Chemical Events in the Atmosphere and their Impact on Environment
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LABORATORY STUDIES OF ATMOSPHERIC RADICAL REACTIONS

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In this paper I will describe some aspects of important environmental problems from the point of view of the chemical reactions that occur in the atmosphere. An overview of the processes involved in stratospheric ozone depletion is given in the papers by Professor Rowland and Professor Anderson, in acid precipitation by Dr. Phillips, and in tropospheric photochemistry by Professor Chameides. It is not practical for me to discuss the details of all of these complicated systems, so I will concentrate on a few issues which are of current interest to me and which I believe touch on some of the key uncertainties in our understanding of the environmental problems. I will also limit my discussion to gas phase reactions, although we know that many liquid phase or heterogeneous reactions are taking place, especially in the troposphere.

THE SO_2 OXIDATION MECHANISM

The topic acid precipitation has received a great deal of public attention in the US, Canada, and Europe recently. In their papers Dr. Brosset, Dr. Knabe, and Dr. Lag discuss various aspects of this critical problem. It is very surprising that we do not know the details of the chemical mechanisms by which gaseous SO_2 is converted to H_2SO_4 in the atmosphere. There have been a number of different proposals for the homogeneous mechanism [1-3] but the only step that is well established is the initial attack of OH on SO_2.

$$OH + SO_2 + M \rightarrow HOSO_2 + M \tag{1}$$

We assume that the bisulfite radical, $HOSO_2$, is the product because the reaction has been shown to be third order. Unfortunately this species has never been detected and nothing is known about its chemistry, so the remaining steps in the mechanism are speculative. A typical scheme is as follows:

$$HOSO_2 + O_2 + M \rightarrow HOSO_4 + M \tag{2}$$

$$HOSO_4 + NO \rightarrow HOSO_3 + NO_2 \tag{3}$$

$$HOSO_3 + H\text{-}R \rightarrow H_2SO_4 + \cdot R. \tag{4}$$

Here the bisulfite radical is oxidized by O_2 to a peroxybisulfate radical which is reduced by NO to a bisulfate radical. The H-R molecule is some species such as H_2O_2 or HO_2 with a relatively weakly bound hydrogen.

In order to model the homogeneous conversion of SO_2 to H_2SO_4 it may not be necessary to know the rate coefficients for each of the steps as long as Reaction (1) is the rate limiting step. However, it is very important to know how many radicals are consumed in the overall mechanism. For example, Reaction (1) consumes one OH, so in the presence of a large concentration of SO_2, a condition that one might find in a power plant plume, the rate of SO_2 oxidation is limited by the rate of OH production. In this situation, a reduction in SO_2 concentration or emission may not be reflected in a proportionate reduction in H_2SO_4 deposition [4], because the rate of H_2SO_4 production is tied to the OH production rate not the SO_2 concentration. Thus a knowledge of the SO_2 oxidation mechanism is required to develop an effective strategy to control acid deposition. When all of the details of the mechanism are not known, it is common to use a simplified scheme such as that described by Atkinson *et al.* [5],

$$OH + SO_2 \rightarrow H_2SO_4. \tag{5}$$

This shorthand version of the mechanism assumes that one odd hydrogen radical (OH) is consumed per SO_2 oxidized. This approach allows modellers to simulate SO_2 oxidation in the troposphere.

Recently there have been two studies which cast serious doubt on the validity of Reaction (5) as a generalized reaction to describe SO_2 oxidation. First, Stockwell and Calvert [6] made a kinetic study of the mechanism of the OH-SO_2 reaction using a photochemical reactor with long-path Fourier transform infrared spectroscopy. Mixtures of CO, HONO, NO, NO_2, H_2O, and SO_2 at ppm concentrations were prepared in synthetic air or N_2 at 700 torr. OH radicals were generated by the photolysis of HONO:

$$\mathrm{HONO} + h\nu \rightarrow \mathrm{OH} + \mathrm{NO}. \tag{6}$$

The OH initiates a chain reaction, the key steps include:

$$\mathrm{OH} + \mathrm{CO} \rightarrow \mathrm{CO_2} + \mathrm{H} \tag{7}$$

$$\mathrm{H} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{HO_2} + \mathrm{M} \tag{8}$$

and

$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{OH} + \mathrm{NO_2}. \tag{9}$$

The chain is terminated by Reactions (10) and (11):

$$\mathrm{OH} + \mathrm{NO} + \mathrm{M} \rightarrow \mathrm{HONO} + \mathrm{M} \tag{10}$$

$$\mathrm{OH} + \mathrm{HONO} \rightarrow \mathrm{H_2O} + \mathrm{NO_2}. \tag{11}$$

The steady state OH concentration was inferred from the rate of CO_2 formation via Reaction (7). The effect of SO_2 on this system was tested by adding SO_2 concentrations up to 172 ppm. The surprising result was that the rate of CO oxidation was not significantly reduced. This observation implies that the oxidation of SO_2 does not terminate the HO_x chain and does not result in the net removal of OH radicals. Therefore the generalized Reaction (5) cannot be correct.

