A MECHANISM FOR HYDROCHLORIC ACID PRODUCTION IN CLOUD

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ABSTRACT

A theoretical model describing the general interaction between atmospheric trace gases, such as SO_2, NH_3, CO_2 and O_2, chemical reactant gaseous product H_2SO_4 and hydrometeors containing NaCl is proposed to study a possible mechanism for hydrochloric acid production in non-precipitating cloud and the determination of the pH value of cloud droplets.

Four different cloud droplet distributions have been used to estimate the upper limit of the amount of gaseous HCl released into the atmosphere resulting from the evaporation of cloud droplets. It is shown that the acid production and the amount of HCl released depend on the following factors: (a) the temperature of the cloud; (b) the oxidation rates; (c) the ambient concentration of SO_2, NH_3, and H_2SO_4; (d) the life cycle of the cloud; and (e) the liquid water content of the cloud.

This proposed chemical model also predicts a pH value spectrum depending on the cloud droplet distribution. Field measurements for the dependence of pH value on particle size and spatial distribution of gaseous HCl are recommended.

I. INTRODUCTION

Recently there is a growing awareness of the acidity of precipitation produced by cloud in a polluted environment. Not only because acid rain has detrimental effects on local fishing industry, agricultural crops and forest ecosystem, but also it has no country boundary.

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One country's industrial activity may produce acid rain in another country. Although in the field of air pollution scientists focus almost exclusively on the emission of SO_2 from burning of fossil fuel and the subsequently low pH value of the rain drop in the polluted atmosphere, sulfuric acid is by no means the unique acid in the rain drop. As a matter of fact, more recently there is an increasing urgency to better understand the role of free hydrochloric acid in the atmosphere due to the following reasons:

(a) HCl plays an important role in the air chemistry. Previous interest in the HCl problem resulted mainly from the research to explain the changing sodium to chlorine ratio from the ocean. (1,2) Indeed, the general tendency of the increase of that ratio with distance from the coast can easily be explained by assuming the release of free hydrochloric acid from cloud nuclei during their courses toward continent. Currently attention has been given to the air chemistry of stratosphere in which HCl will compete if present in the natural stratosphere with NO, OH, etc., in the catalytic destruction chain of ozone ($HCl + OH \rightarrow H_2O + Cl$, $Cl + O_3 \rightarrow ClO + O_2$, $ClO + O \rightarrow Cl + O_2$) (3).

(b) Positive small ions at tropospheric and lower stratospheric levels consist of clusters of the type: $NH_4^+ \cdot (NH_3)_n \cdot (H_2O)_m$ with $n \sim 1\text{-}3$ and $m \sim 1\text{-}10$ depending on temperature and ambient (NH_3) and (H_2O) concentration. The presence of these ions in the atmosphere may induce reactions leading to the formation of aerosols, or at least to the existence of free NH_4Cl molecules whenever traces of ammonia and hydrochloric acid are in collisional contact with ions. Calculation shows that by assuming an ion density of 10^3 cm^{-3} would result in an average lifetime for HCl in the order of 10 days ($HCl \rightarrow NH_4Cl$). If NH_4Cl is absorbed by cloud droplets, the possibility of subsequent HCl formation and release cannot be excluded, i.e., some HCl could be continuously recycled. On the other hand, if aerosol NH_4Cl is formed, that may be a significant sink for atmospheric HCl.

(c) It is believed that most of the gaseous HCl molecules in the atmosphere are the end product of interactions between trace gases and hydrometeors. According to Duce, (4) the annual production rate of HCl in a global scale through this mechanism is 6×10^8 metric tons. Because HCl is highly dissolvable, the subsequent absorption of HCl into the rain drops will further lower the pH value and increase the acidity of acid rain during the rain-out process. Since HCl is vitally linked with other trace gases in the atmosphere and the acidity of rain, a full understanding of HCl will be helpful in understanding the fate of other atmospheric trace gases and the sources of acid rain.

It is the purpose of this paper to suggest a model to estimate the upper limit of the amount of gaseous HCl released into the atmosphere resulting from the interactions between the trace gases and hydrometeors and the evaporation of cloud droplets. The proposed model includes both the liquid phase oxidation mechanism and gas phase oxidation mechanism.

In addition to the interactions between the trace gases such as SO_2, NH_3, CO_2 and O_2 and the hydrometeors containing NaCl, the model also introduces the interaction between chemical reactant gaseous product H_2SO_4 and the hydrometeors containing NaCl. However, it is important to point out here that the accuracy of this model is severely limited by insufficient parameters for most precursor reactions leading to the formation of HCl and governing its fate in the intricate atmospheric system. Though quantitatively our estimations are highly speculative, qualitatively we have identified some of the important parameters that govern the amount of HCl liberated from the evaporation of the cloud droplets, thus providing a framework for further studies in this interesting subject.

This proposed model is also utilized to determine the pH value of cloud droplets. Because of the introduction of the kinetic effect into the model, a pH value spectrum depending on the cloud droplet distribution is found.

In section II, we briefly review various mechanisms proposed to study the production of HCl in the atmosphere. The pH value of the cloud droplets estimated by our model including both the liquid and gas phase oxidation of trace gases is presented in section III. In section IV we utilize our proposed model to estimate the amount of HCl released from cloud droplets. Finally, we discuss the important factors for the production of HCl and recommend future field experiments on this subject.

II. OVERVIEW

In this section, we briefly review various mechanisms proposed to study the production of HCl in the atmosphere.

Cauer (5) suggested that the oxidation of chloride by ozone is responsible for the low pH values of precipitation. In his studies of atmospheric condensation nuclei, he assumes that the sodium and chloride added to the atmosphere by bursting bubbles or breaking waves go through entirely different cycles. In the presence of small amounts of ozone in the lowest strata of the atmosphere (0-100 μgm^{-3}), those chlorine ions contained in sea spray droplets may be oxidized to free chlorine gas, which in turn, under the influence of sunlight and water vapor, can be hydrolyzed to form hydrochloric acid. The proposed reaction scheme to form HCl can be summarized as follows:

$$O_3(g) + Cl^-(aq) \rightarrow O_2(g) + ClO^-(aq)$$

$$ClO^-(aq) + 2H^+(aq) + Cl^-(aq) \rightarrow Cl_2(g) + H_2O\ (liq)$$

$$2Cl_2 + 2H_2O\ (liq) \rightarrow 4HCl\ (liq) + O_2(g)$$

However, these reactions are unlikely to happen in the atmosphere, because experimentally Kohler and Bath (6) have carried out a simulating experiment and found that the reaction is insufficient to account for the observed geographical variation of sodium to chloride ratio.

