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ACID RAIN: SCIENTIFIC AND TECHNICAL ADVANCES

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ACID RAIN: SCIENTIFIC AND TECHNICAL ADVANCES

Edited by R. Perry
R.M. Harrison,
J.N.B. Bell
and J.N. Lester

Carboxylic acids are believed to contribute significantly to rainwater acidity in remote areas, although their contribution is not at all well quantified. In polluted regions they are unlikely to be of much importance.

Strong Acids

Strong acids of major importance in the atmosphere are as follows:

H_2SO_2

HNO_3

HCl

CH_3SO_3H (methyl sulphonic acid)

Sulphuric acid

Atmospheric oxidation of SO_2 proceeds via a range of mechanisms. Consequently, dependent upon the concentrations of the responsible oxidants, the oxidation rate is extremely variable with space and time, but typically lies around 1% h^{-1}.

Several gas phase mechanisms have been investigated including photooxidation, reaction with hydroxyl radical, Criegee biradical, ground state atomic oxygen, $O(^3P)$, and peroxy radicals.

Table 1, based upon the treatment of Finlayson-Pitts and Pitts (2), summarises the rate data and clearly indicates the overwhelming importance of the hydroxyl radical reaction in the gas phase.

Table 1 Homogeneous Oxidation Mechanisms for SO_2 (based on ref 2)

Oxidising Species	Concentration* (cm^{-3})	Rate Constant (cm^3 $molec^{-1}$ s^{-1})	Loss of SO_2 ($\%h^{-1}$)
OH	5×10^6	9×10^{-13}	1.6
O_3	2.5×10^{12}	$<8\times10^{-24}$	$<7\times10^{-6}$
Criegee biradical	1×10^6	7×10^{-14}	3×10^{-2}
$O(^3P)$	8×10^4	6×10^{-14}	2×10^{-3}
HO_2	1×10^9	$<1\times10^{-18}$	$<4\times10^{-4}$
RO_2	3×10^9	$<1\times10^{-18}$	$<1\times10^{-3}$

* Assuming a moderately polluted atmosphere.

The mechanism of the SO_2-OH reaction is not entirely clear, but most probably is as follows:

$$SO_2 + OH \rightarrow HOSO_2$$
$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

In the presence of water droplets, which can take the form of fogs, clouds, rain or hygroscopic aerosols, sulphur dioxide will dissolve, opening the possibility of aqueous phase oxidation. Upon dissolution, the following equilibria operate.

$$SO_2(g) + H_2O \rightleftarrows SO_2H_2O$$
$$SO_2.H_2O \rightleftarrows HSO_3^- + H^+$$
$$HSO_3^- \rightleftarrows SO_3^{2-} + H^+$$

These equilibria are sensitive to pH and HSO_3^- is the predominant species over the range pH 2-7. The other consequence of these equilibria is that the more acidic the droplet, the greater the degree to which the equilibria move towards gaseous SO_2 and limit the concentrations of dissolved S(IV) species. Some rate constants are pH-dependent in addition.

The major proposed oxidation mechanisms for SO_2 in liquid droplets include the following:

(i) uncatalysed oxidation by O_2
(ii) transition metal-catalysed oxidation by O_2
(iii) oxidation by dissolved oxides of nitrogen
(iv) oxidation by ozone
(v) oxidation by H_2O_2 and organic peroxides.

Relative rates for typical specified concentrations of reactive species are indicated in Table II.

Table II Aqueous Phase Oxidation Mechanisms for SO_2

Oxidant	Concentration*	Oxidation rate ($\%h^{-1}$) pH 3	pH 6
O_3	50ppb (g)	3×10^{-2}	5×10^{3}
H_2O_2	1ppb (g)	8×10^{2}	5×10^{2}
Fe-catalysed	3×10^{-7}M (ℓ)	2×10^{-2}	5×10^{1}
Mn-catalysed	3×10^{-8}M (ℓ)	3×10^{-2}	7
HNO_2	1ppb (g)	5×10^{-4}	3

*g and ℓ denote gas and liquid phase concentrations respectively. Conditions are 5 ppb gas phase SO_2 at 25°C with no mass transfer limitations.

