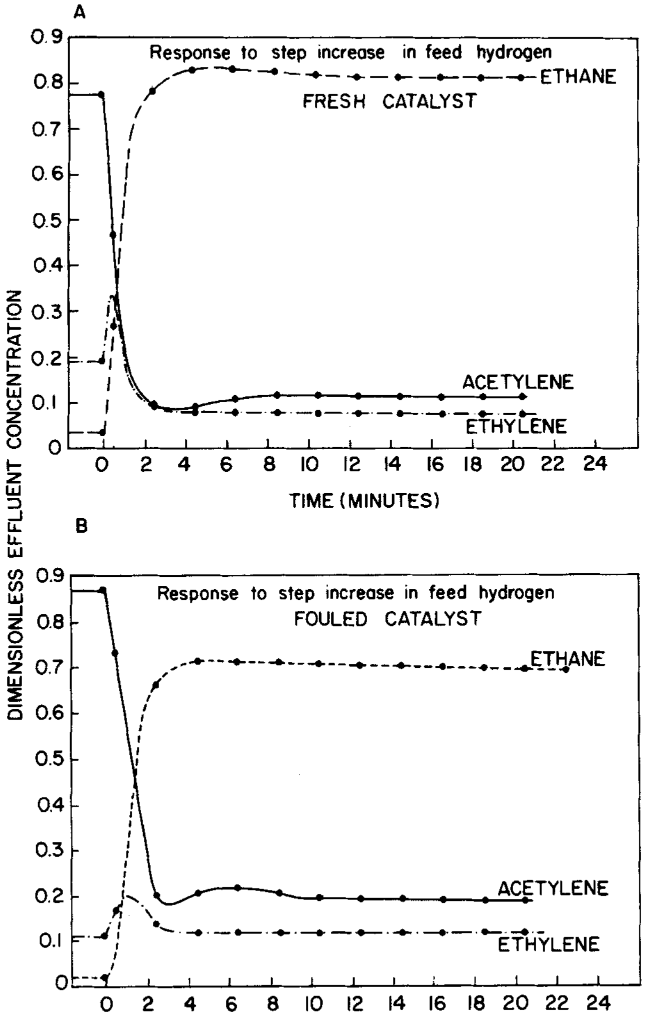

Figure 3. Step increase transients for (A) fresh and (B) fouled catalyst (dimensionless concentrations defined as in Figure 2).

min. The longer transients seen here for fresh catalyst must therefore be caused by slow interactions with and/or reactions on the catalyst surface.

Fouling profoundly alters the dynamic behavior of the reactor, changing both the trajectory shapes and, in the case of the step-down experiment, the time required to achieve steady state. The asymmetric response pattern for fresh catalyst (slower step up, faster step down) is reversed for fouled catalyst.

This work adds to two important themes in the recent literature. First, slow events on the catalyst surface can in some cases dominate reactor transient behavior (Sheintuch and Schmitz 1977). Careful consideration of the possible existence of these features is critical in analyses of catalytic reactor dynamics: the quasi-steady state approximation for surface species should be invoked with care and not casually assumed to be valid. Secondly, it appears that the complex effects of fouling on reactor transients shown above cannot be explained mathematically simply by introduction of scaling factors which multiply the overall rates of the two hydrogenation reactions. In this event, the influences of fouling are impossible to represent using separable kinetics (Butt and Bilimoria 1978, Butt et al. 1978), and a more complex representation of fouling is required for reactor modeling and analysis. Further research along these lines is in progress.

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Gas Phase Ozonation of Aliphatic Sulfur Compounds

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Odors are typically classified as nuisance air pollution problems rather than health hazards. Traditionally, sources of non-toxic odors have been restricted by law to special geographical zones, based on prevailing winds and population growth patterns. This approach follows the widely held concept that the best solution to pollution is dilution. But population growth and air dilution patterns are not always predictable. Moreover, scientific evidence suggests that adverse synergistic effects may result, when pollutants are dispersed into the ecosystem. Hence, present political trends encourage abatement or curtailing of gaseous emissions. Failure to do so may invite civil suits and/or government intervention. Thus, the growing technology for treating gas streams to remove non-toxic odors as well as toxic constituents.