Later on the following route has been suggested for converting particulate chloride to hydrogen chloride or chlorine in the atmosphere (7):

$$NaCl + 2NO_2 \xrightarrow{H_2O} NaNO + MOCl$$

$$NOCl + H_2O \rightarrow HCl + HNO_2$$

$$NOCl \xrightarrow{hV} NO + Cl$$

However, Robbins et al. (8) did not observe the formation of nitrosyl chloride, thus the free HCl in the atmosphere cannot come from direct reaction between sea-salt particles and nitrogen dioxide.

Based on experimental results, Robbins et al. suggested the reaction route via hydrolysis of nitrogen dioxide (NO_2) to form nitric acid (HNO_3) vapor followed by either adsorption of HNO_3 vapor by dry sodium chloride particle at low relative humidities, or by solution droplets containing sodium chloride when relative humidities are high. The final step is the chemical reaction of nitric acid with sodium chloride leading to the desorption of hydrogen chloride, either immediately following the reaction or during subsequent evaporation of the droplets. Since the existence of gaseous HNO_3 in urban areas is well recognized today, we do believe that this HCl-formation mechanism in the presence of HNO_3 produced by gas phase oxidation process is one of the important mechanisms to form HCl and lower the pH value of the cloud droplets containing sodium chloride. However, among all the possibilities, the process most often quoted is summarized by the following chemical reaction sequence:

$$(H_2SO_4 + NaCl)_{aq} \rightarrow (Na_2SO_4)_{aq} + (2HCl)_{gas}$$

This leads us to the still controversial problem in atmospheric chemistry dealing with the production of SO_4^{--} in liquid droplet through the oxidation of SO_2. There are two possible pathways to produce SO_4^{--} in aquaeous solution droplet in the atmosphere. The most recognized pathway is the oxidation of dissolved SO_2 in liquid phase. However, the process involving the oxidation of SO_2 to form gaseous H_2SO_4 and followed by vapor transfer to the liquid droplet should also be considered

For gas phase oxidation, in the presence of third body, gaseous SO_2 can be oxidized in the atmosphere through the following schemes:

(R1a) $SO_2 + OH + M \rightarrow HSO_3 + M$ (Davis, 1974) (9)

(R1b) $HSO_3 \rightarrow H_2SO_4$

(R1b) steps have not been established yet, however the (R1a) is assumed to be rate determining for the formation of H_2SO_4 molecules.

(R2a) $(H_2SO_4)_n + (H_2O)_m \xrightarrow[\text{nucleation}]{\text{heteromolecular}}$ sulfuric acid droplets

(R2b) sulfuric acid vapor transfer to particles or cloud droplets.

On the other hand, organic radicals can also be used to oxidize SO_2:

(R3) $ROO + SO_2 \rightarrow RO + SO_3$ (Cadle 1972) (10)

(R4) $SO_3 + H_2O \rightarrow H_2SO_4$ followed by reaction (R3).

Most authors believe that in the lower troposphere, the most likely source of sulfate is through the oxidation of dissolved SO_2 in cloud droplets:

(R5) $SO_2 \rightarrow$ dissolved in cloud droplets $\xrightarrow{\text{catalysts}} SO_4^{--}$

In the lower troposphere, ammonia is probably one of the best candidates of catalyst for that reaction. In fact, the SO_2-NH_3-CO_2 water system has been treated by Scott and Hobbs (11) and recently by Easter and Hobbs (12) who also critically reviewed the published rate constants entering the reaction scheme.

In this paper, we estimate the amount of HCl production by considering $(H_2SO_4 + NaCl)_{aq} \rightarrow (Na_2SO_4)_{aq} + (2H_2O)_{gas}$ chemical reaction mechanism. Both liquid phase and gas phase oxidation of SO_2 to form SO_4^{--} in liquid droplet will be considered.

III. ESTIMATION OF THE pH VALUE OF THE CLOUD DROPLETS

1. Liquid phase oxidation (see Figure 1a)

As noted earlier, the ammonia catalyzed SO_2 oxidation in the liquid phase is currently considered as the most likely route to produce sulfate compounds. However, if sodium chloride is present in the droplets, free hydrogen and chloride ions will combine and finally be released into the atmosphere in the form of free hydrochloric acid during the evaporation process of cloud droplets in a non-precipitating cloud. We therefore, incorporate this process in our model calculation and determine the pH value of the cloud droplet and the amount of HCl that

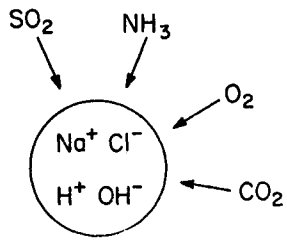

Figure 1a. A diagram to show the interaction between trace gases (SO_2, NH_3, CO_2), O_2 and hydrometeors containing NaCl

could be liberated from the cloud droplets.

Scott and Hobbs (11) have summed up the chemical reaction equations involved and the corresponding equilibrium constants. (See Table 1.)