A second study by McKeen, Liu, and Kiang [7] supports the conclusion that SO_2 oxidation does not consume HO_x. They modelled the oxidation of SO_2 in the stratosphere from the 1982 eruption of the El Chichón volcano. Using one and two dimensional models, they examined the photochemical effects on the injection of several megatons of sulfur into the stratosphere and compared the results with the chemical lifetimes of sulfur obtained from observations of stratospheric SO_2 and sulfate particles. The SO_2 to sulfate conversion scheme they tested assumed that odd hydrogen radicals were consumed (as in Reaction (5)). Under this condition their model predicted that the HO_x species were significantly suppressed and that the chemical lifetime of SO_2 was greater than 100 days. This can be compared with the observations which imply a lifetime of the order of 30 to 40 days. McKeen *et al.* [7] found that it was necessary to assume that HO_x was not consumed by the SO_2 oxidation in order to match the shorter lifetime of the observations. They adopted the scheme proposed by Stockwell and Calvert [6]:

$$OH + SO_2 + M \rightarrow HOSO_2 + M \qquad (12)$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \qquad (13)$$

and

$$SO_3 + H_2O \rightarrow H_2SO_4. \qquad (14)$$

which can be reduced to the generalized mechanism

$$OH + SO_2 + H_2O \rightarrow H_2SO_4 + HO_2. \qquad (15)$$

The major difference between this mechanism and the one given in (5) is that HO_x radicals are not consumed in (15). The major weakness of this scheme is that the best available thermochemical data on sulfur species [8] indicates that Reaction (13) is endothermic by approximately 6 kcal mol^{-1}. This is an uncomfortably large figure but the uncertainty in the heat of formation of $HOSO_2$ is probably large enough that one is not convinced that (15) is incorrect.

There is an additional piece of evidence that O_2 is reactive toward the $OH + SO_2$ adduct. A discharge-flow experiment hy Leu [9] found that OH was regenerated when the $OH + SO_2$ recombination reaction was studied in an O_2 buffer gas. Although the author had no explanation for this observation, it is possible that the NO present in his experiment from the OH source reaction, $H + NO_2 \rightarrow OH + NO$, was contributing to the regeneration of OH via the sequence Reactions (1), (13), and (9). We are presently developing some experiments to test this possibility by directly searching for the products HO_2 and SO_3 in my research group.

If the Stockwell and Calvert proposal that odd hydrogen radicals are not destroyed in the SO_2 oxidation process is correct, a major revision of the models for the homogenous oxidation of SO_2 is required. This revision will certainly change the predicted effects of reducing SO_2 emission rates. The final result may be a clearer view of the strategy for reducing acid deposition rates.

THE CO + OH REACTION

The reaction of carbon monoxide with hydroxyl radicals is a very important reaction in the lower atmosphere. It oxidizes CO, a highly toxic gas

$$OH + CO \rightarrow CO_2 + \dot{H} \qquad (7)$$

to CO_2, it regulates the atmospheric $\dot{H}O_x$, and it contributes to the photochemical production of ozone in the lower atmosphere via the sequence (7), (8), (9), (16) and (17).

$$NO_2 + h\nu\,(\lambda < 380\ \mathrm{nm}) \rightarrow NO + O \qquad (16)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (17)$$

Reaction (7) is also very important in hydrocarbon combustion systems [10] where it has been shown to exhibit an unusual temperature behavior. The first observation of a pressure effect in the CO + OH reaction was reported by Overend, Paraskevopoulos, and Cvetanovič [11] ten years ago. Several different groups subsequently confirmed the observation, but the best quantitative results that have been published are those of Biermann, Zetzsch, and Stuhl [12]. Details of other studies are given in reference 12. Biermann *et al.* used flash photolysis of water vapor to generate OH and observed OH decay rates by uv resonant absorption at pressures between 25 and 750 torr of He or N_2. Their measurements were made at 300 K and showed a significant pressure effect only when O_2 was added. This observation led Biermann *et al.* to conclude that the CO + OH adduct, $HOCO^+$, has three competing paths: (1) direct dissociation to products $CO_2 + H$, (2), stabilization by M and subsequent reaction of the stabilized product with O_2 to give $CO_2 + \dot{H}O_2$ and (3) dissociation back to the reactants. They indicated some concern with their mechanism because the adduct, HOCO, hydroxycarbonyl, is very stable and therefore an O_2 reactant should not be required to observe the pressure enhancement. A satisfactory explanation of this problem has not been given. In the presence of O_2 the Biermann *et al.* result is described by the equation $k(CO + OH) = (1.4 + 1.4\,P) \times 10^{-13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ where P = the pressure of nitrogen in atmospheres. Thus the rate constant doubles between low pressure and one atmosphere pressure.

