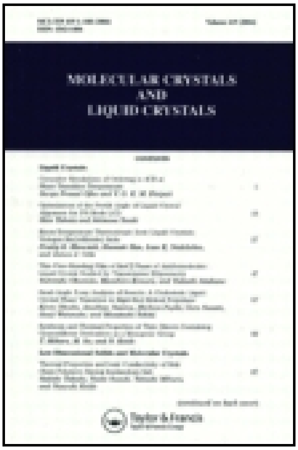

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Reactions of Gases with Irradiated Organic Solids

III. Reactions of Propionamide, *n*-Butyramide, Isobutyramide, Methacrylamide, Valeramide, and Stearamide with Sulfur Dioxide‡

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Abstract—The reactions of γ-irradiated propionamide, *n*-butyramide, isobutyramide, methacrylamide, valeramide, and stearamide with sulfur dioxide have been studied by ESR spectroscopy, gas absorption measurements, and X-ray diffraction. Sulfur dioxide reacts with the radicals originally generated in the irradiated material to give sulphonyl radicals. These propagate in a chain reaction in which further sulfur dioxide is absorbed. In some cases the original radicals can be recovered from the corresponding sulphonyl radicals. The mechanism of the reactions is discussed.

1. Introduction

In a previous paper[1] we reported some preliminary results of an ESR study of the reaction of sulfur dioxide with the radicals induced by γ irradiation in solid propionamide, *n*-butyramide, and isobutyramide. The changes in the spectra indicated that at least a large fraction of the original free radicals, R·, generated in the irradiated solid react with SO_2 to give the sulphonyl radicals, $RSO_2\cdot$. The original radicals, R·, can be recovered at least partially by reevacuating the sample.

In this communication we will present data on the ESR spectra,

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gas absorption, and X-ray diffraction characteristics of the reactions between SO_2 and the radicals induced by γ irradiation in crystalline propionamide, *n*-butyramide, isobutyramide, methacrylamide, valeramide, and stearamide. Except for methacrylamide, these all have the same type of layerlike crystal structure.[2,3] As has been previously shown,[1,4,5] this structure allows for the diffusion of gases with small molecules, such as O_2 and NO, which react with the previously generated free radicals. Methacrylamide has a different type of structure which has not yet been determined. It polymerizes in the solid state when irradiated and shows a limited sensitivity to oxygen diffusion,[6] but the rate of reaction with oxygen is considerably slower than the others. SO_2 has larger molecules than either NO or O_2. Its diffusion into the lattice should therefore be inhibited or much slower than that of the smaller gases. Surfaces, grain boundaries, edge dislocations, and other sites which allow for easier diffusion should therefore play a more prominent role in this reaction. This seems to be true as will be shown below.

2. Experimental

Propionamide, *n*-butyramide, isobutyramide, and stearamide were purified as already reported.[5] Valeramide and methacrylamide were purified by recrystallizing twice from acetone. High purity SO_2 (from Matheson) was used. The irradiations were performed in the underwater Co^{60} irradiation facility of the Brookhaven National Laboratory.[7] Dosimetry was done by the Fricke method.[8] The powdered samples of the amides were evacuated for several hours at 10^{-5} mm Hg and then sealed and irradiated at $-78\,°C$ at dose rates ranging from 6.5 to 11 Mrads/hr to the required total dose, usually between 18 to 23 Mrads. For the Tesla-coil irradiation experiments, the Tesla-coil was brought close to the evacuated tube containing the specimen, which was then irradiated with the coil discharge.[9] Before the reaction with SO_2 the irradiated samples were warmed up to room temperature, pumped under high vacuum for about 15 to 20 min in order to remove the radiolytic gases, and then allowed to react with sulfur dioxide at room temperature.

The reactions were studied by gas-volumetric measurements of the amount of SO_2 absorbed using a conventional manostatic apparatus and by following the changes of the ESR spectra as a function of time. During the evacuation of the samples (after the reaction with SO_2), in order to recover the original radicals from the corresponding sulphonyl ones, the samples were kept in the resonance cavity, with the vacuum line connected to them.