Table 1

Liquid-Phase Reactions in the SO_2 - NH_3 - CO_2 - Water System

Eq.	Chemical Equilibrium Equation	Equilibrium Constant
(1)	$H_2O \rightleftharpoons H^+ + OH^-$	$K_w = [H^+][OH^-]$
(2)	$(SO_2)g + H_2O \rightleftharpoons SO_2 \cdot H_2O$	$K_{hs} = [SO_2 \cdot H_2O] / P_{SO_2}$
(3)	$SO_2 \cdot H_2O \rightleftharpoons H^+ HSO_3^-$	$K_{1s} = [H^+][HSO_3^-]/[SO_2 \cdot H_2O]$
(4)	$HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$	$K_{2s} = [H^+][SO_3^{--}]/[HSO_3^-]$
(5)	$(NH_3)g + H_2O \rightleftharpoons NH_3 \cdot H_2O$	$K_{ha} = [NH_3 \cdot H_2O]/P_{NH_3}$
(6)	$NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$	$K_{1a} = [NH_4^+][OH^-]/[NH_3 \cdot H_2O]$
(7)	$(CO_2)g + H_2O \rightleftharpoons CO_2 \cdot H_2O$	$K_{hc} = [CO_2 \cdot H_2O]/P_{CO_2}$
(8)	$CO_2 \cdot H_2O \rightleftharpoons H^+ + HCO_3^-$	$K_{1c} = [H^+][HCO_3^-]/[CO_2 \cdot H_2O]$

As pointed out by McKay (13), those equilibrium constants are highly dependent upon the temperature. McKay has listed these equilibrium constants at 25 C and 15 C. By assuming constant enthalpy for each set of constants, those constants can be extrapolated to values at other temperatures.

In our model we assume that chemical equilibria between SO_2 and NH_3 and their various dissolved forms in liquid are established at all

time. It is also assumed that, in the aqueous phase, the diffusion of SO_2 is so fast that the oxidation rate rather than diffusion is a controlling factor. We also assume that the cloud is at the 600 mb level and its temperature is 0°C.

The concentration of H^+ ions and SO_4^{--} ions can be estimated by solving the following equations:

$$\frac{d[SO_4^{=}]}{dt} = K[SO_3^{=}] \tag{1}$$

$$[SO_3^{--}] = K_{2s}K_{1s}K_{hs}\frac{P_{SO_2}}{[H^+]^2} \tag{2}$$

$$\{1 + \frac{K_{ha}K_{1a}}{Kw} PNH_3\}[H^+]^3 - 2[SO_4^{--}][H^+]^2$$

$$- \{Kw + K_{hc}K_{1c}Pco_2 + K_{hs}K_{1s}Pso_2\}[H^+]$$

$$- 2K_{hs}K_{1s}K_{2s}P_{so2} = 0 \tag{3}$$

The oxidation rate constant k in Eq. (1) is still a controversial subject. Up to now three different expressions have been suggested. Their differences are so large that further experimentation to clarify this problem is urgently needed.

The first expression was suggested by Scott and Hobbs (11) in 1967. Based upon the experimental results of Van den Heuval and Mason (14) they evaluated the value of k at 25°C was 0.0017 sec^{-1}.

Using the experimental results of Fuller and Crist, (15) McKay (13) in 1971 suggested a rate value depending upon the hydrogen ion concentration. This rate value k at 25°C can be expressed as following:

$$k = 0.013 + 59[H^+]^{1/2}\ sec^{-1}$$

$$= 0.032\ sec^{-1} \text{ at neutrality}$$

In 1972, Miller and de Pena (16) used a different value of k, 0.003 sec^{-1}, to do their calculations.

All these oxidation rate constants depend on the temperature. As suggested by McKay, (13) and Easter and Hobbs, (12) an activation energy of 18.3 k cal $mole^{-1}$ should be used to obtain the rate constant at varying temperatures. Rate constants of k suggested by different authors and calculated at different temperatures are shown in Table 2.

Table 2

Rate Constant k (sec^{-1})

Suggested by Different Authors and at Different Temperatures

Author	25°C	15°C	10°C	0°C	-3°C
Scott & Hobbs	0.0017	0.00058	0.00033	0.0001	0.000069
McKay	0.013+	0.0048	0.0026+	0.00078+	0.00054+
	$59[H^+]^{1/2}$	$20[H^+]^{1/2}$	$11.57[H^+]^{1/2}$	$3.43[H^+]^{1/2}$	$2.44[H^+]^{1/2}$
(at neutrality)	0.032	0.011	0.00628	0.00192	0.00133
Miller & dePena	0.003	0.001	0.0059	0.00018	0.000124

2. Gas phase oxidation (see Fig 1b)

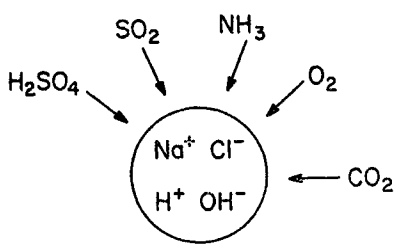

Figure 1b. A diagram to show the interaction between trace gases (SO_2, NH_3, CO_2), O_2 and hydrometeors containing NaCl with the impinging of chemical reactant gaseous production H_2SO_4 molecules.

In order to have a more realistic model, the gas phase oxidation of trace gases to produce acid molecules should not be neglected. As noted earlier, the gas phase oxidation of SO_2 leading to the formation of H_2SO_4 in the atmosphere is through the following scheme:

$$\text{(R1a)} \quad SO_2 + OH + M \rightarrow HSO_3 + M$$

where M is the third body responsible to take away the excess energy produced in the reaction. On the basis of micro-observations (17) the steps following the reaction to produce H_2SO_4 are so fast, we can assume that the rate-limiting process leading to the formation of H_2SO_4 is (R1a). The rate constant of reaction (R1a) can be approximated to be 3×10^{-31} cm^6 sec^{-1}. (9) The OH concentration is taken to be 5×10^6 cm^{-3}. By assuming the cloud is at 2 km, the value of the third body concentration M can be taken as 2.09×10^{19} cm^{-3}. (18) The conversion rate of SO_2 to H_2SO_4 is then expressed as a function of the

environment concentration of SO_2. If we set SO_2 = m ppbv, then the production rate of H_2SO_4 is:

$$P_1 = \frac{d[H_2SO_4]}{dt} = k[OH][M][SO_2]$$

$$= 6.6 \times 10^4 \text{ m molecules cm}^{-3}\text{sec}^{-1}$$

It is obvious that the relative importance of the gas phase oxidation rate is dependent on the ambient concentration.

In order to determine the actual number of acid molecules sticking on the cloud droplets, we assume an accomodation factor of 1 and the impinging rate (i.e., the number of molecules that arrive at the surface of the droplet per unit area per unit time) is estimated by the formula:

$$\beta = \frac{P}{\sqrt{2\pi mkt}} = \left(\frac{kT}{2\pi m}\right)^{1/2} N_B = bN_B, \qquad (4)$$

$$b = \left(\frac{kT}{2\pi m}\right)^{1/2}$$

where P is the pressure of H_2SO_4, k is the Boltzmann constant, m is the mass of one acid molecule, and N_B is the number concentration of the gaseous acid which we can assume equal to the production rate of that species times a certain factor.