DeMore at the Jet Propulsion Laboratory has reexamined the CO + OH reaction system [13]. A sketch of his experiment is shown in Figure 1. A mixture of gases including the CO reactant, water vapor, and Ar, N_2, or SF_6 is continuously irradiated by 184.9 nm light from a mercury lamp. This photolyzes H_2O producing OH:

$$H_2O + h\nu\,(\lambda = 184.9\ \text{nm}) \rightarrow H + OH. \tag{18}$$

The steady state OH concentration that results is measured by laser induced fluorescence. The rate coefficient for Reaction (7) is determined by two methods: evaluating the steady state OH concentration and the amount

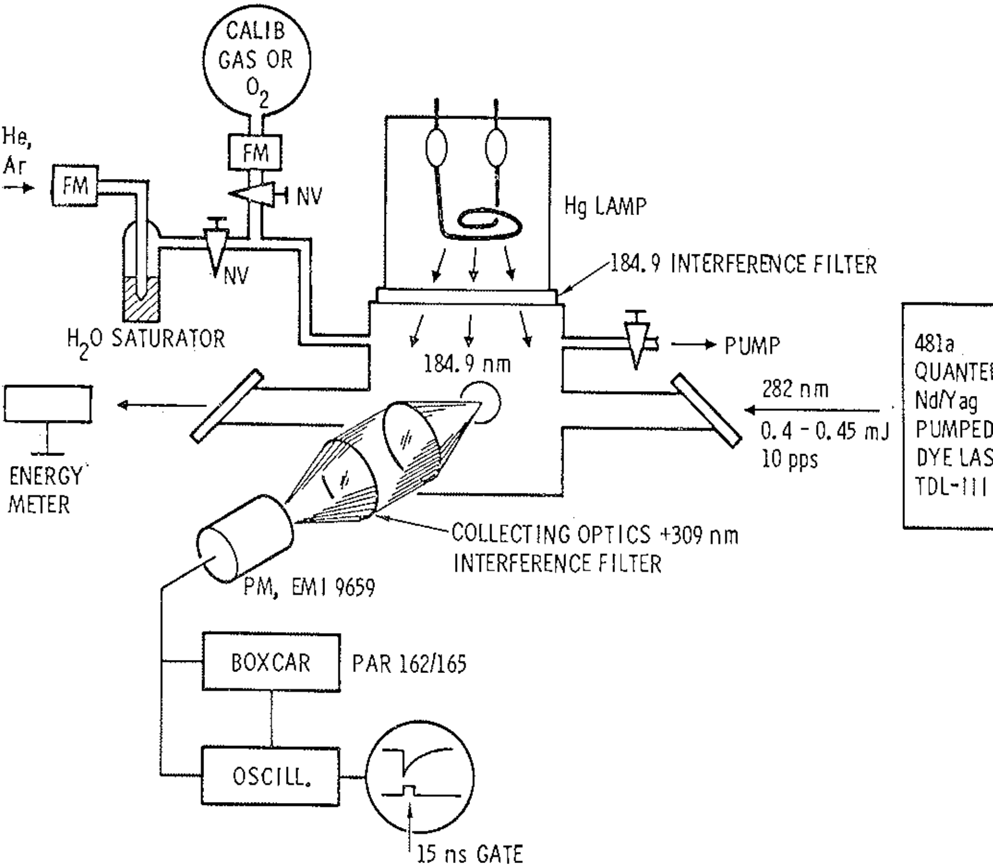

FIG. 1. Schematic of apparatus used by DeMore at Jet Propulsion Laboratory to study the reaction CO + OH. See text for details.

of CO oxidized to CO_2 or by adding a reference reactant such as H_2 or CH_4 and evaluating the ratio of the CO + OH rate to the reference gas + OH rate. Preliminary results from DeMore's study are shown in Figure 2. This gives the factor by which the rate coefficient is increased for three different gases versus the pressure of the added gas. The ratio of the efficiencies of the gases is given by the ratio of their slopes and is in the order one expects for collisional stabilization by Ar, N_2, and SF_6. The efficiency of N_2 is only about 40% of the value reported by Biermann *et al.* [12] DeMore also could not reproduce the O_2 effect reported by Biermann *et al.* DeMore found that small amounts of O_2 did not enhance the CO + OH rate coefficient even at high total pressures. He has proposed that the O_2 enhancement reported by Biermann *et al.* may result from the sequence:

$$H + O_2 + M \rightarrow HO_2 + M, \tag{19}$$

and

$$OH + HO_2 \rightarrow H_2O + O_2. \tag{20}$$

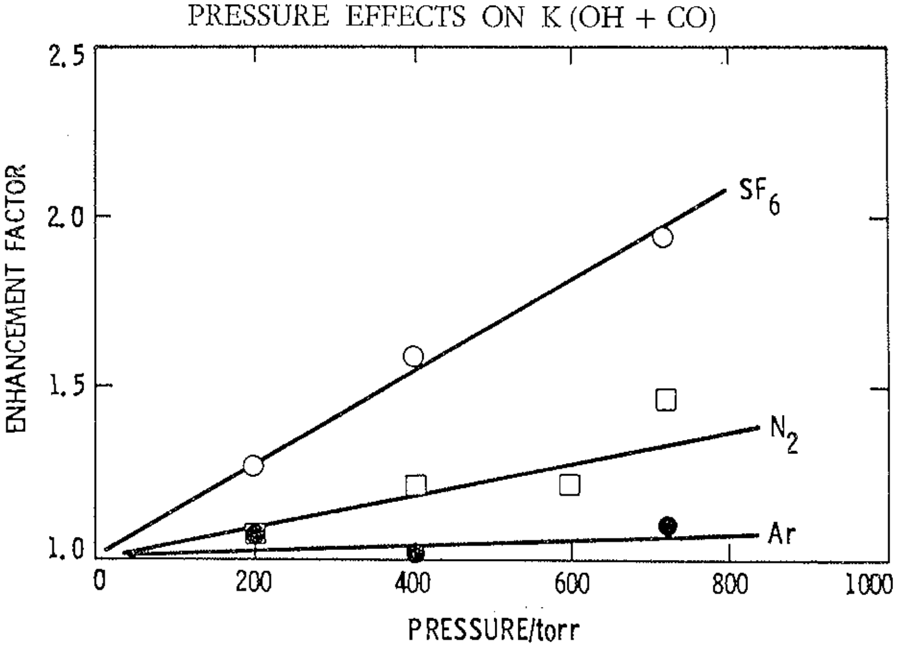

FIG. 2. Preliminary data from studies of the CO + OH reaction by DeMore. This shows the enhancement factor (the number by which the low pressure rate coefficient should be multiplied) as a function of pressure for three different collision gases.

This requires that the radical concentration in the Biermann *et al.* experiment be a factor of 3 to 10 times higher than they reported. A second problem is that Biermann *et al.* could see no enhancement with 750 torr of N_2 when no O_2 was present. According to the data of DeMore there should have been a 40% increase in the rate coefficient. I favor adopting the data from the DeMore study because bis experiment is simpler than that of Biermann *et al.* and because his data is consistent with a straightforward kinetic model. Nevertheless this critical reaction requires some additional direct measurements.

THE $HO_2 + HO_2$ REACTION

The HO_2 disproportionation reaction has a rich measurement history beginning with the classic mass spectrometric study of Foner and Hudson in 1962 [14].

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (21)$$

This reaction is important in the atmosphere as a loss mechanism for hydroperoxyl radicals which are a critical oxidant. It is also the source of atmospheric hydrogen peroxide which may be responsible for the oxidation of SO_2 to sulfuric acid in droplets and on the surface of aerosols. During the last 10 years several rather astonishing observations have been made regarding Reaction (21): (a) a water vapor enhancement [15], (b) a large negative temperature dependence [16], and (c) a significant pressure dependence [17, 18]. In the last few months a series of independent studies in different laboratories have been made on Reaction (21) and at last a clear picture has emerged of the kinetics of this important reaction The key study was made by Kircher and Sander [19] at the Jet Propulsion Laboratory. They used flash photolysis to generate HO_2 radicals and uv absorption to measure their concentration. They investigated the kinetics of Reaction (21) at temperatures between 230 and 420 K, at pressures between 100 and 700 torr, with H_2O vapor at pressures between 0 and 10 torr, and for both the hydrogen and deuterium isotopes. The Kircher and Sander study provides data for the complete range of atmospheric conditions for which Reaction (21) is important.