At high pH, all mechanisms in Table II are capable of oxidising SO_2 at appreciable rates, generally far in excess of those observed in the atmosphere over a significant averaging period. Slower rates are observed because of mass transfer limitations to the rate of introduction of SO_2 and oxidant to the water droplet, and the previously noted effect of pH reduction (due to H_2SO_4 formation) on the solubility of SO_2. At pH 3, only the reaction with hydrogen peroxide is very fast, due to an increasing rate constant at reduced pH compensating for the lower solubility of SO_2. Recent experimental studies indicate that this reaction can be very important in the atmosphere, but is limited by the availability of H_2O_2 which rapidly becomes depleted. The rate of formation of H_2SO_4 is therefore a function more of atmospheric mixing processes than of chemical kinetics in this case.

Several studies have emphasised the importance of SO_2 oxidation upon the surface of carbonaceous aerosols (8,9). Our own work (10), including experiments at high relative humidity and in aqueous suspension indicates that this reaction pathway is likely to make a negligible contribution to atmospheric sulphate formation under most conditions.

Nitric Acid

The main daytime route of nitric acid formation is from the reaction:

$$NO_2 + OH \rightarrow HNO_3$$

The rate constant is 1.1×10^{-11} cm^{-3} $molec^{-1}$ s^{-1} at 25°C (2) implying a rate of NO_2 oxidation of 19.8% h^{-1} at an OH concentration of 5×10^6 cm^{-3} (c.f. Table I). This is thus a much faster process than gas phase oxidation of SO_2. This process is not operative during hours of darkness due to near zero OH radical concentrations.

At nighttime, reactions of the NO_3 radical become important which are not operative during daylight hours due to photolytic breakdown of NO_3. The radical itself is formed as follows:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

It is converted to HNO_3 by two routes. The first is hydrogen abstraction from hydrocarbons

$$NO_3 + RH \rightarrow HNO_3 + R$$

Typical reaction rates imply formation of HNO_3 at about 0.3ppb h^{-1} in a polluted urban atmosphere by this route (2). This is modest compared to daytime formation from NO_2 and OH.

The other nighttime mechanism of HNO_3 formation is via the reaction sequence

$$NO_3 + NO_2 \underset{\leftarrow}{\overset{M}{\rightleftarrows}} N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

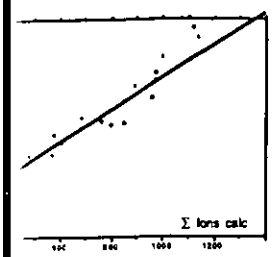
The reaction involving water is rate determining and may be fairly slow at low relative humidity, contributing HNO_3 at ~0.3ppb h^{-1} (2). As humidity increases, and especially in the presence of liquid water, more rapid reactions may be observed. This is presently supported only by indirect evidence and requires further experimental investigation.

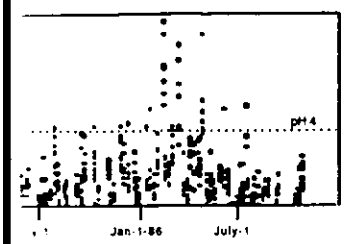
Aqueous phase oxidation of NO_2 is of little importance due primarily to low aqueous solubility of NO_2.

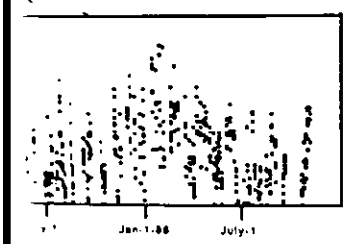
Hydrochloric Acid

HCl differs from H_2SO_4 and HNO_3 in that it is emitted into the atmosphere as a primary pollutant and is not dependent upon atmospheric chemistry for its formation.

Some perspective of its significance as an acidic pollutant may be gained from Table III which shows the estimated emissions of SO_2, NO_x and HCl in the U.K. and the potential hydrogen ion equivalent.







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FREE RADICAL CHEMISTRY OF AQUEOUS-PHASE SO_2.

R.E. Huie

Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, Maryland 20899, United States of America

ABSTRACT

A major mode of oxidation of SO_2 in atmospheric droplets involves a free radical chain. This free radical chain contributes both to the acidification of precipitation and to other possible chemical effects of atmospheric SO_2. This article reviews our present understanding of the aqueous-phase radical chemistry of SO_2 and discusses some of the important reactions in that complex chain.