The concentration of H_2SO_4 in the cloud droplet due to impinging can be expressed as:

$$C = \frac{bs}{AV} \cdot N_B \cdot t \cdot 10^3 \text{ (moles liter}^{-1}\text{)}$$

$$= \frac{3bt}{Ar} \cdot N_B \cdot t \cdot 10^3 \text{ (moles liter}^{-1}\text{)} \qquad (5)$$

where r = radius (cm)

S = area (cm^2)

V = volume (cm^3)

$b = \left(\frac{KT}{2\pi m}\right)^{1/2}$ (cm sec^{-1})

A = Avogadro Number

t = time (sec)

N_B = concentration (cm^{-3})

It is obvious from Eq. (5) that the smaller the droplet size and the longer the time of reaction, the greater the importance of the gas phase reaction followed by impinging to produce H^+ ions in the droplet.

Indeed, the gas phase reaction must be incorporated with the liquid phase reaction since those two processes are acting simultaneously. Consequently, Eq. (3) should be modified to include the gas phase reaction term as following:

$$\{1 + \frac{K_{ha}K_{1a}}{K_w} PNH_3\}[H^+]_t^3 - \{2[SO_4^{--}]_t + \sum_{ji}\sum a_j n_i \frac{3b_j t}{Ar_i} N_j \cdot 10^3\}[H^+]_t^2$$
$$- \{K_w + K_{hc}K_{1c}P_{co2} + K_{hs}K_{1s}P_{so2}\}[H^+]_t - K_{hs}K_{1s}K_{2s}P_{so2} = 0 \qquad (6)$$

where i refers to size index

j refers to species index

n_i is the number of droplets with radius r_i

a_j is the covalence of species j

Eqs. (1), (2), and (6) form a closed set from which concentrations of different species in the droplet can be evaluated as a function of time for a given set of initial concentrations of ambient SO_2 and NH_3. The initial concentration of H^+ is a solution to Eq. (6) with an initial condition where $[SO_4^{--}]$ equals zero. The substitution of the value of $[H^+]$ to Eq. (2) will yield the value of $[SO_3^{--}]$. The $[SO_4^{--}]$ at a later time will then be determined from Eq. (1). The whole calculation scheme may then be repeated and the pH value of the droplet at any instant can then be evaluated.

Fig. (2) is a graph indicating the variation of pH value with the droplet size distribution. Curves A and B correspond to an ordinary cloud at 0°C with ambient SO_2 and NH_3 gas concentrations 1 ppbv and 3 ppbv, respectively. Curves C and D correspond to a polluted cloud with ambient SO_2 and NH_3 gas concentrations 10 ppbv and 3 ppbv, respectively. Curves A and C have included the production of sulfuric acid through gas phase oxidation. In an unpolluted environment, concentrations of gaseous H_2SO_4 molecules have been estimated as 1×10^7.

Here, we estimate the concentration of H_2SO_4 molecules by:

$$N_B = \frac{C_B}{Sb}, \quad b = \sqrt{\frac{kT}{2\pi m}} \qquad (7)$$

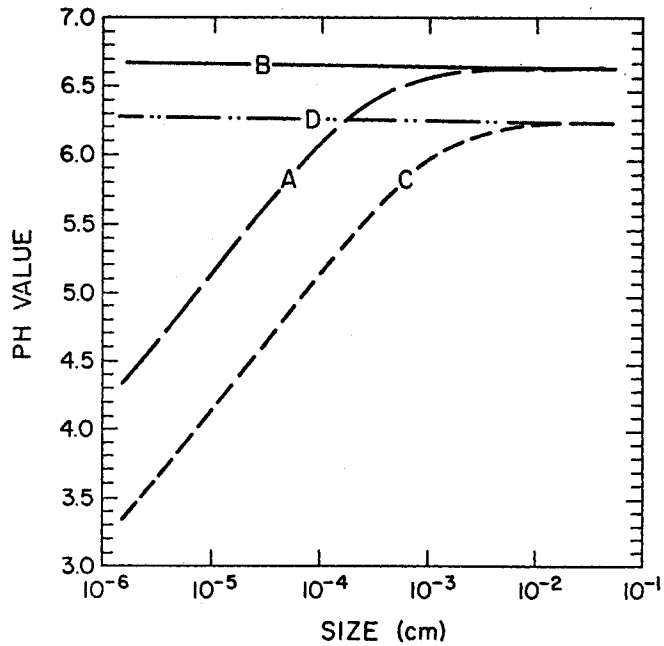

Figure 2. pH value of the cloud droplet as a function of its size. Curves A and B correspond to an environmental SO_2 and NH_3 concentrations 1 ppbv and 3 ppbv respectively. Curves C and D correspond to an environmental SO_2 and NH_3 concentration 10 ppbv and 3 ppbv respectively. Curves A and C are obtained by considering both the gases phase and liquid phase oxidation, but Curves B and D are obtained by considering the liquid phase oxidation alone. All values are obtained by using the oxidation rate suggested by McKay, and by assuming the cloud is at a level of 600 mb and the temperature is 0°C. The time of reaction is 10 minutes.

where C_B is the rate of production of H_2SO_4 and can be obtained by $C_B = k[OH][SO_2][M] = 6.6 \times 10^4$ molecules/(cm sec) for 1 ppb SO_2, and S is the total surface area of aerosol per cubic centimeter ($\simeq 10^2$ $\mu m^2/cm^3$ in rural area and $\simeq 10^3$ $\mu m^2/cm^3$ in urban area (19)). Equation (7) gives a steady state concentration of H_2SO_4. N_BSb is the total rate of the loss of H_2SO_4 to aerosol surface and in a steady state the total rate of the loss is assumed to be equal to the total rate of production (C_B). Thus, in the rural area the steady state concentration of H_2SO_4 is in the order of 10^7 molecules/cm^3. In a polluted environment, their

concentrations are accordingly increased by ten fold. Curves B and D correspond to the result obtained without considering the gas phase oxidation. Results shown in Figure (2) are obtained by assuming a cloud of liquid water content 0.2 gm/m^3 of air and exposed to the trace gases for 10 minutes. Here we used McKay's oxidation rate constant.

