

THE RATE OF REACTION BETWEEN DILUTE HYDROGEN SULFIDE AND OZONE IN AIR

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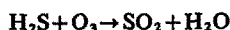
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Abstract—The rate of reaction between dilute hydrogen sulfide and ozone in air was measured. Experimental data were obtained from two tubular, laminar-flow reactors having internal dia. of 3/8 in. and 1/4 in. On the basis of these data the following expression was obtained for the rate of generation of sulfur dioxide by the reaction of hydrogen sulfide with ozone in the absence of light.

$$\frac{dc_{\text{SO}_2}}{dt} = 22.8 \exp(-6500/RT) c_{\text{H}_2\text{S}}^{0.5} c_{\text{O}_3}^{0.5} \frac{\mu\text{moles}}{\text{liter min}}$$

Comparison of data from the two reactors indicated that the reaction was almost totally homogeneous. From the results of previous authors the expression



is thought to represent the true stoichiometry adequately under the experimental conditions of the present study.

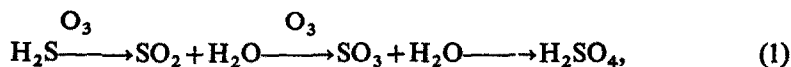
1. INTRODUCTION

GAS-PHASE oxidation by ozone is believed to be an important factor in the removal of atmospheric hydrogen sulfide. In addition, this reaction is thought to be significant in several of the industrial and municipal odor-control processes involving hydrogen sulfide and organic sulfur compounds. In spite of this importance, however, little is known about the mechanism of the reaction, and until recently even its stoichiometry was open to question. Compounding these problems on a practical basis is the ability of ozone to mask odors by olfactory desensitization, thereby leaving the exact nature of many odor-control processes in serious doubt.

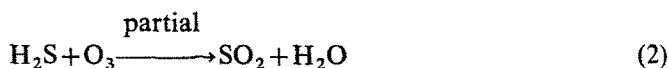
2. PREVIOUS WORK

Early investigations of the reaction between hydrogen sulfide and ozone (HELBIG, 1881; BRESCIANI, 1915) were conducted under poorly-controlled conditions, and produced conflicting results. More recently, more reliable experiments have been performed (GREGOR and MARTIN, 1961; CADLE and LEDFORD, 1966). An analysis of these later experiments (HALES, 1968) appears to indicate that hydrogen sulfide reacts with ozone to form sulfur dioxide, which is consecutively oxidized slowly to form sulfur trioxide.

This reaction, which may be expressed by the form,



goes to completion only when there are excessive quantities of ozone present. For initial ozone concentrations equal to or below those of hydrogen sulfide, the simpler form



appears to describe the reaction stoichiometry satisfactorily.

Cadle and Ledford also attempted to measure rates of the reaction between dilute hydrogen sulfide and ozone in air, using a laminar-flow, tubular, Pyrex reactor. Hydrogen sulfide and ozone were mixed in an air stream at the reactor entrance, and passed through the reactor tube. The reaction was terminated at any of several points along the reactor by injecting nitric oxide, which annihilated the remaining ozone by the extremely fast reaction



Extent of the reaction between hydrogen sulfide and ozone was measured by photometric determination of the nitrogen dioxide. This, assuming the absence of any side reactions involving nitrogen oxides, gave a measure of the ozone remaining at the quench point of the reactor.

In estimating reaction-rate parameters from their data, Cadle and Ledford assumed that the reaction taking place was totally homogeneous. As a result the following expression was obtained for the rate of reaction between hydrogen sulfide and ozone in air:

$$\frac{dc_{\text{O}_3}}{dt} = -4.7 \times 10^5 \exp(-8300/RT) c_{\text{O}_3}^{1.5} \frac{\mu\text{moles}}{\text{liter min}}. \quad (4)$$

Suspecting that a wall reaction may have influenced their results, Cadle and Ledford performed additional experiments with the reactor packed with several lengths of Pyrex tubing. They also tested a reactor that had been coated with potassium chloride. Conversions within each of these systems were about double those observed in the original apparatus, indicating the presence of a fairly rapid surface reaction.