The first step in dealing with odor pollution is always identifying the causative agent or agents. This is followed by an hypothesis on how it is generated, and corrective procedures

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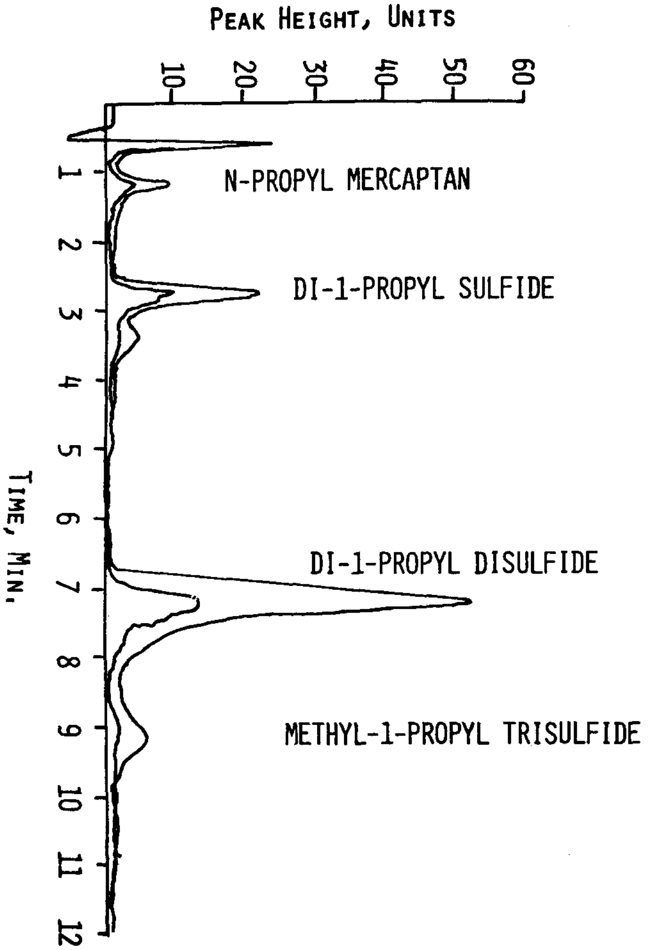

Figure 1. Chromatograms of onion vapor before (upper) and after (bottom) 30 seconds of contact time with ozone. Initial onion vapor concentration was 2 ppm, O_3 200 ppm, total pressure 1 atm and t = 35°C.

can be taken, based on cost effectiveness. Demonstrated cost-effective treatments for a given odor, source, and process conditions are 1) wet scrubbing, 2) incineration, 3) catalytic oxidation, and 4) ozone contacting. Only the first and last approached represent room temperature processes, and of the two, ozone contacting is conceptually the simplest.

The use of ozone to sweeten fouled air is hardly a novel concept. Nebel, et al. (1974), Baratt (1975), and Petherbridge (1975) discuss some of the various problems and processes associated with it. Quane (1974) addresses those aspects specific to pharmaceutical plants; McGowan et al. (1978) investigated onion and garlic dehydration units. Odors emanating from industrial processes associated with food processing and agribusinesses are almost always non-toxic, and usually require only partial oxidation to render them undetectable by olfactory sensation. Still, ozone treatment has not always succeeded in eliminating odors, and there have been a number of symposia on new technology utilizing ozone to treat odor problems. See McCammon (1975), Hardenson and Turk (1977), Rosen (1979).

One specific instance where ozone contacting does not eliminate odors has been in off-gases from dehydration units for onions and garlic cloves. Organoleptic tests conducted with test panels on air fouled with vaporized onion oil revealed odors persisting even after contacting times of 30 seconds (McGowan et al. 1978). The obvious question is, why does ozone work for some odors and not for others?

Murphy (1975) attempted to answer this by studying ozone chemistry. One possible answer is that ozone attack is specific to a particular type of molecule; such as unsaturated hydrocarbons. But most food processing odors are caused by organic aldehydes, ketones, amines, and, in the case of onions and garlics—aliphatic sulfur compounds (Grodnitz 1975, Freeman 1975). Since all of these compounds are saturated, the specificity of ozone for unsaturated bonds does not apply. Obviously other kinetic mechanisms must be functioning. With onion odors, the general assumption is that the ozone is attracted to the sulfur atoms of the odor molecules. If a reaction occurs, and a sulfoxide or sulfone is produced, the odor loses its organoleptic sensitivity, and further oxidation is not necessary. A series of kinetic studies were made to check this and other hypotheses concerning ozone attack on aliphatic sulfur compounds.