A comparison of curves A, C with B, D indicates that the additional consideration of gas phase oxidation will produce a pH value spectrum depending on the droplet size distribution, while the ignoring of gas phase oxidation will produce a pH value which is independent of the droplet size distribution. It is obvious that the consideration of gas phase oxidation in addition to the liquid phase oxidation will produce a lower pH value of cloud droplets.

Curve C indicates that a droplet with radius 0.01μ will have a pH value as low as 3.0. This is true as long as the droplet remains small, because in this case the hydrogen ions in the droplet are mainly due to the impinging of gaseous acid molecules. The concentration of hydrogen ions in the droplet due to impinging is inversely proportional to its radius. In the real atmosphere the droplet will grow. The lower the pH value of the droplet, the smaller is its partial water vapor pressure, and the greater is the number of water vapor molecules impinging on its surface. Consequently, the pH value will increase due to the growth of droplet.

In order to see the effect of temperature on the pH value of the cloud droplets, Figure (3) has been plotted by assuming a temperature of 10°C. A comparison of these two figures indicates that the lower the temperature, the higher the pH value. Figure (4) is obtained with the same environmental conditions as that of Figure (2) except here we use Scott and Hobbs' oxidation rate constant.

Finally, in order to see the effect of time duration on the average pH value of the cloud, a plot of average pH value versus time at 0°C with McKay's rate constant is shown in Figure (5). At the beginning, the difference between the two models, considering both the gas and liquid phase oxidations, and only the liquid phase oxidation is small. However, as the reactions continue, their differences increase. This is because the gas phase oxidation is proportional to time, the longer the time of reaction, the more important is the gas phase oxidation. On the other hand, the liquid phase oxidation is slowed down due to the increasing amount of free hydrogen ions in the droplet as reaction proceeds.

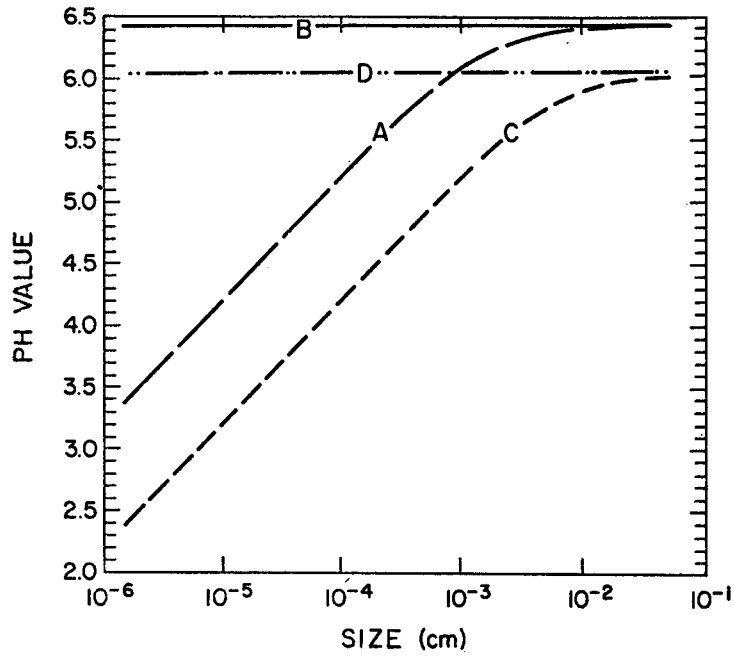

Figure 3. The same as Figure 1, except the temperature of the cloud is 10 C.

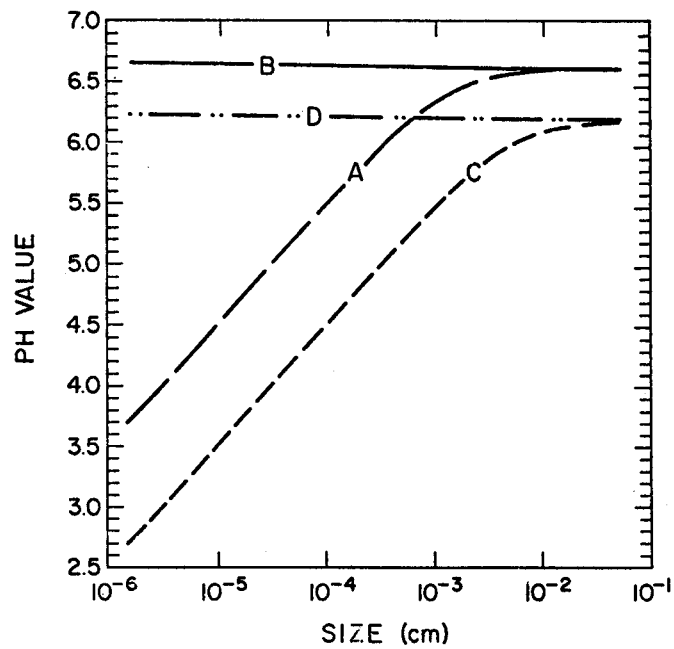

Figure 4. The same as Figure 2, except the oxidation rate is the one suggested by Scott and Hobbs and the H_2SO_4 concentration has been decreased by a factor of 2.