In view of the complicating wall effects, Cadle and Ledford concluded that the reaction in their system was at least partially heterogeneous, and suggested that (4) be used as an estimate of the upper limit of the rate of this reaction in the atmosphere.

3. EXPERIMENTAL DETAILS

The experimental system of the present investigation (HALES, 1968) was designed to resolve some of the difficulties encountered by the previous authors, and to provide a reliable measure of the rate of homogeneous reaction between hydrogen sulfide and ozone. Dimensions of the original system were specified on the basis of conversions expected from Cadle and Ledford's results. It was found, however, that actual conversions were about two orders of magnitude lower than those predicted by (4), making it necessary to rescale the experiment.

Details of the final experimental system are shown in FIG. 1 and TABLE 1. Oxygen from a regulated cylinder passed through an OREC O3V1 ozone generator and into the Teflon injection collars (FIG. 2) of two reactors. Nitrogen, also from a regulated cylinder was mixed with hydrogen sulfide issuing from a Hamilton gas-tight syringe

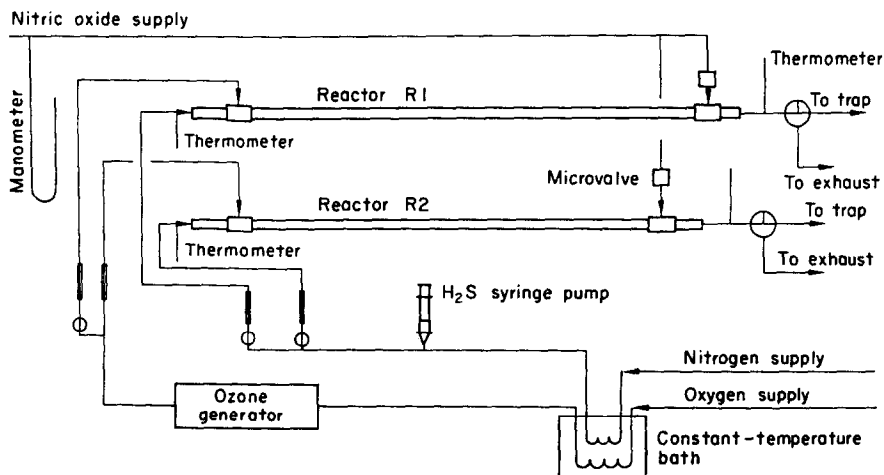


FIG. 1. Experimental reaction system.

driven by a Sage syringe drive. This mixture proceeded to the entrances of the two reactors, where it was mixed with the ozone-oxygen mixtures in the injection collars.

Diameters of the two reactors differed by a factor of 1.5. This made it possible to estimate the relative contributions of homogeneous and heterogeneous reactions by virtue of the associated variation in surface-to-volume ratios. Interior volumes of the reactors were almost totally darkened by wrapping all outside surfaces with black plastic tape and applying insulation.

Reactor effluent streams could be diverted to the exhaust system or switched to the sampling lines by means of threeway stopcocks at the exits. Sampling was accomplished by means of freeze-out traps. As shown in FIG. 3, each trap consisted of an initial section of spiral glass tubing surrounding a larger, secondary section. These

TABLE 1. CHARACTERISTICS OF EXPERIMENTAL SYSTEM

Reactor lengths:	
Reactor 1	168.9
Reactor 2	141.4
Reactor diameters:	
Reactor 1	$3/8 \pm 0.0001$ in.
Reactor 2	$1/4 \pm 0.0001$ in.
Gas flow rates:*	
Nitrogen	80 ml min^{-1}
Oxygen	20 ml min^{-1}
Reagents:	
Hydrogen sulfide	Matheson C. P.
Nitric oxide	Matheson C. P.
Nitrogen	Matheson prepurified
Oxygen	Matheson extra dry

* Measured at ambient conditions of temperature and pressure.