Tests of their results are provided by several independent measurements. Table 1 summarizes the results of four recent studies of the

TABLE 1 - *Summary of $HO_2 + HO_2$ reaction temperature dependence studies at low pressure.*

k (T)	k (298)	Temperature Range	Method	References
$(10^{-13}$ cm^3 molecule^{-1} s$^{-1})$				
(2.0 ± 0.6) exp [(595 ± 120)/T]	15	253-390	DF/LMR	This work[20]
2.25 exp [(610 ± 200)/T]	17	240-417	FP/UV	Kircher and Sander[19]
2.4 exp [(560 ± 200)/T]	16	298-358	FP/IR	Thrush and Tyndall[21]
(2.6 ± 04) exp [(581 ± 44)/T]	18	273-339	MM/UV	Cox and Burrows[22]

DF = discharge flow
FP = flash photolysis
MM = molecular modulation
LMR = laser magnetic resonance
UV = ultraviolet absorption
IR = infrared absorption

temperature dependence of k_{21} at low pressure. The pressure dependence of the reaction is small enough that it can be neglected at pressures less than about 10 torr, so in this region it may be considered purely bimolecular. The first line in Table 1 summarizes measurements made by G.A. Takacs in my laboratory [20]. He used laser magnetic resonance to detect HO_2 radicals in a discharge-flow experiment. Several different methods were used to generate HO_2, including the reactions of F and Cl atoms with H_2O_2 and the reaction of Cl with CH_3OH followed by the reaction of the CH_2OH product with O_2. The HO_2 concentration was calibrated by using Reaction (9) to convert HO_2 to NO_2 or OH which were independently detected and calibrated. The low pressure value of k_{21} given by Kircher and Sander [19] was derived from the $P = 0$ intercept of plots of k_{21} versus pressure. Thrush and Tyndall [21] used flash photolysis production of HO_2 radicals and infrared absorption with a diode laser for their detection. The 1979 study by Cox and Burrows [22] used uv absorption for detection of HO_2 in a molecular modulation experiment. The agreement of the results from these four studies is remarkable. All values of the rate coefficient at 298 K fall within the range $k_{21} = (1.5 \text{ to } 1.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Similarly the temperature coefficients, E/R, are in excellent agreement among the data sets, although the Thrush and Tyndall and Cox and Burrows studies cover relatively small temperature ranges.

From the slope of plots of k_{21} versus pressure Kircher and Sander determined the termolecular rate coefficients and their temperature dependence for M = Ar and N_2. The values of these are $k(Ar) = 8.4 \times 10^{-34} \exp(1100\ K)$ and $k(N_2) = 1.9 \times 10^{-33} \exp(980/T)$ in cm^6 molecule^{-2} s^{-1}. Thus the termolecular rate coefficient in N_2 is about 5.1×10^{-32} at 298 K. The effect of one atmosphere of N_2 is to increase the effective bimolecular rate coefficient from about 1.6×10^{-12} to about 2.9×10^{-12} cm^3 molecule^{-1} s^{-1}. If water vapor is present, a further enhancement about 70% is found with 10 torr H_2O at 298 K. The recommended expression for modelling the $HO_2 + HO_2$ reaction in air at high pressures and in the presence of water vapor is given by the expression:

$$k_{21} = (2.3 \times 10^{-13} \exp(590/T) +$$
$$+ 1.7 \times 10^{-33} \exp(1000/T)[M])(1 + 1.4 \times 10^{-21} \exp(2200/T)[H_2O])$$

This equation, largely derived from Kircher and Sander [19], brings together the results from many different studies of this critical and complex reaction.

NO_3 CHEMISTRY

Several years ago Noxon *et al.* [23] first observed NO_3 radicals in the atmosphere by means of its absorption at 662 nm of lunar light. Many subsequent measurements [24, 25] have been made and the general conclusion can be drawn that the observed atmospheric concentrations of NO_3 are not accurately reproduced by attempts to model its chemistry with the available reaction rate data. This conclusion has stimulated a great deal of interest and activity involving NO_3 chemistry.

The nitrate radical is most abundant during the nighttime because it is very rapidly photolyzed by sunlight. Its source is the slow reaction of NO_2 with ozone:

$$NO_2 + O_3 \rightarrow NO_3 + O_2. \qquad (22)$$

It is known to react with NO_2, forming N_2O_5:

$$NO_2 + NO_3 + M \rightleftarrows N_2O_5 + M. \qquad (23)$$

These reactions demonstrate the key role that NO_3 plays in atmospheric chemistry. It is a critical intermediate in the formation of N_2O_5, a potential reservoir and sink for NO_x. Since other NO_x species, NO and NO_2, have a dominant part in tropospheric and stratospheric chemistry, the possibility of a significant nighttime chemistry involving NO_3 must be investigated. Several groups including ours at NOAA are starting research on NO_3 kinetics.