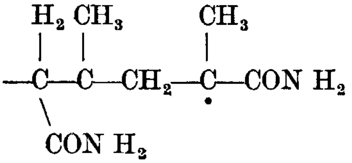
The ESR spectra were recorded on a X-band Varian spectrometer, having a 100-kc modulation and a cylindrical cavity.

The X-ray diffraction diagrams of the samples before and after irradiation and reaction with SO_2 have been made with a G.E. X-ray diffractometer using $Cr_{k\alpha}$ radiation.

3. Results

A. THE NATURE OF THE INITIATING RADICALS

Except in the case of methacrylamide and stearamide, the room temperature, the ESR spectra of the γ-irradiated powdered amides can best be interpreted in terms of the free radicals formed by the loss of the hydrogen atom alpha to the amide group.[1,5,10,11] The room temperature ESR spectra of the γ-irradiated methacrylamide is the one that is generally observed for polymethylmethacrylate macroradicals and which can be described as the superposition of two series of hyperfine structure lines: a quintet and a quartet, with a binomial intensity distribution in each series. According to the interpretation of Ingram and Abraham *et al.*,[12] which has been supported by more recent experiments,[13] the sets of lines correspond to two different conformations of the same macroradical, namely to the growing chain radical:



arising because of the hindred rotation for the alpha methylene group. However, the exact interpretation of this spectrum is not important to our work. The room temperature ESR spectrum of the γ-irradiated stearamide appears to be a composite of two radicals: one decaying more rapidly and also reacting more rapidly in the presence of reactive gases than the other one. The more stable one seems to result from the loss of the hydrogen atom alpha to the amide group, as in the other amides. The more labile radical has the unpaired spin nearer the other end of the hydrocarbon chain.[5] These spectra are shown in Figs. 1a to 6a.