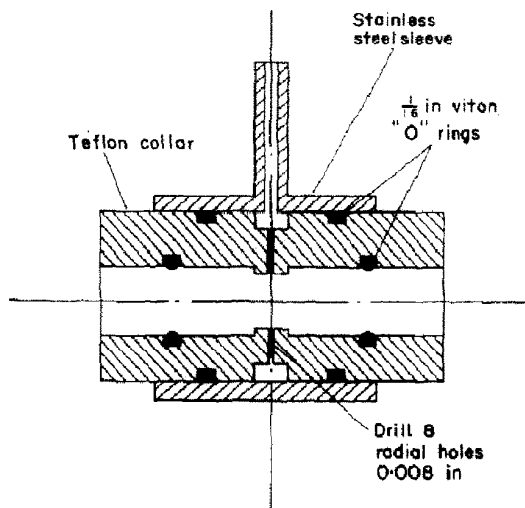


FIG. 2. Schematic of gas injector.

traps were placed in Dewar flasks, and were refrigerated with a solid-liquid slush of isopentane (-160.5°C). Preliminary tests verified the effectiveness of the traps for quantitative sampling of sulfur dioxide.

Conversions were consistently below 10 percent throughout the study. This precluded the use of reactant exit concentrations as a reliable measure of reaction progress. Furthermore, the possibility of contamination from the atmosphere prevented accurate measurement of water formed by the reaction. Consequently, the

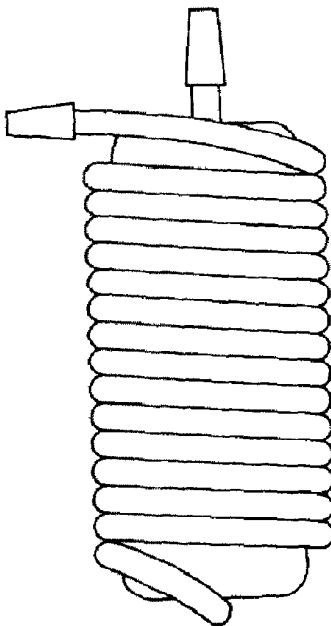


FIG. 3. Schematic of freeze-out trap.

reaction-product sulfur dioxide was the only compound leaving the reactors to be measured.

Measurement of sulfur dioxide was accomplished with a modified Fisher-Gulf 160 chromatograph, using a 12-ft TCP column. Upon collecting a freeze-out sample, the trap was evacuated, and the residual ozone was selectively evaporated off. The remaining contents of the trap (SO_2 , H_2O , and some H_2S) were vacuum-distilled into the chromatograph sampling loop, the sulfur dioxide being measured upon subsequent injection to the chromatograph column.

Inlet ozone concentrations were measured by bubbling the reactor inlet stream through an alkaline potassium iodide solution, acidifying, and titrating with standard thiosulfate. Inlet hydrogen sulfide concentrations were calculated directly from known flow rates through the syringe pump.

Provision was made to quench the reaction at the reactor outlets by injection of nitric oxide with a technique similar to that used by Cadle and Ledford. This consisted of introducing a controlled flow of nitric oxide through injection collars that were identical to those used at the reactor inlets. Nitric oxide was obtained from a regulated cylinder source, and controlled by two Matheson model 151 micro-flow valves. Preliminary tests, however, showed that observation of the hydrogen sulfide-ozone reaction would be occluded by side reactions arising from the presence of nitric oxide in the system; hence this type of quenching procedure was discontinued, the microvalves being permanently shut off.

Since the use of nitric oxide as a quench was discontinued, the freeze-out traps served the secondary purpose of quenching the reaction. This, of course, modified the treatment of resulting data, since the hydrogen sulfide-ozone mixture then could react over the additional volume between the former quench point and the effective quench point within the trap. These additional volumes were found to be approximately 7.5 and 5.4 ml for reactor 1 and reactor 2, respectively. Effectiveness of the traps for quenching the reaction was verified through preliminary experiments, wherein the reactants were introduced immediately at the trap entrances.

For experiments near room temperature, the temperatures of the reacting fluids were held constant to within $\pm 0.5^\circ\text{C}$ by external insulation and by controlling the temperature of the laboratory. At higher temperatures a Plexiglas, insulated jacket was employed. This housed the reactor, and was warmed by a constant-temperature stream of hot air supplied by a conventional hair dryer. Temperatures of the system were observed by thermometers, as shown in FIG. 1.