Atkinson, Pitts, and coworkers at the University of California at Riverside are in the process of publishing a series of papers on NO_3 chemistry. I will briefly describe a few of their results. Their method involves the use of a smog chamber experiment with long path infrared absorption measurements of reactant concentrations [26]. Their kinetic measurements are based on the competition between two different reactants for the NO_3 radical. N_2O_5 is used as a source of NO_3. Table 2 summarizes some of their data for reactions of NO_3 with selected organic compounds. Most of these materials are present in significant concentrations only in polluted urban environments. For the alkene compounds the rate coefficients follow the general trend found for the addition reactions of O and OH. This supports the proposal that the mechanism involves addition to the double bond. A dramatic increase in reactivity is observed with the

TABLE 2. - *NO_3 radical reaction rate coefficients at 298 K* (from Atkinson *et al.* [26], UC Riverside).

Compound	k (cm^3 $molecule^{-1}$ s^{-1})
ethene	$(6.1 \pm 2.6) \times 10^{-17}$
propene	$(4.2 \pm 0.9) \times 10^{-15}$
1-butene	$(5.4 \pm 1.2) \times 10^{-15}$
isobutene	$(1.7 \pm 0.19) \times 10^{-13}$
cis-2-butene	$(1.89 \pm 0.22) \times 10^{-13}$
trans-2-butene	$(2.11 \pm 0.24) \times 10^{-13}$
2-methyl-2-butene	$(5.1 \pm 1.6) \times 10^{-12}$
2,3-dimethyl-2-butene	$(3.1 \pm 1.0) \times 10^{-11}$
benzene	$\leq 1.1 \times 10^{-17}$
toluene	$(2.0 \pm 1.1) \times 10^{-17}$
m-xylene	$(7.6 \pm 3.5) \times 10^{-17}$
napthalene	$(6.4 \pm 2.5) \times 10^{-15}$
formaldehyde	$(3.23 \pm 0.26) \times 10^{-16}$
acetaldehyde	$(1.34 \pm 0.28) \times 10^{-15}$

addition of methyl groups. The aldehydes apparently react mainly by H atom abstraction and the expected product, HNO_3, was observed. The reaction mechanism for the aromatic compounds is not known, but may involve abstraction also.

If one assumes a nitrate radical concentration of about 300 ppt [25] the lifetimes of these organic compounds range from about 1/3 year for materials with a rate coefficient of 10^{-17} cm^3 $molecule^{-1}$ s^{-1} to about 13 seconds for materials with a rate coefficient of 10^{-11}. It is possible that the faster reactions play a significant role in defining the atmospheric lifetimes of both nitrogen oxides and some organic materials. Atkinson *et al.* [26] have raised the point that the addition reaction products of some of the compounds may be highly toxic, especially the dinitrate products. An additional interesting point is that the reactions may provide a nighttime source of other reactive radicals such as OH or HO_2 or that a compound such as HNO_2, nitrous acid, may be formed. HNO_2 is a source of OH and NO radicals as soon as the sun comes out.

FUTURE STUDIES

The interest in atmospheric environmental problems has stimulated a great deal of laboratory research on chemical kinetics. New research tools, especially lasers, have aided in increasing the quantity and quality of data. A major problem that is limiting the development of this research area is that often the reactions that need to be studied are not easily identified. For example, it is not possible to assess the effect of a reaction on model calculations until one has an estimate of the rate coefficient. Also it is not possible to tell which previous studies may be in error. One must speculate on reactions to which model predictions are very sensitive or for which there are inconsistencies in the data.

There is one other topic which should be pursued. This is the study of reaction products. I believe much more emphasis should be placed on this part of laboratory kinetics. For example, the key termination reaction for nitrogen oxides is:

$$OH + NO_2 + M \rightarrow HNO_3 + M. \qquad (24)$$

where it is assumed that HNO_3 is nitric acid. It is possible that an isomer of this compound is formed, namely, peroxynitrous acid, HOONO. Two isomers are observed on the similar system of Cl addition to NO_2: ClONO and $ClNO_2$ Also it is known that HOONO is stable and that it is formed in solution. If this isomer is formed, its existence introduces a new species to the list of atmospheric trace constituents. I believe there are many similar "well known" reactions that must be investigated to confirm such details.

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DISCUSSION

Anderson

Could you briefly discuss the mechanism involved in the water vapor insertion into the $HO_2 + HO_2$ reaction?

Howard

Yes. I deliberately omitted many such gory details because I had visions of finding a comatose audience when the lights were turned back on. Recall that the $HO_2 + HO_2$ reaction has a pressure-dependent component, and so what is happening is that the water vapor molecule acts as a chaperon in the association reaction. The HO_2 radical has a very large dipole moment, about 2.1 Debye. It is even larger than the dipole moment of water. This molecule associates with a water molecule through a hydrogen bond and forms a complex.

$$HO_2 + H_2O + M \rightarrow HO_2 \cdot H_2O + M$$

A second reaction occurs between the HO_2 — water complex and HO_2:

$$HO_2 \cdot H_2O + HO_2 \rightarrow HO_2 \cdot HO_2 + H_2O.$$

Presumably this is a fast bimolecular reaction. It gives the same product, $HO_2 \cdot HO_2$, that is obtained by the thermolecular reaction in the absence of water vapor. This product must decompose to H_2O_2 and O_2 quite rapidly. Kircher and Sander discuss some of the details of this mechanism in their paper and David Golden and coworkers at SRI International have also analyzed it in terms of kinetic theories. Both have papers coming out very soon in the Journal of Physical Chemistry.