EXPERIMENTAL

Three of the major constituents of onion oil were secured in relatively pure form. These are n-propyl mercaptan, di-n-propyl sulfide, and di-l-propyl disulfide. A flow reactor was designed to vaporize the pure liquid compound from a steam-heated plate and disperse it in a flowing-air stream. Concentrations in the range of 2 to 10 ppm were controlled by a microsyringe pump, which gave a metered flow to the hot plate. Once the odor was dispersed in an air stream at atmospheric pressure, it was contacted with ozone and air in the flow reactor. The ozone at a concentration of 150 ppm was generated on site, with a commercial laboratory unit.

The flow reactor had sampling ports, which for total flow rates 0.02 m^3/s gave space times of 1, 2, 4, 6, and 7 seconds. Analysis of the gas stream for odor molecules was performed by gas chromatography, with a sulfur specific photometric cell. The column was temperature-programmed and flame ionization gave minimum detection limits of 0.3 ppm. Ozone analysis was performed using the standard KI method. Conversions of odor molecules to partially oxidized products were determined from peak area reductions on chromatograms. Figure 1 shows chromatograms of the treatment process for onion oil after a contacting time of thirty seconds. The reactor was essentially isothermal with a temperature of 35°C.

THEORETICAL ANALYSIS

The general assumptions made in studies of ozone reactions with organic molecules are that the reactions are irreversible, complete, and can be monitored by following the disappearance of the ozone. In our studies, since destruction of the odor molecule was the objective, only partial oxidation was needed. Since we had an analytical procedure for following its concentration, we chose to base our studies on the odor molecules. The ozone was kept at high excess concentrations. For levels of 150 ppm O_3 to 10 ppm for the odor molecule, the ozone concentration essentially remained unchanged during the seven seconds of contacting times for a total pressure of one atmosphere.

Because the data are very preliminary in nature, a very general and simplistic math model was developed, to empirically correlate the data. This simple approach assumed a biomolecular reaction between ozone and the odor with the formation of an intermediate complex and a non-chaining reaction.

$$mA + nO_3 \underset{k_2}{\overset{k_1}{\rightleftarrows}} B^* \qquad (1)$$

$$B^* \xrightarrow{k_1} P(s) \qquad (2)$$

A represents the odor molecule, O_3 the ozone, B^* the intermediate complex, and P the initially ozidized product or products. The rate of disappearance of the odor molecule can be represented by the following differential equation assuming the mechanisms given by Equations (1) and (2).

$$-d[A]/dt = k_1[A]^m[O_3]^n - k_2[B^*] \qquad (3)$$

Using the steady state approximation on B^*, the following simplifications can be made