Interior surfaces of the reactors and associated glassware were cleaned using the following procedure:

1. Wash and rinse with soap and tap water.
2. Allow to stand for 1 hr in hot, concentrated cleaning solution, (potassium dichromate-sulfuric acid).
3. Rinse with tap water.
4. Allow to stand for 1 hr in hot, concentrated KOH solution.
5. Rinse with dilute HCl.
6. Rinse repeatedly with distilled water.
7. Cover and allow to air dry.

The reactor interiors were sealed from the outside atmosphere when not in use to prevent contamination by ambient dust particles.

Experiments were initiated by setting all flow rates at the desired levels, and allowing the ozone concentration to assume a steady-state value. The hydrogen sulfide syringe pump was then turned on. After allowing sufficient time for all transients to decay, the reactor exit stream was switched to pass into the freeze-out trap. Upon allowing sufficient time for a measurable sample to be collected (7–20 min), the reactor exit stream was switched to the exhaust line, the freeze-out trap removed, and the sample transferred to the chromatograph. Ozone concentration at the reactor inlet was measured immediately after removing the freeze out trap.

4. EXPERIMENTAL RESULTS

Production of sulfur dioxide by the reaction between hydrogen sulfide and ozone was measured in the experimental reactor system at 28.5°C and 48°C. The results of these measurements are summarized in TABLES 2 and 3, and in FIGS. 4 and 5. The tables provide the basic data, giving sulfur dioxide concentrations at the reactor exits for corresponding values of the inlet hydrogen sulfide and ozone concentrations, and reactor space-times. Exit concentrations of sulfur dioxide were computed from experimental measurements by assuming that the degree of conversion beyond the reactor exits was proportional to the additional volumes between the exit points and the freeze-out traps.

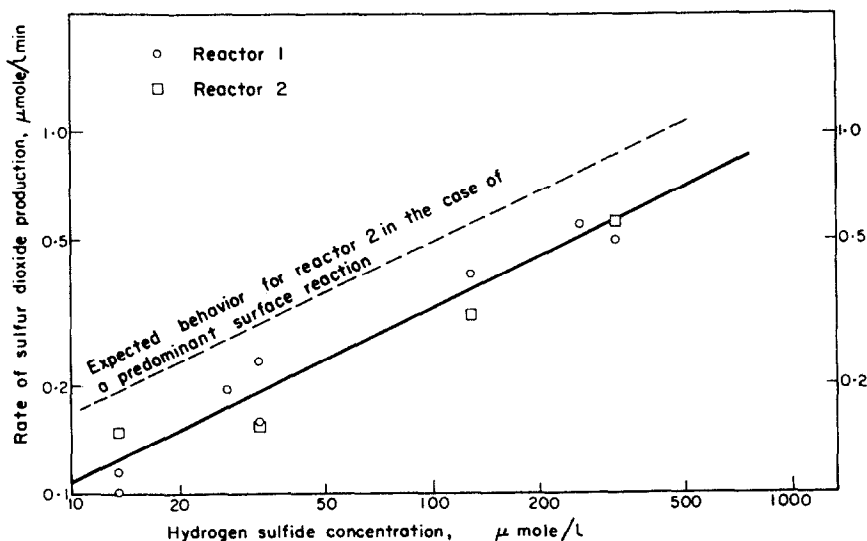


FIG. 4. Rate of generation of sulfur dioxide by reaction between hydrogen sulfide and ozone at 28.5°C in the absence of light; $c_{O_3} = 17.6 \mu \text{ moles l}^{-1}$.

FIGURES 4 and 5 show rates of production of sulfur dioxide, computed from the tabulated results. Because of the small conversions, the system could be described as an initial-rate (differential) reactor, (concentration of reactants invariant with axial position), without introducing serious error. Accordingly, the reaction rates shown in FIGS. 4 and 5 were computed assuming initial-rate behaviour and a totally homogeneous reaction.