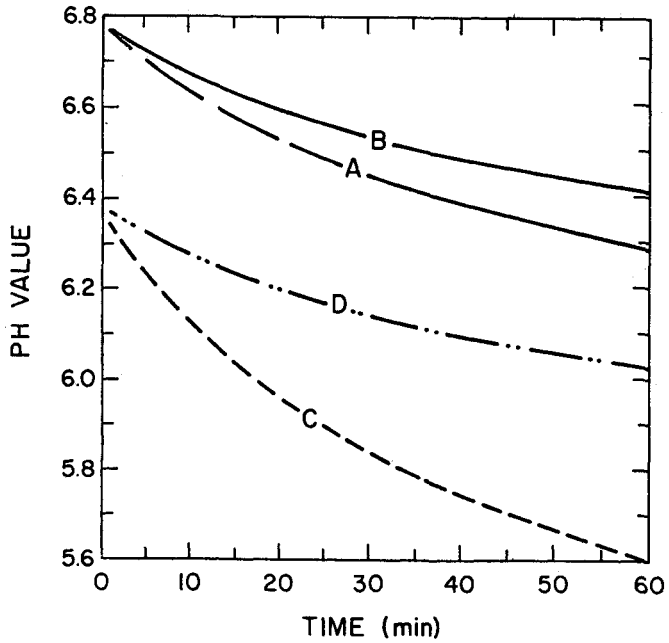

Figure 5. The average pH value of the cloud as a function of time Curves A and B correspond to an environmental SO_2 and NH_3 concentrations 1 ppbv and 3 ppbv, respectively. Curves C and D correspond to an environmental SO_2 and NH_3 concentrations 10 ppbv and 3 ppbv respectively. Curves A and C are obtained by considering both the gas phase oxidation and the liquid phase oxidation, but curves B and D are obtained by considering the liquid phase oxidation alone. All values are obtained by using the oxidation rate suggested by McKay and by assuming the cloud is at a level of 600 mb and the temperature is 0 C.

IV. ESTIMATION OF THE AMOUNT OF HCl RELEASED FROM THE CLOUD DROPLETS (See Figure 6)

In order to estimate the amount of HCl released into the atmosphere we must know the distribution of cloud droplets containing NaCl. Though different forms of sea-salt nuclei distributions have been suggested, four types are widely used. (Arnason and Greenfield). (20)

Based on nuclei distributions in the trade wind region (Woodcock)

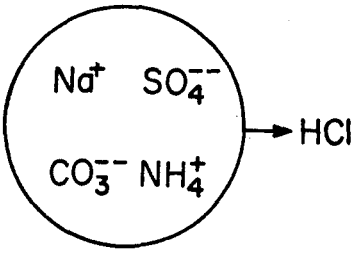

Figure 6. A diagram to show the release of HCl into the atmosphere from the hydrometeors during the evaporation process.

(21) Eriksson (22) suggested the following analytical form:

$$\frac{dn}{dr} = n(r) = a_1 \mathrm{Exp}(-br^{1/2})$$

where n is the number of sea-salt particles per cubic centimeter of radii smaller than r, and a_1 and b are constants having the values 6.31×10^2 and 6.9 respectively, when r is measured in microns. Another distribution, given by Mordy (23) in his numerical simulation of condensation, represents maritime conditions also based on observation by Woodcock. The third distribution, also maritime, is used by Warner (24) in a computation of droplet growth by condensation.

In contrast to the above three maritime distributions, the fourth one is more or less typical of continental conditions (25):

$$\frac{dn}{dr} = n(r) = \frac{c}{2,30} r^{-4} \tag{9}$$

where c is a constant in the order of 10^{-7} to 10^{-8} if r is given in microns.

The equilibrium radii in response to a change in supersaturation S can be computed by means of the following equilibrium equation (26):

$$S - \frac{a}{r} + \frac{b}{r^3} = 0 \tag{10}$$

where a $\frac{3.3 \times 10}{T}$, (T is absolute temperature), and b $\approx$ 4.3i m/M.

The amount of hydrogen chloride released into the atmosphere from a cloud at a supersaturation S after it moves to an unsaturated environment can be estimated by the following formula:

$$M_j = 36.5 \times 10^{-3} \sum_{K=1}^{n} \frac{4}{3} \Pi \left(\frac{r_s^k + r_s^{k+1}}{2}\right)^3 \cdot \Delta N_j^k \cdot [H^+]_k \tag{11}$$

where M_j is the amount of HCl released into the atmosphere in units of $\mu g/m^3$ of air

r_s^k is the equilibrium radius at supersaturation S with group index k

ΔN_j^k is a particular distribution (j) of nuclei per cubic centimeter for a range r with group index k to k+1

$[H^+]$ is the concentration of H^+ ions for a particular cloud at the end of its life cycle and its unit is in moles/liter.

The amount of HCl released into the atmosphere as a function of life cycles of the cloud at 0°C for different types of nuclei distribution at an environment of zero percent supersaturation is shown in Figures (7) and (8). Curves A, B, C and D in Figures (7) and (8) correspond to the results obtained by using the above mentioned four types of nuclei distributions respectively. Here we use McKay's oxidation rate and assume the ambient concentration of SO_2 and NH_3 are 1 ppbv and 3 ppbv respectively. Graphs in Figure (7) are results obtained by considering both the gas and liquid phase oxidation of SO_2. Graphs in Figure (8) are results obtained by considering only the liquid phase oxidation of SO_2. A non-precipitating cloud may go through more than one cycle and more HCl will be released from an "older" cloud (recycled cloud condensation nuclei). Here the life cycle is assumed to be one hour.

Figures (9) and (10) are obtained by assuming the cloud is at a polluted environment; i.e., the ambient concentration of SO_2 and NH_3 are 10 ppbv and 3 ppbv respectively. Results in Figure (9) are obtained by considering both the gas and liquid phase oxidation of SO_2. Results in Figure (10) are obtained by considering only the liquid phase oxidation of SO_2.

As the supersaturation of the environment changes the liquid water content of the cloud will change accordingly. Consequently, the amount of HCl released from such cloud will change. In order to see the effect of liquid water content of the cloud on the amount of HCl released into the atmosphere, plots of the amounts of HCl released as a function of the liquid water content of the cloud for different environmental conditions at the end of the first life cycle of the cloud are shown in Figure (11). Results are obtained by considering both the liquid and gas phase oxidation of SO_2. Here we assume that the concentration of ambient SO_2 is 1 ppbv, and curves A, B, and C correspond to concentration of NH_3 1 ppbv, 2 ppbv and 3 ppbv respectively. The increases of environmental NH_3 concentration will decrease the production of HCl from a non-precipitating cloud.