INTRODUCTION

Sulfur dioxide dissolves into water to produce sulfite, bisulfite, and hydrated sulfur dioxide, with pK_a's of 7.19 and 1.86 (1). Over the pH range of greatest importance to atmospheric chemistry, then, aqueous SO_2 exists as bisulfite, HSO_3^-. In an atmospheric water droplet, HSO_3^- can be oxidized in a two-electron process involving atom transfer by such oxidants as H_2O_2 and O_3

$$H_2O_2 + HSO_3^- \rightarrow H_2O + HSO_4^-$$

$$O_3 + HSO_3^- \rightarrow O_2 + HSO_4^-$$

The reaction with hydrogen peroxide is faster for HSO_3^- than for SO_3^{2-} and continues to get faster as the pH is lowered below the pK_a of HSO_3^-, down to the pK_a of $SO_2 \cdot aq$ (2). The rate constant for the ozone reaction is faster for SO_3^{2-}, but is still significant for HSO_3^- (3). Since these reactions involve an oxygen atom transfer, there is no initiation of the free radical chain.

The oxidation of HSO_3^- by one-electron oxidants does lead to the initiation of the free radical chain. Examples of these reactants include free radicals such as OH, and oxidized transition metal ions such as Mn^{+3}

$$OH + HSO_3^- \rightarrow H_2O + SO_3^-$$

$$Mn^{+3} + HSO_3^- \rightarrow Mn^{+2} + SO_3^- + H^+$$

Rate constants for many of these reactions have now been determined.

Under typical aerobic conditions, the sulfite radical, SO_3^-, would react with O_2 to form the peroxysulfate radical

$$SO_3^- + O_2 \rightarrow SO_5^-$$

Subsequent reaction of this radical can propagate the chain or terminate it. The rates and mechanisms of the reactions of this radical are then needed to determine the importance of the free radical chain in the oxidation of HSO_3^-.

The final important radical in the autoxidation chain reaction is the sulfate radical, SO_4^-. It can be formed in the reaction of SO_5^- with HSO_3^-

$$SO_5^- + HSO_3^- \rightarrow SO_4^- + HSO_4^-$$

or in the self-reaction of SO_5^-

$$SO_5^- + SO_5^- \rightarrow SO_4^- + SO_4^- + O_2$$

This is a very reactive radical, which can react with HSO_3^- or with many other possible constituents of the droplet, including halide ions.

OXIDATION OF BISULFITE BY FREE RADICALS

One-Electron Oxidation

Both SO_3^{2-} and HSO_3^- are oxidized by free radicals in one-electron transfer reactions to produce the SO_3^- free radical. Rate constants for selected reactions are given in Table 1. In all of these cases, the reaction of a radical with SO_3^{2-} is faster than its reaction with HSO_3^-. For very strongly oxidizing radicals such as OH, the difference is small; for weakly oxidizing radicals such as I_2^-, the difference becomes quite large. Very weak oxidants such as CH_3O_2 do not appear to oxidize HSO_3^- at a measurable rate (7). Of considerable importance is the observation that whereas the SO_5^- radical oxidizes SO_3^{2-} with a rate constant of 1.3×10^7 $M^{-1}s^{-1}$, the rate constant for reaction with HSO_3^- is $<3 \times 10^5$. This result may help explain much of the pH dependence reported for the autoxidation of aqueous SO_2.

Table 1. Rate Constants for Some Reactions of Free Radicals with Sulfite and Bisulfite

Reaction	pH	$k(M^{-1}s^{-1})$	reference
$OH + HSO_3^-$	4.4	4.5×10^9	4
$OH + SO_3^{2-}$	11.2	5.2×10^9	4
$SO_4^- + SO_3^{2-}/HSO_3^-$		$>2 \times 10^9$	5
$Cl_2^- + HSO_3^-$	3	3.4×10^8	4
$Br_2^- + HSO_3^-$	4.2	6.9×10^7	6
$Br_2^- + SO_3^{2-}$	10	2.6×10^8	6
$I_2^- + HSO_3^-$	3	1.1×10^6	6
$I_2^- + SO_3^{2-}$	11	1.9×10^8	6
$SO_5^- + HSO_3^-$	4.9	$<3 \times 10^5$	4
$SO_5^- + SO_3^{2-}$	8.7	1.3×10^7	4
$NH_2 + SO_3^{2-}$	11	$<10^5$	6

There is presently no evidence that $SO_2 \cdot aq$ can be oxidized by one-electron transfer. The rate constants determined for the reaction of Mn(III) with aqueous SO_2 in strong (2-6 M) acid could be explained as reaction of the metal ion with HSO_3^- (8). $SO_2 \cdot aq$ does reacts with strong one-electron reductants, such as the 2-hydroxy-2-propyl radical, to yield SO_2^-. In an aerobic system, SO_2^- would react rapidly ($k=2.4 \times 10^9$ $M^{-1}s^{-1}$) with O_2 to give HO_2 (9).