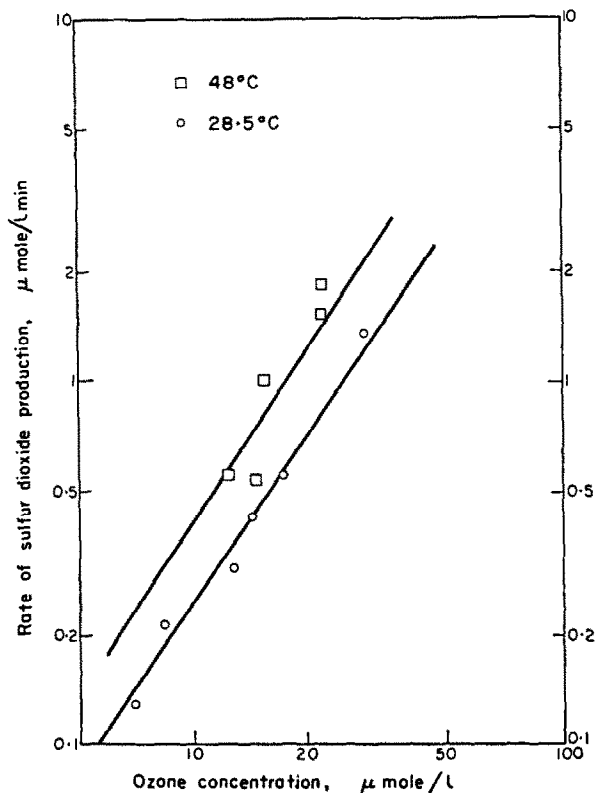


FIG. 5. Rate of generation of sulfur dioxide by reaction between hydrogen sulfide and ozone in the absence of light $C_{H_2S} = 256 \mu \text{ moles l}^{-1}$.

TABLE 2. EXPERIMENTAL RESULTS OBTAINED FROM REACTOR SYSTEM AT 28.5°C IN THE ABSENCE OF LIGHT

Initial ozone	Concentration $\mu \text{ moles l}^{-1}$. Initial H_2S	Exit SO_2	Reactor	Space time (min)
17.6	260	0.651	1	1.20
17.6	130	0.472	1	1.20
17.6	26.9	0.231	1	1.20
17.6	13.4	0.123	1	1.20
17.6	33.6	0.273	1	1.20
17.6	13.4	0.137	1	1.20
17.6	325	0.586	1	1.20
17.6	325	0.250	2	0.449
17.6	130	0.138	2	0.449
17.6	13.4	0.067	2	0.499
17.1	33.0	0.078	2	0.499
17.1	33.0	0.180	1	1.20
6.9	256	0.153	1	1.20
8.3	256	0.253	1	1.20
12.8	256	0.362	1	1.20
14.5	256	0.500	1	1.20
28.9	254	1.60	1	1.19

These figures pertain to constant ozone and hydrogen sulfide concentrations of 17.6 and 256 $\mu\text{mole/l}$, respectively. The plots are based on an assumed ability of observe conversions at a constant concentration of one of the reactants while the concentration of the other is varied—a practical impossibility because of fluctuations in ozone generator output and atmospheric pressure, in addition to differences in degree of conversion. These effects, however, were minor, and were compensated prior to constructing the plots.

TABLE 3. EXPERIMENTAL RESULTS OBTAINED FROM REACTOR 1 AT 48°C IN THE ABSENCE OF LIGHT

Initial ozone	Concentration ($\mu\text{ moles l}^{-1}$)		Exit SO_2	Space time (min)
	Initial H_2S			
16.0	242		1.08	1.11
23.6	242		1.98	1.11
15.0	239		0.565	1.11
23.2	239		1.63	1.11
12.7	241		0.592	1.11

FIGURE 4 is of particular interest because it indicates that results from reactors 1 and 2, when computed as homogenous reaction rates, fall on the same curve within the limits of experimental error. Since the surface-to-volume ratios of these two reactors differed by a factor of 1.5, a deviation between 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, 1.5 times higher than the line representing results obtained from reactor 1. Because of the behavior of these results it was concluded that the observed data represent the true homogeneous reaction within the limits of experimental error.

Linear regressions were performed on the results shown in FIGS. 4 and 5. At 28.5°C, these showed the reaction orders to be 0.495 and 1.562 in hydrogen sulfide and ozone, respectively. Assuming the true reaction orders to be 0.5 and 1.5, a least-squares fit of the complete results was found to give the following expression:

$$\frac{dc_{\text{SO}_2}}{dt} = 22.8 \exp(-6500/RT) c_{\text{H}_2\text{S}}^{0.5} c_{\text{O}_3}^{1.5} \frac{\mu\text{moles}}{\text{liter min}} \quad (5)$$

If (2) is valid, then (5) also represents the rate of depletion of hydrogen sulfide and ozone by this reaction.

