Some recent measurements of H_2S oxidation rates and their implications to atmospheric chemistry[1]

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ABSTRACT

The general belief that significant fractions of atmospheric sulfur are donated naturally from the earth's surface in the form of hydrogen sulfide and/or its organic homologs implies that atmospheric breakdown of these materials must be a rather fast process. It has been expected that oxidation of these materials by atmospheric ozone should contribute significantly in accomplishing this breakdown; and experimental measurements have been published which do, indeed, indicate rapid ozone oxidation rates, corresponding to lifetimes of the order of hours under typical tropospheric conditions. This paper discusses some later experimental measurements on H_2S ozone reaction rates which disagree with former determinations, predicting typical H_2S lifetimes of the order of months—much too long for this reaction to be a significant mechanism of atmospheric removal. The results also indicate the H_2S ozone reaction should be expected to proceed homogeneously in the atmosphere, with catalytic effects being of little or no importance. The reaction proceeds thermally; light in the visible region does not affect its rate appreciably. These measurements indicate that some mechanism(s) other than ozonation must be responsible for atmospheric breakdown of reduced sulfur compounds. Final portions of the paper examine some possibilities for these mechanisms.

It is generally believed that the majority of sulfur contributed to the atmosphere by natural sources is emitted as H_2S or its organic homologs, RSH and RSR′. As noted by Junge (1963), Conway (1943) has performed a global material balance for sulfur which, assuming a steady state exists, implies that sulfur entering oceans via the rivers must be accounted for in large part by re-emission to the atmosphere, ostensibly in the form of H_2S. Subsequent material-balance estimates (Erikkson, 1959; Robinson & Robbins, 1968; Wilson et al., 1960, 1971; Junge, 1963; Kellogg et al., 1972) have generally adhered to this idea, although they reflect a growing expectation that organic sulfides and mercaptans may play a prominent role in the exchange process. Lovelock et al. (1972) recently have published some interesting evidence in this regard, suggesting that dimethyl sulfide ($(CH_3)_2S$) may be an important factor in the natural transport of sulfur to the atmosphere.

Experimental measurements of H_2S levels in the atmosphere have been limited in quantity. In addition, it has been shown recently that most existing results are highly questionable, owing to the possibility of errors in chemical analysis (Kellogg et al., 1972). Regardless of these difficulties, the data that do exist indicate that removal of H_2S and its organic homologs from the troposphere must be a fairly rapid process to account for observed atmospheric concentration levels in context of expected source magnitudes. It has been ac-

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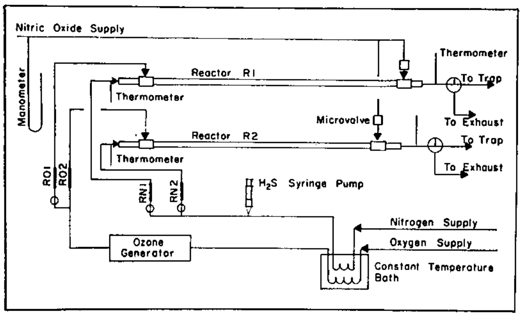

Fig. 1. Experimental reactor system.

cepted generally that the most likely mechanism for removal of these compounds from the troposphere is an initial oxidation process followed by dry deposition or precipitation scavenging. Cadle (1960) and Cadle & Ledford (1966) postulated that ozonation should be a significant reaction in the oxidation process, and performed measurements of the rate of the reaction

$$H_2S + O_3 \rightarrow SO_2 + H_2O \tag{1}$$

which supported this concept. The resulting rate expression, which may be written as

$$\frac{dc_{H_2S}}{dt} = 2.5 \times 10^8 \exp(-8\,300/RT)\, c_{O_3}^{1.5} \text{ moles/ml sec} \tag{2}$$

indicates a rapid oxidation, giving mean H_2S lifetimes of the order of hours under normal tropospheric conditions. These results, however, were thought to be complicated by competing heterogeneous reactions occurring on the reaction-vessel walls. In addition, they were in apparent qualitative disagreement with earlier stoichiometric measurements (Gregor & Martin, 1961). In view of the apparent complication of the wall effect, expression (2) has been suggested as an "upper limit" for the rate of this reaction in the atmosphere.