$$-d[B^*]/dt = 0 = k_1[A]^m[O_3]^n + k_2[B^*] + k_3[B^*] \qquad (4)$$

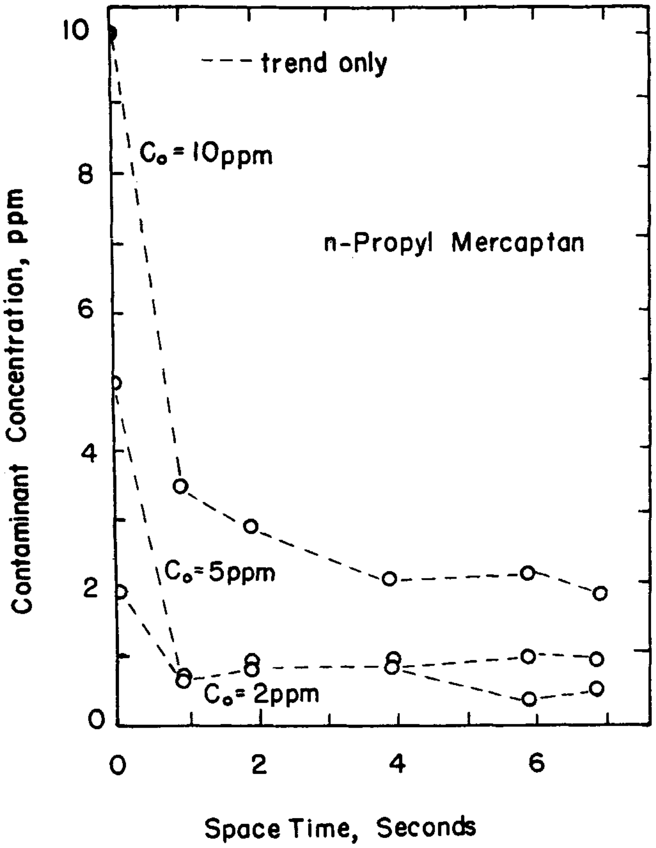

Figure 2. Initial rate studies for n-Propyl Mercaptan. O_3 concentration was constant 150 ppm. Total pressure atmospheric and 60°C.

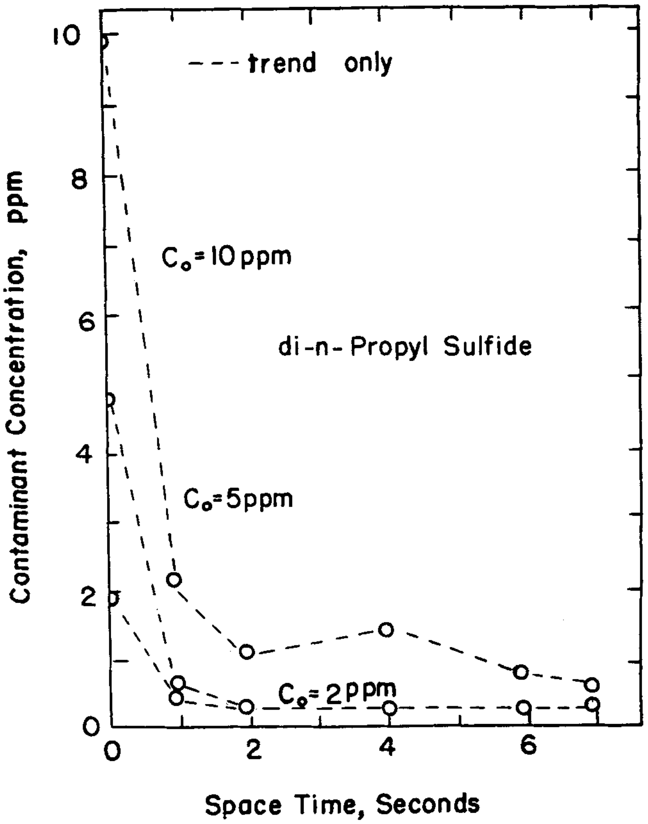

Figure 3. di-n-Propyl Sulfide Studies. $O_3 \approx 150$ ppm, atmospheric pressure, 60°C.

$$[B^*] = \frac{k_1[A]^m[O_3]^n}{k_2 + k_3} \tag{5}$$

Equation (5) is substituted into Equation (3)

$$-d[A]/dt = k_1[A]^m[O_3]^n - \frac{k_2\,k_1}{k_2 + k_1}[A]^m[O_3]^n \tag{6}$$

$$-d[A]/dt = k_1[A]^m[O_3]^n\left(\frac{k_3}{k_2 + k_3}\right) \tag{7}$$

$$-d[A]/dt = K_0[A]^m[O_3]^n \tag{8}$$

Equations (3) and (8) represent two different expressions for the disappearance of odor A by the relationships shown in Equations (1) and (2). Since the experiments were run with a large O_3 excess, the concentration of O_3 remained constant throughout. Under these conditions Equations (3) and (8) can be further simplified

$$\frac{-d[A]}{dt} = k_1'[A]^m - k_2'[B^*] \tag{9}$$

$$\frac{-d[A]}{dt} = K_0'[A]^m \tag{10}$$

Equation (9) predicts that the rate of disappearance of the odor molecule will reach a steady state value as its concentration approaches zero, while Equation (10) predicts that the rate goes to zero as the concentration, $[A]$, goes to zero. Both equations are of the same form when $[B^*]$ is zero. This would be the case in the initial stages of the reaction, before $[B^*]$ became appreciable. Based on this assumption we used the (first 3 pts.) initial slopes of the curves in Figures 2, 3, and 4 to make log-log plots of the initial rate $d[A]/dt$ versus $[A]$. In all cases, the least squares fit of the data gave, m, statistically equal to unity. This result was not unexpected, since most other investigators have found the reaction to be first order with respect to the odor molecule. With $m = 1$ the data in Figures 2, 3, and 4 were next fit to equations of