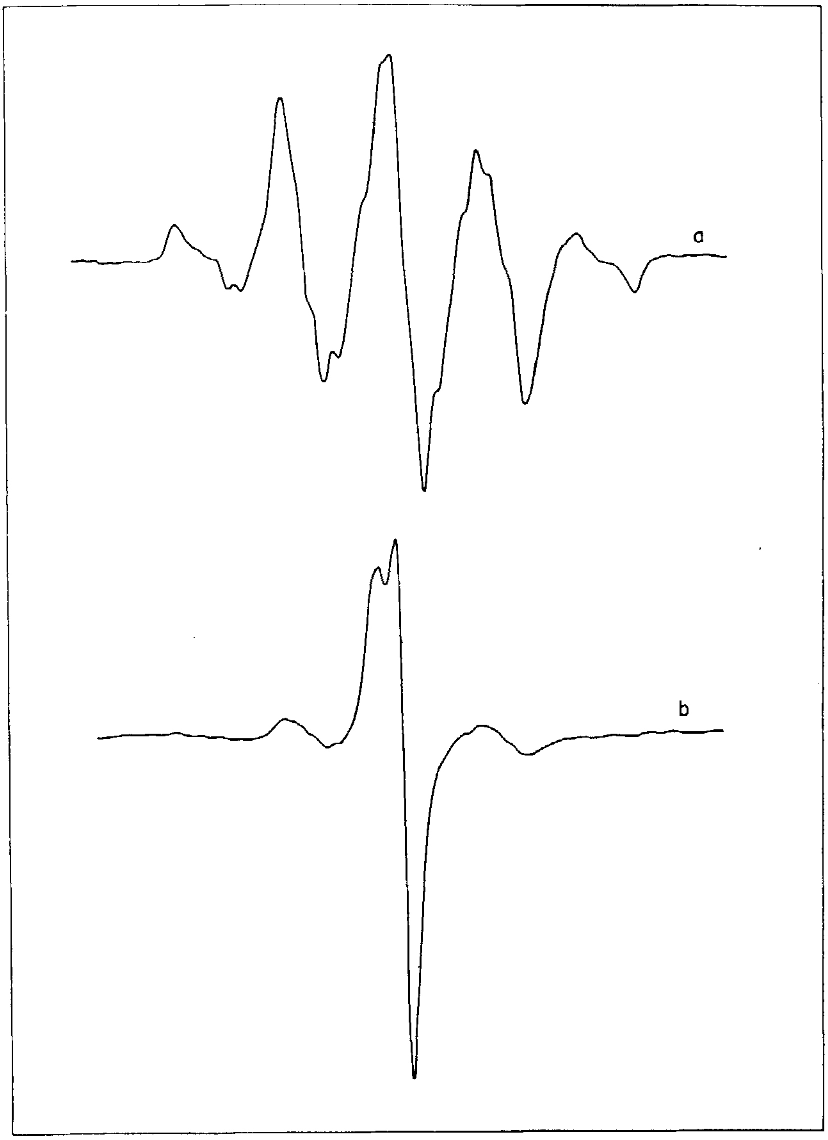


Figure 1. ESR spectrum of irradiated propionamide.
(a) Before admission of SO_2, Amplification factor 160; (b) 6 minutes after addition of SO_2, Amplification factor 80.

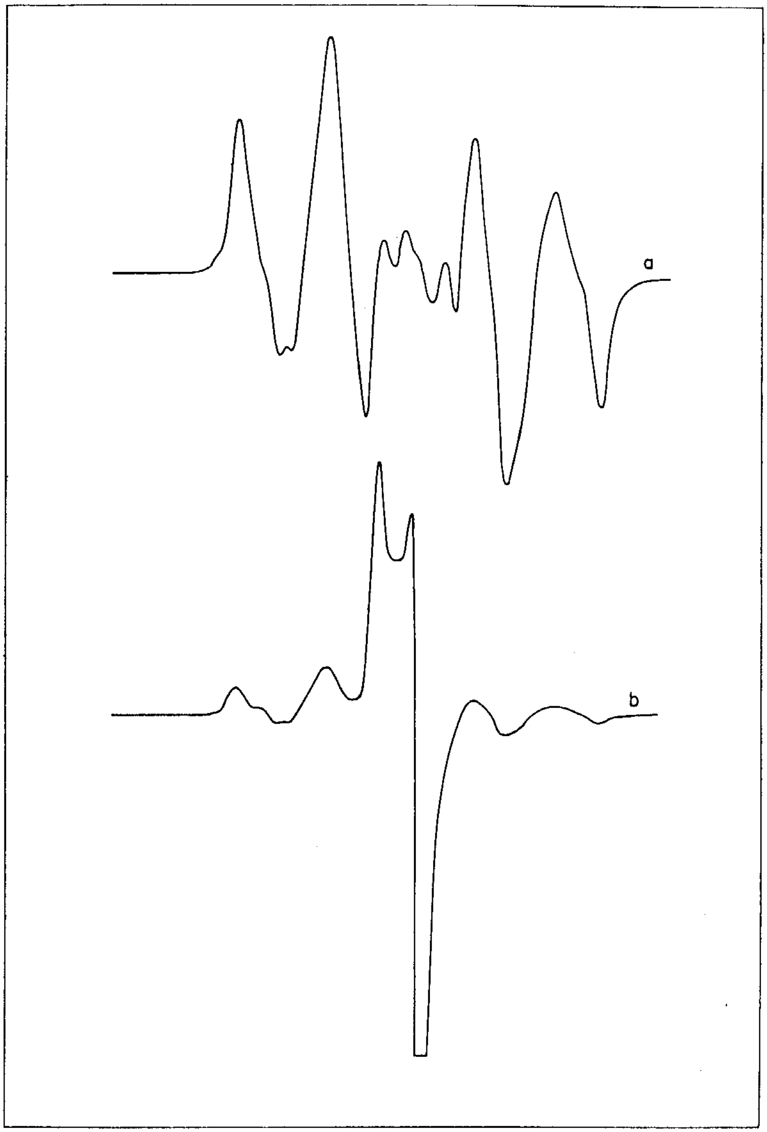


Figure 2. ESR spectrum of irradiated *n*-butyramide.
(a) Before admission of SO_2, Amplification factor 160; (b) 6 minutes after admission of SO_2, Amplification factor 40.