Subsequent authors have applied these results extensively in analyses of atmospheric behavior. Robinson & Robbins (1969), for example, have utilized them in an attempt to separate the homogeneous and heterogeneous contributions for application to an analysis of H_2S oxidation in aerosol-laden atmospheres. We have performed measurements of the rate of reaction (1) (Hales et al., 1968, 1969), in an attempt to overcome the apparent surface-reaction difficulties experienced by the previous workers. Shown schematically in Fig. 1 the system employed two reactors of different radius, so that the bulk and wall effects could be separated on the basis of variation of surface to volume ratios.

Details of this experiment are given in the previous reports. Essentially, it consisted of introducing ozonized oxygen and H_2S-containing nitrogen into the reactors through the rotameters RO1, RO2, RN1 and RN2 as shown in the figure. Upon passing through the reactors, the laminar-flow streams were emitted through freeze-out traps for quenching of the reaction and collection of the reaction products. Preliminary attempts to quench the reaction by introduction of nitric oxide at the reactor exits were discontinued upon experiencing serious side-reaction difficulties with this technique.

Experiments were initiated by operating the reactors at constant flow rates and reactant concentration levels until a steady state was attained. The exit stopcocks were then switched to divert the flows from the exhaust lines to the freeze-out traps. Upon sampling for a timed period, the traps were removed from the reactors, and the reaction products analyzed using a gas-chromatograph. Ozone concentrations in the inlet oxygen were measured using a KI oxidation technique; H_2S concentrations were determined directly by measured flow rates through the syringe-pump source.

Numerical solutions to the rigorous continuity equations, describing laminar flow, diffusion, and surface and wall reactions in a cylindrical reactor were obtained initially for data analysis (Hales, 1968). Subsequent experimental measurements, however, indicated that reaction rates were about two orders of magnitude lower than those expected from Cadle's and Ledford's results. Under such conditions, the rigorous equations of continuity describing the reactor system approach simplified limiting forms asymptotically, and a much simpler method of analysis is possible. In fact, the low rate of reaction permitted analysis by assuming negligible depletion of reactants in the reactor, allowing rate parameters to be evaluated simply by plotting conversion rates versus concentration on logarithmic paper. Such plots are shown in Figs. 2 and 3, which indicate the rates and corresponding condi-

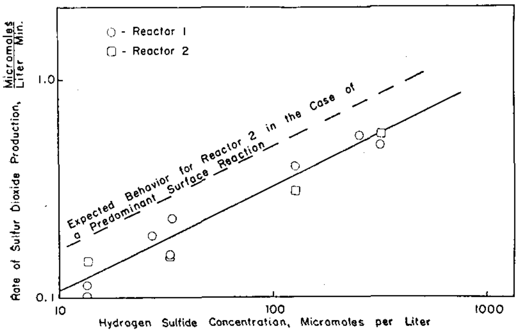

Fig. 2. Rate of generation of sulfur dioxide by reaction between hydrogen sulfide and ozone at 28.5°C. $c_{O_3} = 17.6$ micromoles per liter.

tions for the measurements. Least-squares fits of these data were utilized to obtain the following rate equation:

$$\frac{dc_{H_2S}}{dt} = -3.8 \pm .5 \times 10^8 \exp\left(\frac{-6\,500}{RT}\right) \times c_{H_2S}^{0.5}\, c_{O_3}^{1.5} \text{ moles/ml sec} \qquad (3)$$

where the error limit on the rate constant indicates the overall standard deviation of data points about the fitted expression at 28.5°C. As indicated by Figs. 2 and 3, the concentration ranges of study were 6.9×10^{-6}–28.9×10^{-6} molar, and 13.4×10^{-6}–325×10^{-6} molar for ozone and H_2S, respectively.