Bisulfite also can be oxidized in a one-electron process by transition-metal ions in their higher oxidation states. These reactions have been investigated for many years, but the interpretation of the results is complicated by the ability of HSO_3^- to complex the metal ions, often forming quite stable complexes (10). Also, the interpretation frequently is complicated further by the reverse reaction, the oxidation of the reduced metal ion by SO_3^-. The rate constants for these reactions do appear to follow the same pattern as for the free radicals: the reaction with SO_3^{2-} is far faster than with HSO_3^-. Indeed, rate data are usually interpreted by assuming that only SO_3^{2-} is reactive. Since metal ion complexes are typically relatively weak oxidants ($E < 1V$), this assumption is probably justified. For stronger oxidants such as Mn(III), the assumption would not be valid.

Two-Electron Oxidation

We have recently measured rate constants for the reaction of NO_2 with HSO_3^-/S over the pH range 5.3 to 13 (9). The rate constant increases with pH from 1.2 to 3×10^7 $M^{-1}s^{-1}$, but the increase does not appear to be associated with the p HSO_3^-. In an earlier paper (11), the reactivity of NO_2 was compared with tha ClO_2. In all cases, except for their reactions with SO_3^{2-}, ClO_2 reacted faste NO_2. This exception was interpreted as due to the occurrence of an oxygen-ato transfer in the reaction of NO_2, rather than electron transfer. This is in agreement with the observation that whereas NO_2, when bubbled through a SO_3^{2-} solution, will oxygenate the sulfite, it will not initiate its autoxidation (1

REACTIONS OF SULFITE RADICALS

Rate constants for the reactions of SO_3^- with a wide variety of organic compou have been determined, a few of which are listed in Table 2. The sulfite radica found to react readily with easily oxidized reactants such as the ascorbate dianion, but reacts slowly if at all with reactants such as ascorbic acid, whi are known to be more difficult to oxidize. The one-electron reduction potentia SO_3^-

$$SO_3^- + e^- + H^+ \rightarrow HSO_3^-$$

was estimated to be 0.84V at pH 3.6 (14). Making use of the pK_a of HSO_3^-, the reduction potential for the SO_3^-/SO_3^{2-} couple is then calculated to be 0.63 V.

Table 2. Rate Constants for Some Reactions of SO_3^-

Reactant	pH	$k(M^{-1}s^{-1})$	reference
Ascorbic acid	<3	$<10^6$	13
Ascorbate ion	5-10	9×10^6	13
Ascorbate dianion	>12	3×10^8	13
Phenol	11.1	6×10^5	14
Hydroquinone	8.9	4.5×10^6	15
	10.5	5.4×10^7	
	12.9	3.2×10^8	
p-Phenylenediamine	3.4	$<5\times10^5$	6
	5.3	4.2×10^6	
	9.3	5.0×10^7	
Oxygen	6.8	1.5×10^9	14

From the reduction potential of SO_3^- and the two-electron reduction potential of SO_3^{2-} (-0.92V), we can calculate a one-electron reduction potential of -2.47V for the process

$$SO_4^{2-} + H_2O + e^- \rightarrow SO_3^- + 2OH^-$$

This suggests that SO_3^- can act as a strong reductant, yet there is no experimenta evidence to support this. This calculation probably seriously overstates the actua reducing power of SO_3^- since the initial product of the electron transfer would be SO_3, not SO_4^{2-}, which results from subsequent hydrolysis. Taking into account the enthalpy difference between SO_3 and SO_4^{2-} (16), the reduction potential for the couple SO_3/SO_3^- is estimated to be 2.8V, so that it would be very difficult to oxidize SO_3^- in a simple one-electron reaction.

REACTIONS OF THE SULFATE RADICAL

The SO_4^- radical is a very strong one-electron oxidant, with a reduction potential of between 2.5 and 3.1 V (17). It is also capable of reacting by hydrogen-atom abstraction or by addition to carbon-carbon double bonds. A few representative rate constants are given in Table 3. The rate constant for the reaction of SO_4^- with SO_3^{2-}/HSO_3^- is an estimate, and is higher than previously published values. It appears likely that those results were complicated by a chain reaction which regenerated SO_4^- (4).