Anderson

Have you estimated the bond strength in the first step, that is, between water and HO_2?

Howard

Yes. In fact, in some of the studies of the water vapor effect there is a measurement of that from the temperature dependence of the water vapor effect. The bond energy is somewhere around 7 or 8 kcal mol^{-1}. It is a relatively strong hydrogen bond.

ANDERSON

Have you looked for the disappearance of HO_2 in the LMR experiment resulting from the attachment of water?

HOWARD

Yes. But there is a problem in that kind of experiment. What happens is that there is a pressure broadening of the HO_2 line on addition of H_2O vapor. The sensitivity of the experiment is derived from the narrowness of the rotational line. In the presence of tiny amounts of water vapor, an enormous broadening of the HO_2 line develops, making it impossible to measure the HO_2 accurately. This is an indication perhaps of a strong interaction between the HO_2 molecule and the water vapor. So in our Laser Magnetic Resonant experiment we cannot study the association reaction. The previous work on these complexes has all been done at high pressure with uv absorption detection.

CRUTZEN

The reaction $HO_2 + NO$ is of course a key question in the atmosphere. Are there similar problems there with water vapor adducts? And also the possibility that the HOONO molecule which you formed by $OH + NO_2$ may be formed there.

HOWARD

Yes. So far as I know, no one has investigated the effect of water vapor on the $HO_2 + NO$ reaction. What you are suggesting is that in the presence of water vapor $HO_2 + NO$ could lead to HOONO?

CRUTZEN

Yes, this would make the possibility greater that you end up with the HOONO molecule because the water vapor could carry off the excess energy, which otherwise would make it difficult for HOONO to form.

HOWARD

Yes. That is a possibility, and as far as I know, no one has ever looked for such a thing. That the $HO_2 + NO$ reaction would form HOONO is unlikely otherwise, because there is too much energy to be removed before you can form stable HOONO. But you are correct that it would help to associate HO_2 with water.

LIBERTI

There was a lot of discussion about the carbon monoxide in the atmosphere. You pointed out that through free radicals carbon monoxide is oxidized to carbon dioxide. Do you believe that this is the real sink for carbon monoxide, in other words, that the scheme you described is really representative for sink for carbon monoxide?

HOWARD

Yes, I do. I do not know of any other mechanism, certainly no other homogeneous mechanism that is significant.

ROWLAND

I would comment here that there is a related experiment that was carried out by Professor Ehhalt's group in Germany in which they were looking at the radioactive carbon monoxide, carbon 14, monoxide formed by cosmic ray produced carbon 14. They measured the concentration of carbon-14 monoxide in Germany and found that its concentration varied with the season and the concentration was higher in the winter and lower in the summer, as you would expect because the concentration of hydroxyl is lower in the winter and higher in the summer. And they were able to model the actual lifetime of the carbon 14 monoxide quite well with models of the hydroxyl concentration as a function of season. They then checked this by making one measurement in Florida, where the hydroxyl concentration would be even higher, and the concentration of carbon 14 monoxide was lower, as expected from that kind of modeling.

MALONE

If I read the table correctly, there was a difference of about six orders of magnitude in the rate constants for the NO_3 reactions. Is this true? It must require an extraordinary measurement technique. Is it quite credible?

Howard

Yes, that's right, that the rate constant for ethylene was in the 10^{-17} range and the one for the tetramethyl ethylene was around 10^{-11}. So there is about a six-decade factor. There are different tricks for accomplishing the measurement of rate constants over this range. First one can vary the reactant concentration, in this case the hydrocarbon concentration, by quite a large factor, by probably about a factor of 10^5 or 10^6. Also the reaction time can be varied by a factor of 10 to 100 in a chamber experiment. And finally, if they want to try to measure one very accurately — it is possible to put in another material whose rate coefficient is similar in magnitude and to look at the two reactants in competition.

Knabe

We have a steady increase in the exhaust of NO and transformation of NO_2 by the excessive automobile traffic. Is there any effect expected on the radical formation on this changing relation between NO, NO_2 and SO_2 in the atmosphere? In Europe we observed many unusual effects on the vegetation and so on. My question is: are any radicals formed maybe by that new conservation which were not there before?