Fig. 2 is of particular interest. It indicates that reaction rates measured by Reactor 1 and Reactor 2 fall upon the same curve with respective standard deviations of 13.5% and 12.5%. The surface-to-volume ratios of these two reactors differed by 50%, and, on the basis of geometric effects, a noticeable deviation of the results of Reactors 1 and 2 would be expected if a significant heterogeneous reaction were present. Indeed, if the reaction were totally heterogeneous, the "rates" predicted by Reactor 2 should fall on the dotted line, 50% higher than the line representing results obtained from Reactor 1. Because of the behavior of these results we have concluded that the observed data represent the true homogeneous reaction within limits of experimental error.

Eq. (3) predicts normal tropospheric conversion rates of H_2S that are approximately three orders of magnitude lower than those predicted from Cadle & Ledford's eq. (2). This corresponds to H_2S lifetimes of the order of months, rather than hours as expected previously. We have performed tests which indicate that side reactions may have been a factor in determining the outcome of the previous work; however, this conjecture is purely speculative at the present time.

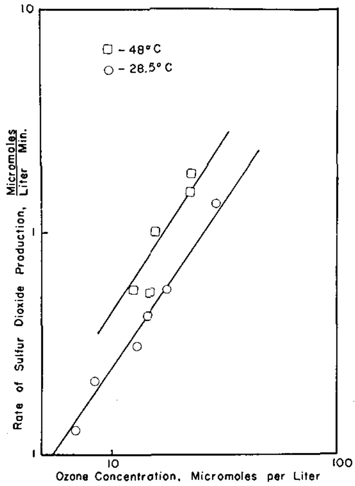

Fig. 3. Rate of generation of sulfur dioxide by reaction between hydrogen sulfide and ozone. $c_{H_2S} = 256$ micromoles per liter.

The fractional reaction orders in empirical rate expression (3) indicate that the chemical conversion occurs by a rather complex mechanism involving free radical chain reactions. Supporting evidence in this regard is provided by results of studies (cf. Liuti et al., 1966) which indicate that H_2S is attacked readily by atomic oxygen. Thermal ozone-decay is known to produce ground-state oxygen atoms as follows:

$$O_3 \rightarrow O_2 + O(^3P) \qquad (4)$$

and from the previous mechanistic studies it appears probable that these atoms in turn attack H_2S to initiate chain reactions involving $HO_2^{\cdot}$, $HS^{\cdot}$, $HO^{\cdot}$, $H^{\cdot}$, and $SO^{\cdot}$, ultimately terminating with the major reaction products SO_2 and H_2O.

The complexity imposed by the possible occurrence of competing chain reactions precludes any comprehensive examination of mechanistic behavior on the basis of the present data. It also serves to illustrate the questionable nature of extrapolating these results, using the empirical expression (3), for prediction of behavior at tropospheric concentrations; further data obtained at lower concentrations would be of high interest in this regard.

Two qualitative observations of the experiments are also of interest; the first of these concerns the influence of light upon the system. Although all results reported in Figs. 2 and 3 were obtained from a darkened system, several preliminary experiments were performed with the reactors subjected to normal laboratory illumination. No differences in rate behavior were observed during these experiments, indicating that photochemical processes are unimportant, at least for wavelengths in the visible region.

The second observation concerns the prospect of catalysis of reaction (1) by solid surfaces. For normal experimental runs the reactors were cleaned scrupulously in an attempt to avoid surface catalysis. Later experiments, however, were conducted with intentionally contaminated surfaces (laboratory dust, potassium chloride, sulfur). Although these tests did indicate the presence of a direct reaction between ozone and sulfur, there was no evidence of any significant catalysis of reaction (1).