Table 3. Rate Constants for Some Reactions of SO_4^-

Reactant	pH	$k(M^{-1}s^{-1})$	*reference*
Formic acid	~0	1.4×10^6	18
Formate ion	7	1.7×10^8	19
Methanol	7-8	3.2×10^6	20
Fumarate ion	7	1.6×10^7	21
Nitrite ion	7	8.8×10^8	22
Chloride ion	6.8	3.1×10^8	23
Bromide ion	7	3.5×10^9	19
Bicarbonate ion	7.5-8.5	9.1×10^6	24
Ammonium ion	7.0	3×10^5	25
SO_3^{2-}/HSO_3^-		$>2 \times 10^9$	5

Of considerable importance are the possible sources of SO_4^-. Two reactions to generate SO_4^- are likely: the reaction of SO_5^- with HSO_3^-/SO_3^{2-} and the self-reaction of SO_5^-. In both cases, alternate paths are possible

$$SO_5^- + HSO_3^- \rightarrow SO_4^- + HSO_4^-$$
$$\rightarrow HSO_5^- + SO_3^-$$

$$SO_5^- + SO_5^- \rightarrow SO_4^- + SO_4^- + O_2$$
$$\rightarrow S_2O_4^{2-} + O_2$$

In neither case are the branching ratios accurately known.

REACTIONS OF THE PEROXYSULFATE RADICAL

The most important reaction of the SO_3^- radical in an atmospheric droplet is likely to be its reaction with O_2, forming SO_5^-. Rate constants for several reactions of this radical are given in Table 4, and they show that SO_5^- is a somewhat stronger oxidant than SO_3^-, but far weaker than SO_4^-. Its one-electron reduction potential has been estimated to be about 1.1 V at pH 7 (14).

In the autoxidation of aqueous SO_2, the key chain-carrying reaction is usually considered to be the reaction of SO_5^- with SO_3^{2-} or HSO_3^-. Although the rate constant for the reaction with SO_3^{2-} is reasonably fast, the reaction with HSO_3^- is too slow to determine by the approach used. This suggests that the self-reaction of SO_5^- becomes the key reaction at low pH. Additionally, reactions of SO_5^- with reduced transition-metal ions are likely to become important.

The one-electron reduction of SO_5^- leads to the production of HSO_5^-, peroxymonosulfate or Caro's acid. This is a strong oxidant, with a two-electron reduction potential of 1.82V (27). If this product accumulates in a droplet, and the droplet evaporates, the resulting aerosol particles will be oxidizing.

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Peroxymonosulfate also can undergo subsequent reactions with other constituents of the droplet. It can oxidize HSO_3^- to HSO_4^- in an atom-transfer reaction, react with many organic compounds (28), or can oxidize reduced transition-metal ions, for example

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + OH^- + SO_4^-$$

This type of reaction would be particularly important in the autoxidation of aqueous SO_2, since it leads to the production of two oxidizing equivalents, thus branching the chain.

Table 4. Rate Constants for Some Reactions of $SO5^-$

Reactant	pH	$k(M^{-1}s^{-1})$	reference
Ascorbic acid	2	2×10^6	13
Ascorbate ion	6.7	7.8×10^7	13
Hydroquinone	6.6	2.7×10^6	15
	9.5	2.0×10^7	
Aniline	13	$\sim 3 \times 10^6$	6
Ethanol	9	$<10^3$	26

CONCLUSIONS

The possible effect of aqueous-phase radical chemistry on the oxidation of SO_2 in atmospheric droplets has been investigated by chemical modeling for several years now (29,30). The kinetic data base, however, has been incomplete, with many uncertainties remaining in the rates and mechanisms of key reactions (31). The data summarized here begin to fill many of these gaps. Major problems still exist, particularly in the mechanisms of important reactions. For example, the branching ratio chosen for the self-reaction of SO_5^- has a major effect on the calculated production of sulfate in a cloud droplet (4). These details become particularly important as impurities are added to the system. Whereas SO_3^- and SO_5^- would react with easily oxidized organic species such as phenolic compounds, these are unlikely to be important in normal droplet chemistry. SO_4^-, however, can react with a much larger array of species, including many likely to be present in atmospheric droplets.

To understand the effect of likely atmospheric constituents on bisulfite autoxidation, careful modeling is needed. These effects can often be quite subtle. For example, the addition of halogen ions might improve the autoxidation efficiency, if other impurities are also present. This is illustrated by the effect of halides on carboxylic acid degradation during sulfite autoxidation (32). The halide ion reacts with SO_4^-, preventing decarboxylation of the carboxylic acid, and forms the dihalide radical, which is still capable of reacting with HSO_3^-.