There were a number of sources of experimental error that contributed to the scatter of points in FIGS. 4 and 5. An analysis of these errors has shown the most serious to be that associated with sample loss during the vacuum transfer process. Sulfur dioxide samples were generally less than 1 μmole , and it was extremely difficult to predict what errors might arise from sorption, contamination, sample carryover, and additional reaction. From the resulting data it appears that such errors were as high as 10–15 per cent for very small samples, but became smaller with increasing sample size.

Errors arising from the sample analyses were significant, but were within acceptable

limits. Errors associated with the thermal decay of ozone with the reactor were estimated by measuring ozone decay rates across the reactors in the absence of hydrogen sulfide. These tests showed that essentially no ozone was lost by thermal decay in the reactors at 28.5°C; at 48°C the loss was about 4 per cent.

The assumption that conversion within the reactor exit sections was proportional to the volumes of these sections was tested by performing an experiment wherein the ozone-oxygen mixture was injected at the quench point of the reactor, rather than at the entrance. This indicated that a systematic error of as much as 7 per cent may have arisen from this assumption. This error is seemingly explained by the low activation energy exhibited by this reaction, indicating that the effective quench point should be farther inside the trap than would be the case had the reaction been more temperature sensitive.

Since the experimental technique was designed originally (on the basis of Cadle and Ledford's results), to deal with sample sizes much larger than those actually encountered it gave rise to experimental errors somewhat larger than would otherwise be expected. This increase in error arose mainly because of the necessity to perform sampling and analysis at the limits of the technique. Also, because of the restricted temperature range and the thermal decay of ozone, the activation energy in (5) should be regarded only as a rough estimate.

In view of these difficulties, the resulting data were considered to be of acceptable quality. Because of its general reproducibility and because of the agreement among results obtained from the two reactors, the rate expression given by (5) is believed to provide a reasonably accurate representation of reaction behavior over the range of variables of study.

DISCUSSION

Equations (4) and (5) are similar in that they indicate a reaction that is 1.5 order in ozone, yet they differ in values of the reaction order in hydrogen sulfide and in the activation energy. Furthermore, absolute rates predicted by (4) are about two orders of magnitude higher than those of (5) over the range of hydrogen sulfide concentrations studied. In addition to these differences, Cadle and Ledford observed a strong surface reaction in their system, whereas the reaction observed in this study was thought to be almost totally homogeneous.

Because of these factors, it would seem that differences between (4) and (5) could be most easily explained on the basis of the presence or absence of a wall-catalyzed reaction. Initially it was suspected that differences in reactor-cleaning procedures might give rise to a difference in catalytic activity between the reactors used in the present and former studies. This was tested by performing an experiment using a Pyrex reactor that had not been cleaned in any manner prior to use. Other experiments were performed using a reactor that had been coated with potassium chloride. Conversions within each of these reactors were about the same as those observed with the initial system, indicating that catalytic activity was not pronounced in either case.

These results led to the suspicion that the nitric oxide quench gas used by Cadle and Ledford may have conditioned the reactor wall in a way such that it became catalytically active. An attempt was made to test this suspicion by exposing a reactor tube to a dilute mixture of nitric oxide and hydrogen sulfide in air. As a result of this exposure,

the walls acquired a faint translucent sheen, which ranged from blue to red in color. This coating was undoubtedly sulfur; however, the origin of its color was unknown, although it could possibly have arisen from the presence of fragmented sulfur molecules, or from the thin-film properties of the coating. Most of the color disappeared within one day after exposure.

Reactors conditioned in the above manner were used to measure the reaction rates between hydrogen sulfide and ozone, and initial conversions were found to increase by a factor of about ten. Upon running subsequent tests with such reactors, the wall activity was shown to decay over a period of about 2 hr, and approach that of the original system.