The results of these experiments indicate that the present understanding of atmospheric sulfur chemistry and of the global sulfur balance is not so complete as had been thought previously. While deviating strongly from previously anticipated behavior and from the findings of Cadle and Ledford, these results seem to be supported qualitatively by the previous stoichiometric study of Gregor & Martin (1961) which indicated that the destruction of H_2S via ozonation is slow compared to the thermal decay of ozone itself. In addition the more recent measurements of Cox Penkett (1971) have provided further evidence that ozone oxidation of H_2S is indeed too slow a process to be of large significance to the global sulfur balance.[1]

These findings imply that either H_2S (and its organic homologs) do not enter into the atmospheric sulfur balance to the extent presently expected, or that some mechanism(s) other than ozone oxidation are responsible for the rapid removal rates. Several alternative mechanisms are possible. The previously mentioned paper by Lovelock et al. (1972), for example, suggests that dimethyl sulfide is the prime agent, and the primary breakdown mechanism of this agent may be a direct photolysis reaction. We suggest that photochemical oxidation by nitrogen oxides may play an additional important factor in this respect, i.e.,

$$NO_x + RR'S \xrightarrow{h\nu} \text{products} \tag{5}$$

Previous researchers in addition to ourselves have observed that nitrogen oxides effect the breakdown of H_2S much more rapidly than does ozone, often forming free sulfur as a reaction product. Other qualitative experiments performed in our laboratories using methyl mercaptan and dimethyl sulfide have also indicated comparatively rapid reaction rates.

Reaction of this class apparently do not occur by direct reaction of NO_x with the reduced sulfur compounds; it is likely, rather, that intermediates of NO_x photolysis are the responsible agents. Since NO does not undergo photolytic decomposition at wavelengths normally encountered in the troposphere, its activity as a decomposition agent is probably related to its reaction with oxygen to form NO_2. NO_2, however, absorbs in the visible and near ultraviolet ranges to produce ground-state atomic oxygen:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{6}$$

Moreover, it is expected that singlet molecular oxygen is formed by several reactions involving $O(^3P)$ and excited states of NO_x. Such behavior gives rise to the possibility of a host of chain reactions involving all of the free radical intermediates mentioned previously in the context of ozone-induced reactions, ostensibly leading to the overall behavior indicated by eq. (5).

A literature survey has shown the limited information concerning reactions of nitrogen oxides with gaseous, reduced sulfur compounds to be relatively uncertain and conflicting. Strangely, the bulk of this literature is confined to a rather early period; later reports have consisted largely of casual references to these reactions when encountered during the course of otherwise unrelated investigations. The very early experiments of Thompson (1820) indicated that dry nitric oxide and hydrogen sulfide

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[1] The author is indebted to Dr S. A. Penkett for his helpful comments on this subject.

react vigorously. In 1847 Leconte (cf. Mellor, 1957) found that nitrogen dioxide, also, reacts with hydrogen sulfide to form sulfur, nitric oxide, and water. Cooke (1887) observed that concentrated mixtures of nitric oxide and hydrogen sulfide will explode when sparked.

Additional experiments at lower concentrations were conducted by Pierce (1929), who observed nitric oxide to react with hydrogen sulfide in glass vessels to form free sulfur, nitrogen, and water. This reaction was catalyzed partially by the reactor walls and exhibited a negative activation energy. Tominaga (1931) also reported that the reaction was partially catalyzed by glass. This author, however, indicated that water was required to promote the reaction. In contrast to the findings of Pierce, Tominaga reported an increase in reaction rate with temperature.

Early experiments of the interactions between hydrogen sulfide and nitrogen oxides in water solution also show conflicting results. Kemper's work (as reported by Mellor (1957)) indicates that no reaction occurs between purified nitric acid and hydrogen sulfide, unless a trace of nitrogen dioxide is present; under these conditions the hydrogen sulfide decomposes completely to form sulfur, sulfuric acid, ammonium sulfate, and nitric oxide. Dunnicliff & Mohammed (1929), on the other hand, found no reaction—even in the presence of nitrogen oxides. Dunnicliff et al. (1931) investigated the reaction between nitric oxides and hydrogen sulfide-containing water. The products of this reaction were found to be ammonium thiosulfate, ammonium nitrite, sulfur, nitrous oxide, and nitrogen. Bagster (1928) studied this same reaction and reported finding a variety of products, including nitrous oxide, hydroxylamine, free sulfur and sulfate.