There are likely to be environmental effects resulting from SO_2 emissions, in addition to acid formation, which can be explained from an understanding of the chemistry of HSO_3^- autoxidation. For example, the formation of an oxidant such as HSO_5^- would magnify the effect of SO_2 on plants. The reactive intermediates formed during the autoxidation also can contribute to physiological effects. Indeed, it has been shown that benzo[a]pyrene is epoxidized during SO_2 autoxidation (33).

Computer models of the radical-induced autoxidation of SO_2 in atmospheric droplets can lead to a better understanding of the importance of the various possible pathways for acid formation. Even with the best available laboratory rate constants for the reactions chosen for the mechanism employed, the results are only going to

be as good as that mechanism. Validation is needed. There have been many laboratory studies of the metal-ion catalyzed autoxidation of SO_2, and some on the radical-induced autoxidation. The models being applied to the atmosphere should first be verified by being applied to these simpler systems.

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ATMOSPHERIC AEROSOLS AND ASSOCIATED GASEOUS COMPONENTS: MEASUREMENTS AND CHEMISTRY.

A.G. Allen, A.M.N. Kitto & R.M. Harrison
Institute of Aerosol Science, University of Essex, Colchester CO4 3SQ, United Kingdom

ABSTRACT

Measurements of airborne concentrations of aerosol SO_4^{2-}, Cl^-, NO_3^-, NH_4^+ and H^+, and of gaseous HCl, HNO_3 and NH_3 have been made at sites in eastern England. Substantial daily variations are seen in concentrations, and in the relative amounts of H_2SO_4, HCl and HNO_3 in the atmosphere. Ammonia has predominantly local sources and varies substantially between sites, whilst SO_4^{2-}, NO_3^- and NH_4^+ have a common source in long-range transport and are highly correlated in concentration. Atmospheric concentrations of HCl and HNO_3 appear to be controlled by the dissociation equilibria of their ammonium salts.

INTRODUCTION

In polluted regions, strong atmospheric acidity normally takes the form of a mixture of sulphuric, nitric and hydrochloric acids in varying proportions. Sulphuric acid, formed from sulphur dioxide oxidation, is of low vapour pressure and thus exists in the atmosphere as a fine aerosol. Reaction with ammonia leads to neutralisation in two stages by formation of ammonium bisulphate and ammonium sulphate in an essentially irreversible process

$$H_2SO_4 + NH_3 \rightarrow NH_4HSO_4 + NH_3 \rightarrow (NH_4)_2SO_4$$

Nitric acid, which is formed predominantly from NO_2 oxidation, and hydrochloric acid are both of appreciable vapour pressure and exist in the atmosphere in vapour phase form. They are also neutralised by ammonia, but in both cases the reaction is reversible.

$$HNO_3 + NH_3 \rightleftarrows NH_4NO_3$$
$$HCl + NH_3 \rightleftarrows NH_4Cl$$

These equilibria have been investigated theoretically quite extensively (1,2,3,4), but rather few atmospheric measurements have been carried out from which to evaluate the extent of conformity of concentrations with theoretical predictions. The prime influences upon gaseous concentrations of HNO_3 and HCl are expected to be air temperature, relative humidity and ammonia concentration.

Vapour phase airborne acids are dry deposited effectively since their deposition velocities are high and typically of the order of 2-6 cm s^{-1}. They are also highly soluble in rainwater, although below-cloud scavenging of gases is not very efficient and hence wet deposition, unless by rainout, is unlikely to be of great importance. Nitric and hydrochloric acids are thus expected to make their contribution to acid deposition primarily via the dry deposition pathway. Sulphuric acid, however, being an aerosol, has a very much lower dry deposition velocity, at least one order of magnitude smaller than for the acid gases. It is a highly effective cloud condensation nucleus and may also be scavenged in

the below-cloud layer. Deposition of this species is expected to be most effective in the wet mode. Deposition may be enhanced by within-cloud oxidation of SO_2 leading directly to incorporation of sulphuric acid in cloudwater.