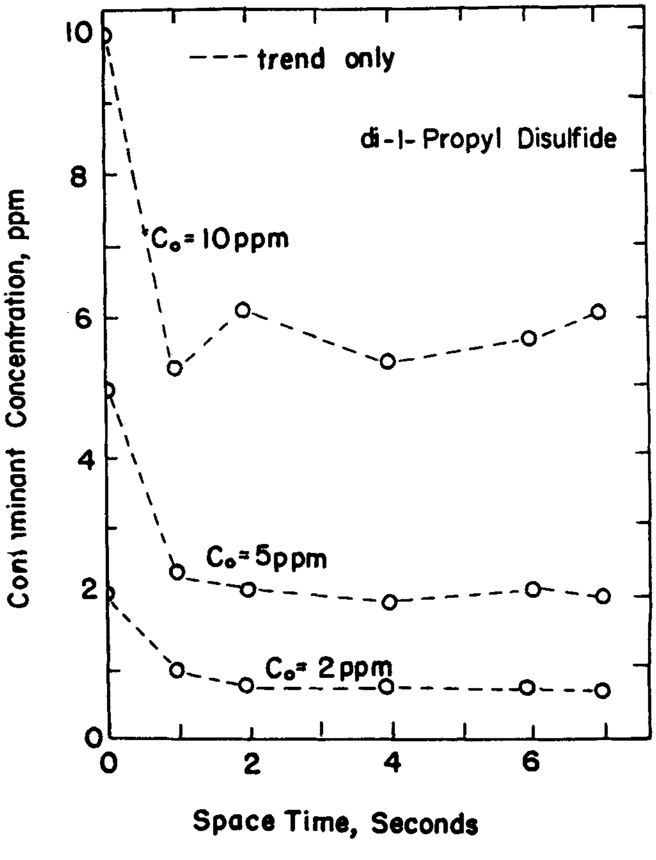

Figure 4. di-1-Propyl Disulfide Studies. $O_3 \approx 150$ ppm, atmospheric pressure, 60°C.

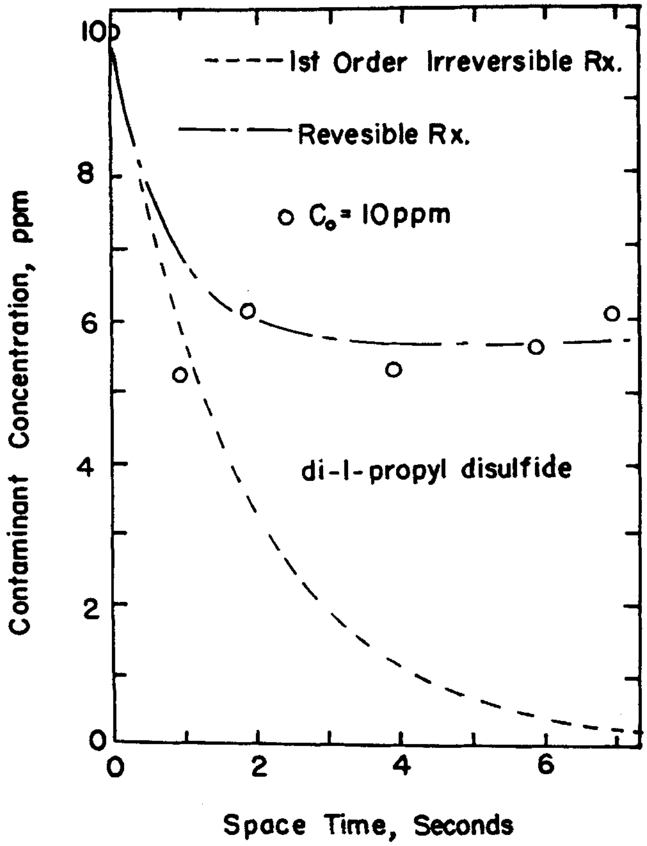

Figure 5. Data for di-1-propyl disulfide fit to Equations 9 and 10 when $C_0 =$ 10 ppm, the reaction is first order with respect to the odor molecule, and O_3 is constant 150 ppm.

