0	2.8	18.0

Table 2: Kinetic Results. **Reaction 1:** $ClONO_2 + HCl$

Reaction 2: $ClONO_2 + H_2O$

Exp. No.	Radius (cm)	k"	γ	Reaction No.
1	0.94	507	0.20	1
2	0.91	327	0.06	1
3	1.01	530	0.35	1
4	1.10	278	0.05	2
5	1.13	201	0.03	2
6	1.18	187	0.03	2
7	1.21	258	0.05	2
8	1.28	137	0.02	2
9	1.18	248	0.04	2
10	0.92	170	0.02	2
11	0.84	202	0.03	2
12	0.84	153	0.02	2
13	0.84	155	0.02	2

Figure 1: Experimental Apparatus



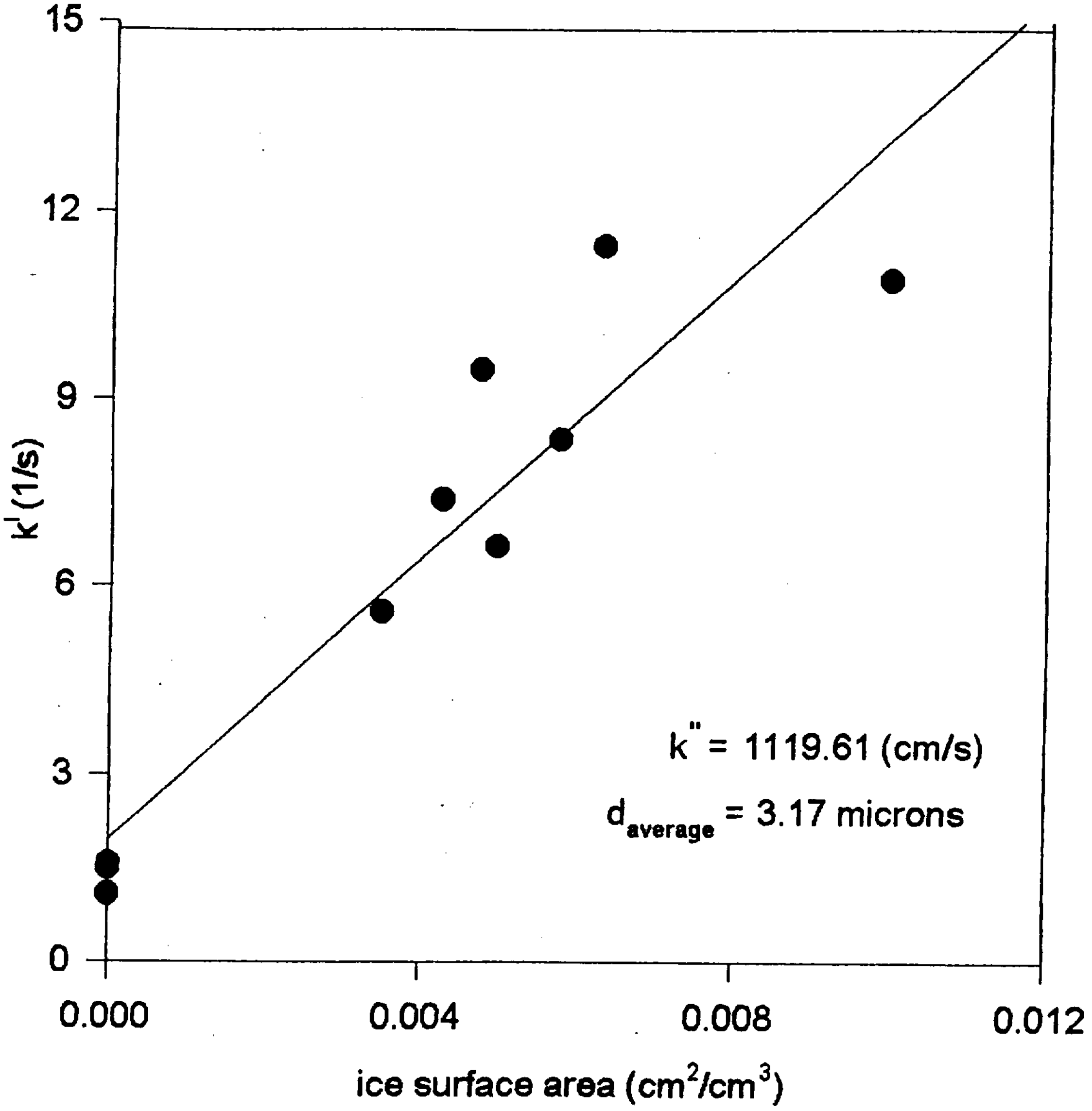


Figure 2: First order decay constant vs. surface area. Slope gives k'' in units of cm/s.