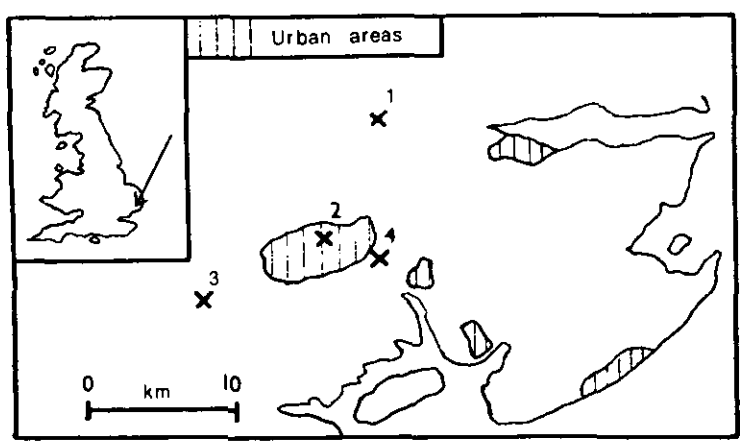
Because of the existence of these various physico-chemical forms and depositional modes of strong acid species, it is essential to define reliably the atmospheric concentration field of strong acids in order to make prediction of deposition processes.

Sampling of airborne acids is fraught with difficulty due to possible neutralisation of aerosol acidity by gaseous ammonia upon the filter surface after collection, and due to volatilisation of ammonium nitrate and chloride after collection, with subsequent inadvertent collection of the associated strong acid. In this work, both denuder and filter pack sampling methods have been utilised as judged most appropriate to artefact-free collection of low concentrations of strong acids from the atmosphere.

EXPERIMENTAL

Air samples were collected at four sites near Colchester in the eastern U.K.; these included two rural locations, one semirural and one urban (fig. 1). Aerosol NH_4^+, Cl^-, NO_3^- and SO_4^{2-}, and gaseous HCl, HNO_3 and NH_3 were collected over periods of 3 hours, 24 hours and 7 days. Deposition samples (total and wet-only) were taken on a weekly basis.

FIG. 1 LOCATION OF SAMPLING SITES



SITE	GRID REF	DESCRIPTION
1	TM 046 331	Rural, ½ km A12 road, occasional grazing
2	TM 003 254	Urban, central Colchester
3	TL 887 218	Rural, arable area
4	TM 029 239	Semi-rural, University library roof

Air samples were collected using a three-layer solid PTFE filter pack, loaded with a PTFE membrane prefilter for particulates (Whatman, 47 mm, 0.5 μm pure size), a nylon membrane for gaseous

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TABLE I

Struture of total annual SO2 emissions
(1980)

	1000 t SO2/year	%
large combustion plants	280	85.4
- power plants	99	30.2
- refineries	20	6.1
- industrial boilers	161	49.1
Other sources	48	14.6
Total SO2 emissions	328	100.0

Although the new installations (those authorized after the 1st of July 1987) must have a Flue Gas Desulphurazation system, the actual installations do not possess any SO2 control devices and the fuel used is oil and coal, with sulphur contents around 3.5 and 1.5%, respectively.

Table II, presents the SO2 emissions evolution from 1970 to 2005.

TABLE II
Estimated annual total SO2 emissions

Year	1970	1973	1977	1978	1979	1980	1983	1985	1990	1995	2005
SO2 1000 t/y	116	178	181	187	237	328	342	353	391	414/437	406/415 (1)

(1) Depending on demand scenario

These emissions have been increasing and will reach their maximum value in 1995. After that the emission levels must start to decrease, but this is so mainly because older power plants will close.

Since the previsions indicates a maximum emission value lower than 450 Kts/year, it will not be necessary to enforce rigorous programs to reduce the emissions. Nevertheless, any convenient strategy to reduce SO2 emissions in Portugal should begin by the desulphurazation of fuels.

As showed also in this table, the major air pollutants associated with man's industrial activities are sulphur and nitrogen oxides, particulates and hydrocarbons. Emitted by both stationary sources as power plants, industrial installations or residential and commercial buildings and mobile sources as vehicles, these pollutants occur chemical changes in the atmosphere and then return to the earth in rain, snow or dry deposition.

On the regional scale of the industrialized regions of Europe man-made emissions of both sulfur and nitrogen oxides are overwhelmingly dominant.

An exception may be Italy where volcanoes and geothermal activities provide an important natural source of SO_2 (2). The volcanic sources inject their sulfur compounds into atmospheric layers, where they do not directly influence the immediate vicinity of man's environment but contribute to the atmospheric burden on a much wider scale.

FORMATION OF ACIDS

In Europe and in our Country the most important primary acidifying and acid gases are:

- Sulfur dioxide (SO_2),
- Nitrogen oxide (NO) and nitrogen dioxide (NO_2),
- Hydrochloric acid (HCl).

The most important secondary pollutants formed from those primary emissions are:

- Sulfuric acid (H_2SO_4) and sulfates,
- Nitrogen dioxide (NO_2),
- Nitric acid (HNO_3) and nitrate,
- Ozone (O_3).