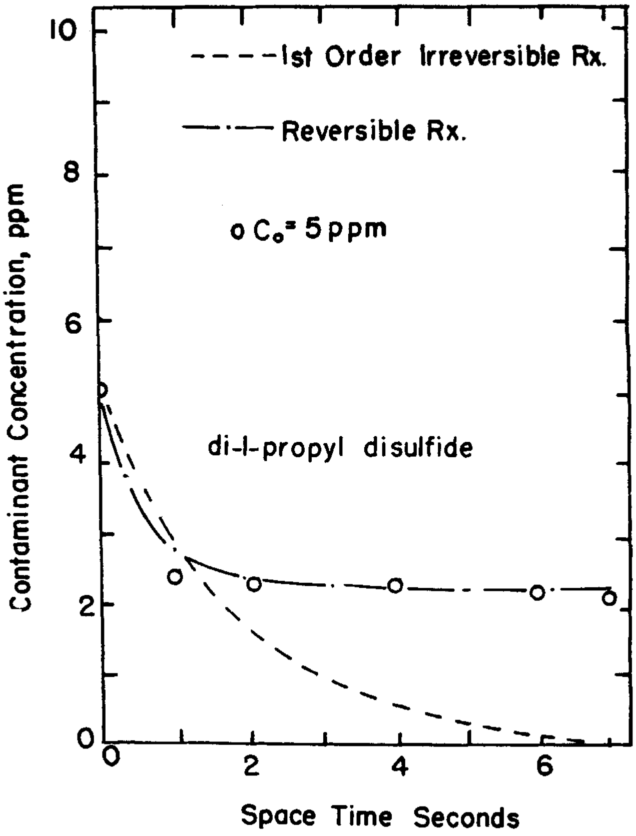

Figure 6. Data for di-1-propyl disulfide fit to Equations 9 and 10 when $C_0 =$ 5 ppm.

the form given by 9 and 10. The results for the disulfide, which were the most divergent, are shown in Figures 5, 6, and 7. Obviously, the mechanistic approach hypothesized by Equation (9) fits these data much better than does that used to derive Equation (10). This observation led to our early supposition that the intermediate complex(s) which forms is stable for reasonably long periods at this experimental temperature.

DISCUSSION OF RESULTS

These data offer an explanation as to why some odors cannot be destroyed by ozone attack. The polysulfide aliphatic compounds appear to complex with the ozone (rather than react) to form a sulfone or sulfoxide. This hypothesis is supported by the observation of several other investigators. Hampson and Garirn (1975), for example, found such complexes while modelling atmospheric chemistry. In fact, sulfur-containing gases were found by Slater (1977), Glavas (1975), Kaduk (1977), and Kirchner et al. (1971) to be particularly good complex formers. The observation was that there is a rapid initial reaction, which tapers off as the concentration of complex builds. Based on the atmospheric chemistry. In fact, sulfur-containing gases were found by Slater (1977), Glavas (1975), Kaduk (1977), and Kirchner et al. (1971) to be particularly good complex formers. The observation was that there is a rapid initial reaction, which tapers off as the concentration of complex builds. Based on the chromatograms produced in our study, there is some indication that, if the di- and tri-sulfides may in fact be partially oxidized, they form mono and disulfide compounds which must again be oxidized if the odors are to be destroyed. This finding is again supported by the National Bureau of Standards models of air pollution problems.