Reports concerning this class of reactions appearing in the more recent literature are sparse, and rather qualitative in nature. Cadle & Ledford (1966) observed a sulfur-producing reaction to occur between mixed nitrogen oxides (NO and NO_2) and hydrogen sulfide in the presence of light; this reaction could be controlled by maintaining the light source below a minimum frequency. We have observed this reaction also, and have found traces of sulfur dioxide as an additional reaction product. In a totally-darkened reactor this reaction was attenuated, but could not be stopped completely. The sulfur-producing reaction was observed to proceed rapidly when light was present, going essentially to completion within the three-second residence time of the reactor. In a recent study Blackwood (1970) utilized a flow reactor to reproduce these qualitative results for dilute mixtures of NO_2 and H_2S. Further investigation with a stirred-vessel system, however, indicated that the reaction was slower than anticipated. There were indications also that the system was insensitive to visible light and almost totally homogeneous in nature. This highly paradoxical behavior is without explanation at the present time.

There is some fragmentary circumstantial evidence supporting the concept that reaction(s) (4) may indeed be important to the global sulfur balance. The recent finding that substantial quantities of submicron aerosol particles (down to and below 0.01 μ) in the mid-troposphere (cf. Junge, 1972), certainly indicates that trace-gas reactions may be important in aerosol generation here. Although this implies nothing with specific regard to NO_x–H_2S (or related) reactions, it does indeed indicate that they could occur. More direct evidence in this regard is given in the discussion of tropospheric H_2S behavior by Junge (1963). Although his general analysis was limited by the quality of H_2S measurements that existed at the time, his observation of constant H_2S levels along the countryside which dropped markedly as urban areas were approached is probably a valid one. Such behavior fits in well with reaction (4), which suggests that atmospheric H_2S levels should be reduced whenever concentrations of NO_x are increased. Additional evidence in support of reactions (4) is given by the noted occurrence of elemental sulfur in air-filter samples and by the qualitative observation that NO has an odor-reducing effect on trace levels of H_2S and mercaptans in ambient atmospheres (cf. Haagen-Smit, 1967).

From this analysis we conclude that agood possibility exists that reaction(s) (4) play an important, perhaps dominant, role in the tropospheric removal of H_2S and its organic homologs. Additional experiments involving the measurement of the associated reaction rates under appropriate conditions of concentration and illumination would be of high interest in this regard.

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НЕКОТОРЫЕ НЕДАВНИЕ ИЗМЕРЕНИЯ СКОРОСТЕЙ ОКИСЛЕНИЯ H_2S И ИХ СЛЕДСТВИЯ ДЛЯ АТМОСФЕРНОЙ ХИМИИ

Общее мнение, что значительные фракции серы в атмосфере поступают естественным путем с поверхности земли в форме сероводорода и/или его органических гомологов, подразумевает что разрушение этих веществ в атмосфере должно быть довольно быстрым процессом. Ожидалось, что окисление этих веществ атмосферным озоном должно давать существенный вклад в это разрушение, и опубликованные до сих пор экспериментальные данные на самом деле указывают на быстрые скорости окисления озоном, соответствующие временам жизни порядка часов в типичных тропосферных условиях. В данной статье обсуждаются некоторые дальнейшие измерения реакции H_2S с озоном, которые не согласуются с предыдущими, предсказывая типичные времена жизни H_2S порядка месяцев, что слишком долго, чтобы эта реакция была существенным механизмом их удаления из атмосферы. Эти результаты также указывают, что реакция H_2S с озоном должна протекать однородно в атмосфере, причем каталические эффекты играют малую или никакую роль. Реакция протекает термически, а свет в видимом интервале не влияет заметно на ее скорость. Эти измерения указывают, что некоторый механизм (или механизмы) иной, чем озонизация, должен быть ответственным за разрушение компонент, содержащих серу. В конце статьи обсуждаются некоторые возможные механизмы.