Suspecting that free sulfur produced by reaction of the quench gas and hydrogen sulfide may have been the active agent, a further test was conducted using a reactor that had been coated with pure sulfur. Coating in this case was accomplished by applying a solution of sulfur and carbon disulfide to the tube wall, and allowing the solvent to evaporate. Conversions within this reactor were slightly higher than those predicted by (5), but not nearly as great as those observed in the previous experiments.

An additional point of conjecture is the difference in activation energies predicted by the two studies. Although the low activation energy appearing in (5) seems reasonable for such a highly exothermic reaction, one would expect the activation energy of its catalyzed counterpart to be lower, rather than higher, as is the case in (4). This leads to the suspicion that a side reaction occurring at the wall, rather than a wall catalysis, might have been responsible for the discrepancy in the results. Cadle and Ledford checked for the influence of side reactions to the extent allowed by their experimental system; therefore, any side reaction that did occur would have to proceed in a rather subtle manner, appearing outwardly to be (2).

One possible reaction of this type would be the ozone oxidation of free sulfur produced by action of the quench. This would cause a decay of ozone in the system that would be difficult to discern from (2), and would account for all of the surface behavior observed by Cadle and Ledford. Cadle and Ledford reported observing the formation of free sulfur upon exposing mixtures of nitrogen dioxide and hydrogen sulfide to light, but were able to control this reaction by keeping the radiation above a given wavelength. The present study, however, indicates that this reaction may proceed to a limited extent even in a totally dark reactor. If sulfur formed in this manner were deposited on the wall as relatively active S_8 fragments, which were rapidly consumed by the ozone, the high depletion rates of ozone could be explained.

The experiments performed in the present analysis were certainly gross approximations to Cadle and Ledford's system, and any conclusions pertaining to the results of these authors would be highly speculative. On the basis of these results, however, the use of nitric oxide quench would seem highly suspect as a factor in distortion of experimental results.

In addition to these considerations, it should be noted that the previous authors measured progress of the hydrogen sulfide-ozone reaction by observing depletion of ozone, whereas this study involved measurement of sulfur dioxide production. Comparison of (4) and (5), therefore, implies the acceptance of the stoichiometric equation (2), which, as discussed previously, evidently describes the true stoichiometry under the conditions of these experiments. Because of the low conversions experienced in this study, it was not possible to check stoichiometry by comparing depletion of

reactants with production of sulfur dioxide. All evidence obtained while performing the experiments, however, suggested that the stoichiometry was well-represented by (2).

The purely stoichiometric investigations of Gregor and Martin and of Cadle and Ledford are also useful for further analyzing the validity of the observed rate behavior. The excess quantities of ozone decomposed thermally in these experiments indicated that annihilation of ozone by reaction with hydrogen sulfide was not extremely rapid compared with the thermal decay. For ozone decay rates in the expected range, Cadle and Ledford's expression would appear to predict rates much too high to explain the observed behavior. Rates based on (5), qualitatively at least, conform with these results in an acceptable manner.

Equation (5), which represents the formation of sulfur dioxide by (2) in clean air in the absence of light, obviously applies to rather specialized conditions. Care should therefore be exercised in its application to practical situations. Furthermore, because of the apparent complexity of the reaction mechanism, one should recognize that extrapolations of (5) beyond limits of existing data may give rise to highly dubious results.

In spite of these limitations, it is interesting to apply (5) to certain hypothetical odor-control situations. Consider, for instance, a factory stack wherein hydrogen sulfide is being emitted at 150°C with a concentration of 500 ppm. A process has been patented (LIMERICK, 1958) for removing odors from stacks containing sulfur gases wherein ozone is injected at the base of the stack, and allowed to react with the contents along its length. Assuming no spontaneous decay of ozone and a stack residence time of 10 sec, (5) predicts that only about 2 per cent of the hydrogen sulfide will be oxidized upon applying a stoichiometric quantity of ozone. True stack environments are admittedly highly complex, and the implications of this analysis are questionable. Nevertheless they do tend to indicate that any odor-control process depending upon the homogeneous contact of hydrogen sulfide and ozone for limited periods of time probably takes its effect more from the odor-masking properties of ozone than from actual removal of hydrogen sulfide.

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