In order to evaluate the significance of the production of HCl through the mechanism discussed in this paper, here we present a rough

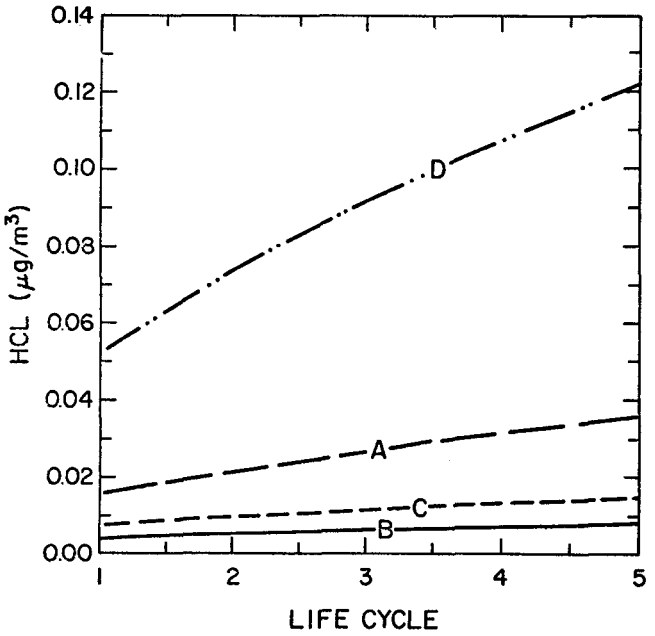

Figure 7. Amount of HCl released into the atmosphere from the cloud as a function of its life cycle. The cloud is at 600 mb and its temperature is 0 C. The environmental SO_2 and NH_3 concentrations are 1 ppbv and 3 ppbv respectively. The life cycle is assumed to be one hour. The results are obtained by using McKay's oxidation rate and considering both the liquid and gas phase oxidation of SO_2. Curves A, B, C and D correspond to nuclei distributions suggested by Erikson, Mordy, Warner and Junge respectively.

estimation of the global production of HCl through the interaction between trace gases and hydrometeors. We assume an average cloud thickness of 2000 meters and the mean global cloud cover as 0.54 (27). We further assume that the life cycle of a cloud is one hour and a cloud can go through five cycles which takes ten hours. If the SO_2 and HN_3 concentrations are both 1 ppbv and we only consider liquid phase oxidation, the global production of HCl is 1.73×10^8 tons/year. However if additionally we consider the gas phase oxidation, the global production of HCl changes to 2.2×10^8 tons/year. If we assume the SO_2 concentration is 10 ppbv and the NH_3 concentration is 1 ppbv and consider both the gas and liquid phase oxidation, the global production of HCl is 9.32×10^8 tons/year. Our estimation is of the same order of magnitude as the annual production rate of 6×10^8 tons calculated by Duce (4).

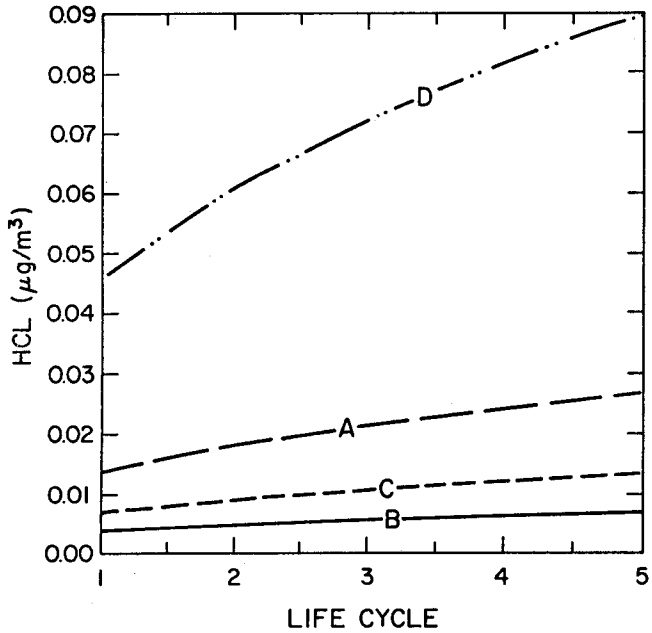

Figure 8. The same as Figure 7, except only the liquid phase oxidation of SO_2 has been considered.

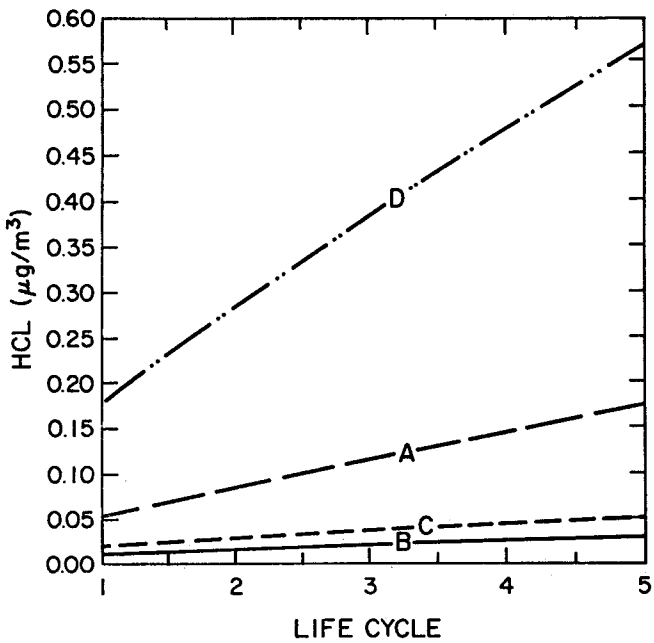

Figure 9. The same as Figure 7, except the cloud is at a polluted environment in which the concentrations of SO_2 and NH_3 are 10 ppbv and 3 ppbv respectively.