Sulfuric acid and nitric acid are formed to a large extent by oxidation of SO_2 and NO_x, which are the principal precursors of these acids.

The deposition of the primary pollutants and that of their products are governed by different mechanism.

For example, atmospheric oxidation is a natural process which is largely driven by photochemistry; but there are many chemical pathways through which SO_2 and NO_x can be oxidized into sulfuric acid and sulfates and into nitric acid and nitrates.

Oxidation of these gases in the atmosphere occurs by homogeneous gas phase reactions, on aerosol surfaces and in aqueous droplets.

The importance of gas - and droplet - phase reactions depends essentially on meteorological conditions as:

- intensity of solar radiation,
- presence of clouds,
- relative humidity,
- presence of other pollutants as hydrocarbons, etc.

In the northern Italy all of these processes are important for acid generation.

Figure 1 shows a simplified reaction scheme for sulfate particle

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formation due to homogeneous SO_2 - gas phase oxidation.

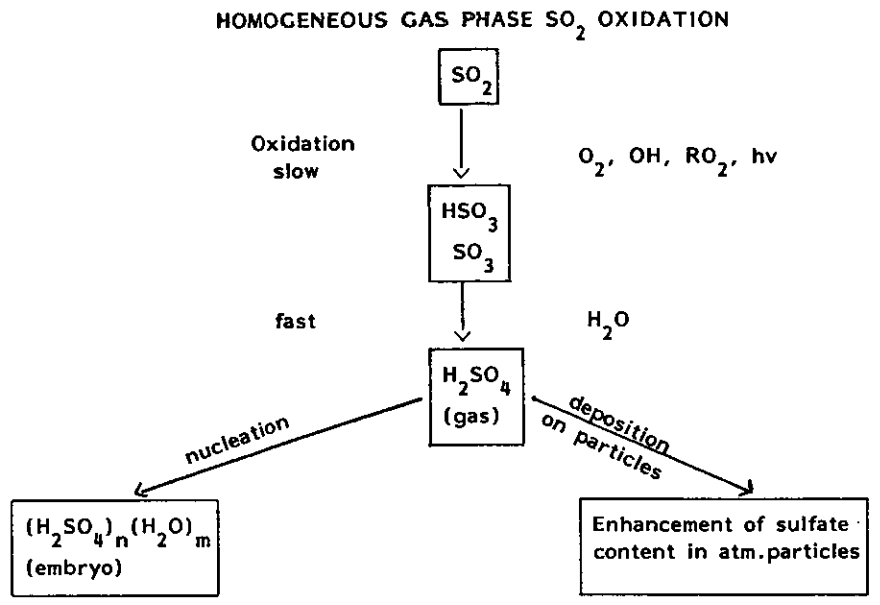

Figure 1: Simplified reaction scheme for sulfate particle formation due to homogeneous SO_2 - gas phase oxidation

Figure 2 shows a simplified reaction scheme of the most important NO_X oxidation mechanisms by homogeneous gas phase reactions.

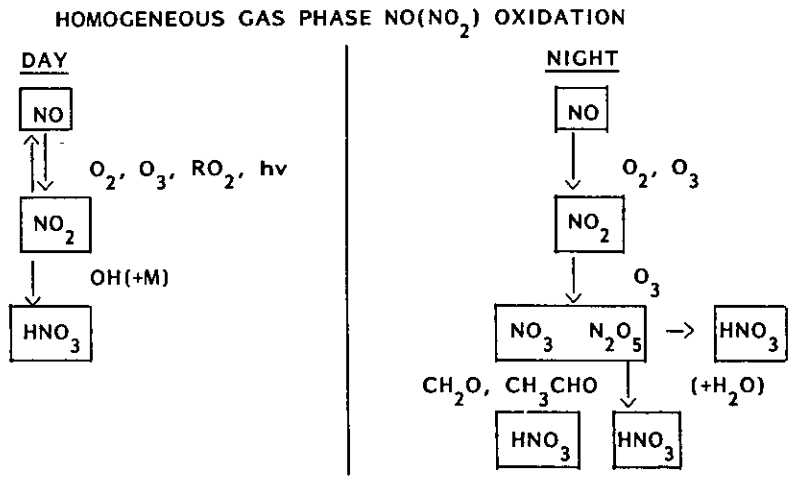

Figure 2: Simplified reaction scheme for HNO_3 generation due to homogeneous gas phase oxidation of NO_x.