Howard

Not that I know of. I think the complement of radicals that we have now is large enough to account for the chemistry that occurs.

Rowland

My impression is that he may have asked the question: Have you changed the concentrations of old radicals in such a way that it would have biological effects?

Howard

Oh, yes. In fact one of the things from the study that I described on nitrate radicals was that they observed some molecules that are toxic compounds. For example, some nitrate compounds which involve the addition of two nitrate radicals to an organic substrate. Apparently those are very toxic, so I would say the likelihood of forming such molecules would be increased as you increase the concentration of nitrogen oxides, because you have to have attached to one organic substrate.

ROWLAND

The comment I would add to that — and it is especially downwind from places where you have sources of nitrogen oxide, that you would expect these effects.

CRUTZEN

This was something which was considered in the Academy report in the United States, an older paper which I was involved in, whether the nitrogen oxides actually would gobble up so much hydroxyl radicals that the oxidation of SO_2 would be effected. There are some slight indications in Europe that may have occurred in the forest, but it does not seem to be right for the United States, so different regions may have different problems here.

CHAMEIDES

I have a question concerning the SO_2 reaction which perhaps is somewhat speculative. The new mechanism for SO_2 homogeneous oxidation, presumably converts an OH radical to an HO_2 radical. Could that combined with the recent observation by Becker and his group that the $SO_2 + OH$ reaction is dependent on oxygen concentrations and which imply that that reaction is practically five times faster in the lower troposphere than had been thought previously? And I wonder if perhaps this $SO_2 + OH$ reaction, if this fast rate constant is correct and the mechanism is correct, could actually be a significant way of converting OH to HO_2 and producing ozone and oxygen. Would you care to comment on that?

HOWARD

Sure. First, I am not familiar with the work of Becker. The little bit I have heard seems to be in general consistent with the observations of Calvert and Stockwell. That SO_2 could be the source of an oxidant by such a mechanism is an interesting idea. It is something that could be very directly tested in a small chamber experiment or by modelling. It will depend upon the concentration of SO_2 relative to other oxidant forming species such as CO or hydrocarbons. But it is something that in my opinion could be directly tested.

LIBERTI

Because of the importance of OH and the large amount of work you have done in this field, which analytical procedure do you suggest for atmospheric OH determination?

HOWARD

I think there is probably not a single method that one would want to trust in such an important measurement. Probably something like what Anderson, Davis, and Wang are trying to do with lasers to measure it in a direct way in one location, plus some kind of less direct measurements of the type that Ehhalt and Campbell use, looking at the oxidation of some species. I think we are going to have to have several methods to do it. It is such a difficult problem, and there is so much variability in the conditions under which you would like to measure it from the stratosphere down to the surface that one is really going to have to use several different methods.

ARNOLD

I should greatly like to comment on the homogeneous SO_2 oxidation. You have pointed out that the problem is the fate of the HSO_3 intermediate radical, and you have mentioned the recent suggestions including the O_2 reaction. I assume that the kinetics is now known for this reaction. From our stratospheric and recent tropospheric observations of the HSO_3 and H_2SO_4 gases we can estimate the lifetime of HSO_3 in the atmosphere, and it turns out to be much shorter than to be expected for instance for the hydroxyl radical reaction as a sink alone. It also turns out that the lifetime is such that we cannot exclude that heterogeneous removal may have a role. It is just of the order which you may expect for heterogeneous removal, assuming an efficient high sticking probability. And if you assume that the O_2 reaction is the main sink, you may get an estimate on the effective rate coefficient for this process from such observations. And finally I should like to add that the fact that HSO_3 clusters very efficiently to ionic clusters being composed of sulphuric acid and water, the same composition as is expected for the aerosols, implies that we should not forget about the possibility that HSO_3 radicals may also undergo heterogeneous removal in the atmosphere.

HOWARD

I could comment on that. You may recall from yesterday that Professor

Arnold has observed chemical species in the stratosphere associated with negative ions, that he interpreted these as being $HOSO_2$ — and if that were correct, then I think that the Stockwell and Calvert mechanism is not correct. I do not think there should be any $HOSO_2$ in the atmosphere, if their mechanism occurs, according to the scheme that they have developed. If Arnold's identification is correct, then I think that the Stockwell and Calvert scheme is not significant. Maybe the observed ion cluster species is SO_3 not $HOSO_2$.

ROWLAND

But what about at much lower pressures?

HOWARD

But you still have O_2 present. One fifth of the air is O_2 where Arnold makes his measurements. The $HOSO_2$ should still convert to HO_2 and SO_3.

CRUTZEN

It was not clear to me at what pressures were these Stockwell and Calvert measurements made.

HOWARD

At one atmosphere. I think the reason they do most of their work at one atmosphere is because their chamber probably leaks...