Our attempt to find a pseudo-order for ozone by contacting copious quantities of odor with low levels of ozone in the experimental isothermal reactor was not very satisfactory. The failure seems to arise from an interference of the odor molecules

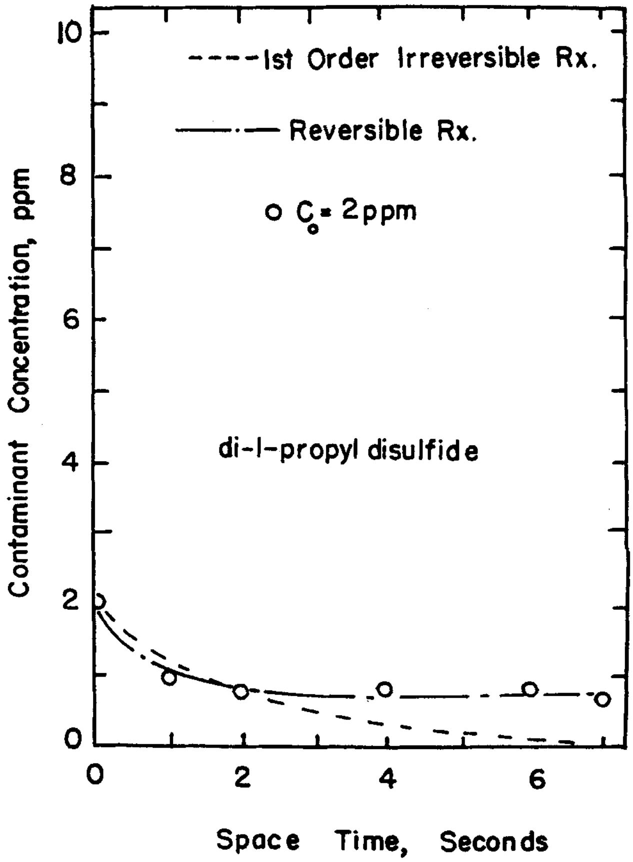

Figure 7. Data for di-1-propyl disulfide fit to Equations 9 and 10 when $C_0 =$ 2 ppm.

with the KI-total oxidant chemistry. An average of all the data gave only a fractional order for ozone based on initial rates. This was not expected, and more studies are underway. The fractional order would seem to support the hypothesis that complexes are formed, however, and is consistent with some of the results reported by Kaduk and Toby (1977) when O_2 is present with O_3 during oxidation.

In summary, we attempted to discover why certain onion and garlic odors are not destroyed by partial oxidation with ozone. The observation that complexes are formed suggests that a "nonisothermal" flow reactor must be employed. An optimum temperature progression requires some knowledge of the temperature dependence of the reaction. When this is available, it may be possible to design an ozone contactor which effectively removes odors from these industrial process streams, as well as others, which heretofore have been less than adequate.

NOTATION

A = odor molecule
m, n = stoichiometric coefficients
O_3 = ozone molecule
B^* = intermediate complex molecule
$P(s)$ = product(s) molecule(s)
k, K = reaction rate constants
t = time

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Nonradioactive Tagging Method of Measuring Particle Velocity in Pneumatic Transport

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In transport-line reactors, e.g. in the hydropyrolysis of coal particles, particle residence time, as determined by particle velocity, is of major importance. Direct measurement of particle velocity in pneumatic transport of pulverized coal was accomplished through radioactive tagging by Hall (1966), Huff and Holden (1966), and Stewart (1962). The tagged particles are injected into the flowing mixture, then detected at two downstream positions. The detector locations and lag-time allow determination of the velocity.

Radioactive tagging has several advantages, compared with other reported methods of particle velocity determination in gas-solids transport. The detectors are external to the transport system, and can be readily moved to any desired location. There are no probes or induced flow disturbances. Because particle velocity is measured directly, calibration is not required. The experimenter can investigate the effects of particle size, shape, etc., by injecting and measuring the velocity of the particles selected. The required amounts of radioactivity are low and radioisotopes with short half-lives do not cause equipment contamination or disposal problems. Health physics problems are negligible, according to Hall (1966), because total personnel exposure was calculated as less than one millirad per month, and film badges and dosimeters have not shown any exposure.

Although radioactive tagging with certain short-lived radioisotopes is reported to be safe and can be conducted by non-technical personnel, general restrictions applying to the use of all radioisotopes may render the method impractical in some cases. In addition, the cost of precision measurements is about \$5000 (Hall 1966). A less expensive method of particle-

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