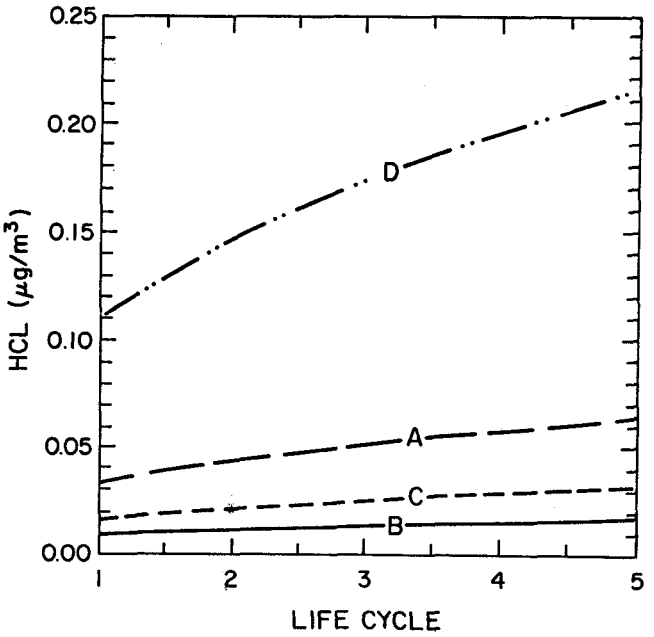

Figure 10. The same as Figure 9, except only the liquid phase oxidation of SO_2 has been considered.

It is important to point out here that the above calculations for the amount of HCl production due to the interactions between the trace gases and hydrometeors is based on the assumptions that the HCl gaseous molecules are released from the cloud droplets only when the cloud droplet is undergoing evaporation process. For a non-evaporating cloud droplet the amount of HCl released from the cloud droplet is depending on the concentration of HCl in the air around the cloud droplet and the partial pressure of HCl in the cloud droplet. If the partial pressure of HCl in the air is much less than the partial pressure of HCl in the cloud droplet, our calculation would be essentially correct. Therefore, the calculation presented in this paper represent an upper limit for HCl production. A more accurate calculation for the production of HCl by the proposed mechanism should consider the difference of the partial pressures of HCl in the cloud droplet and its surrounded air.

V. CONCLUSIONS AND DISCUSSIONS

We have discussed the differences between the chemical models considering only the liquid phase oxidation of trace gases and the more realistic model considering both the gas and liquid phase oxidations. The additional consideration of gas phase oxidation of trace gases will further lower the pH value of the cloud droplets and will produce a pH

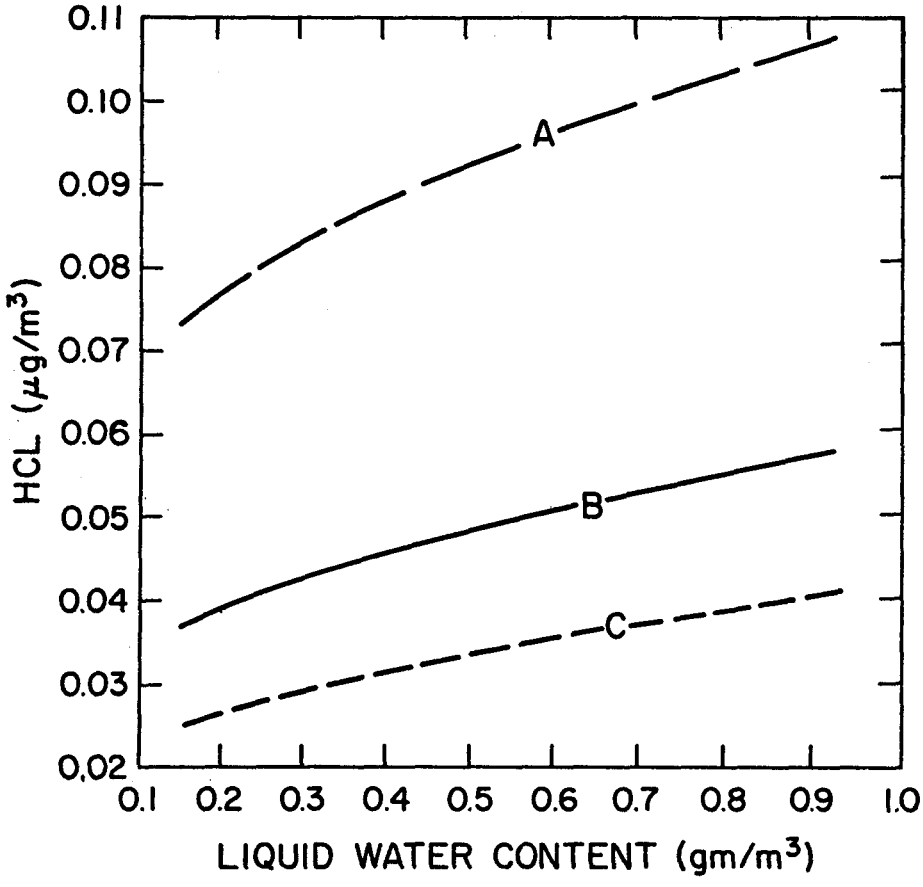

Figure 11. Amount of HCl released into the atmosphere from the cloud as a function of its liquid water content. The environmental SO_2 concentration is 1 ppbv and curves A, B and C correspond to environmental concentration of NH_3 1 ppbv, 2 ppbv and 3 ppbv respectively. Here results are obtained by considering both the liquid and gas phase oxidation of SO_2.

value spectrum depending on the drop size distribution. Generally speaking, the relative importance of these two mechanisms depends on the size distribution of droplets, the time duration of the reaction, the relative abundance of trace gases, and the assumed oxidation rate.

We have demonstrated that non-precipitating clouds containing NaCl can produce a source of free HCl in the atmosphere. The amount of HCl liberated from cloud droplets depends on the following factors: (a) the temperature of the cloud; A higher temperature of the cloud will produce more HCl; (b) the assumed oxidation rate; By using McKay's oxidation rate constant will produce more HCl; (c) the ambient concentration of SO_2 and NH_3; More SO_2 in the environment will produce more HCl, however more NH_3 in the environment will produce less HCl; (d) the

concentration of gaseous acid molecules; More gaseous acid molecules in the environment will produce more HCl; (e) the life cycle of the cloud; More HCl will be released from an "older" cloud; (f) the liquid water content of the cloud; A cloud with higher liquid water content will produce more HCl.

The amount of HCl released into the atmosphere is a combined result of the intricate physical and chemical processes occurring inside the cloud. Due to the complexity of the problem, here we consider only the case in which the droplet is static and does not grow. The macro- and micro-physical processes of a cloud will certainly influence the pH value of the cloud droplets and the effectiveness of HCl production mechanism. Field measurements are urgently needed to reveal the droplet size distribution of the pH value and the spacial distribution of HCl.

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