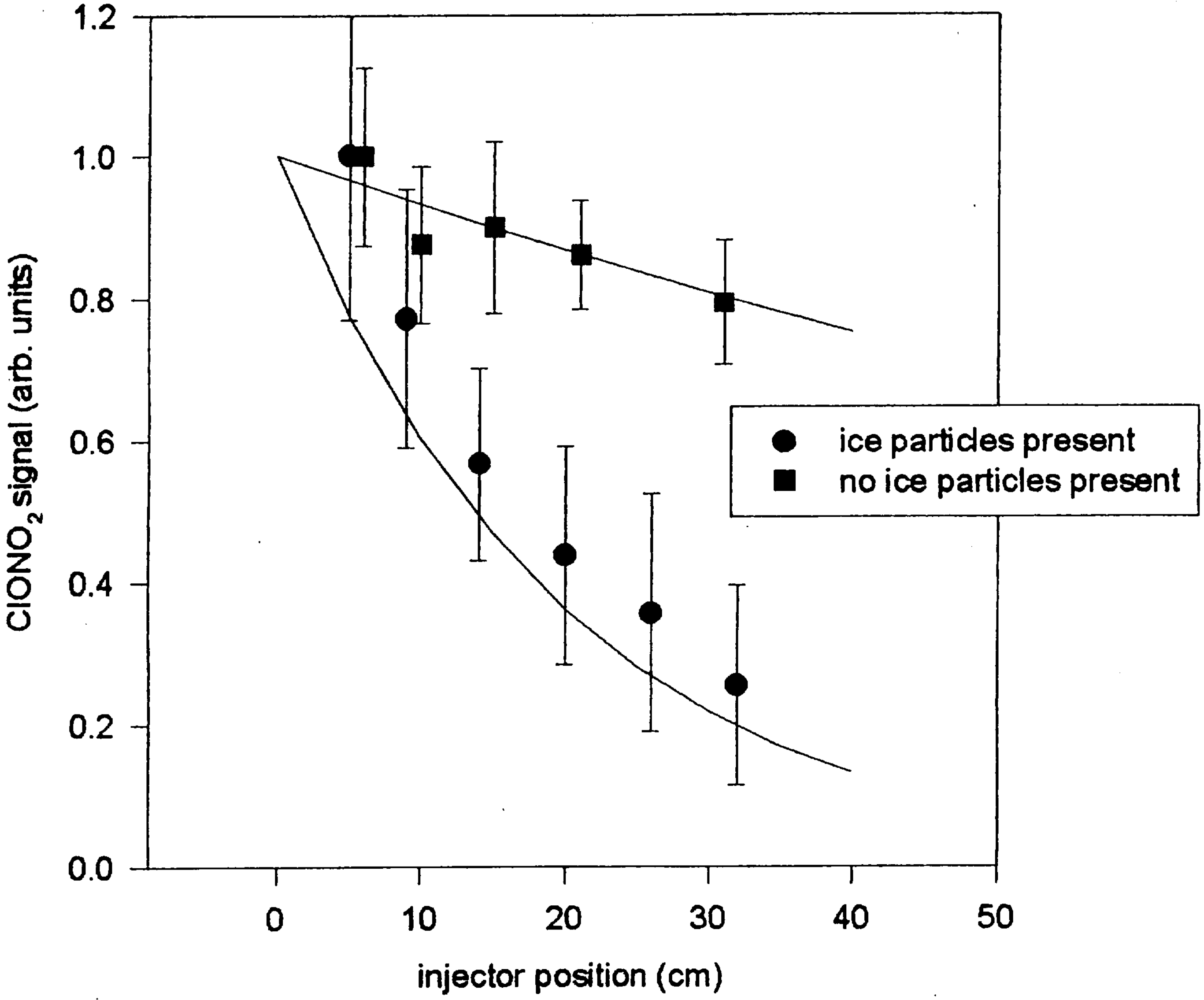


Figure 3: Reactant signal as a function of injector position with and without ice particles.