Figure 3. ESR spectrum of irradiated isobutramide.
(a) Before admission of SO_2, Amplification factor 40; (b) 50 minutes after addition of SO_2, Amplification factor 32.

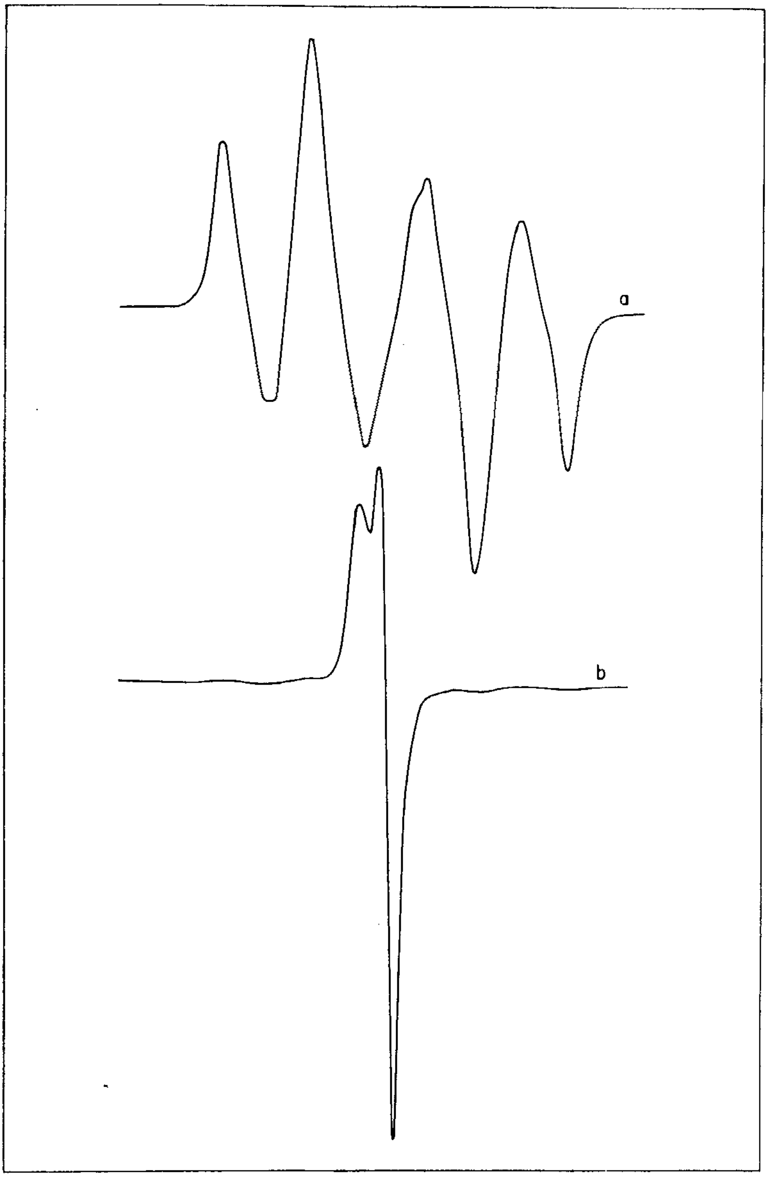


Figure 4. ESR spectrum of irradiated valeramide.
(a) Before admission of SO_2, Amplification factor 50; (b) 2 hours after admission of SO_2, Amplification factor 20.

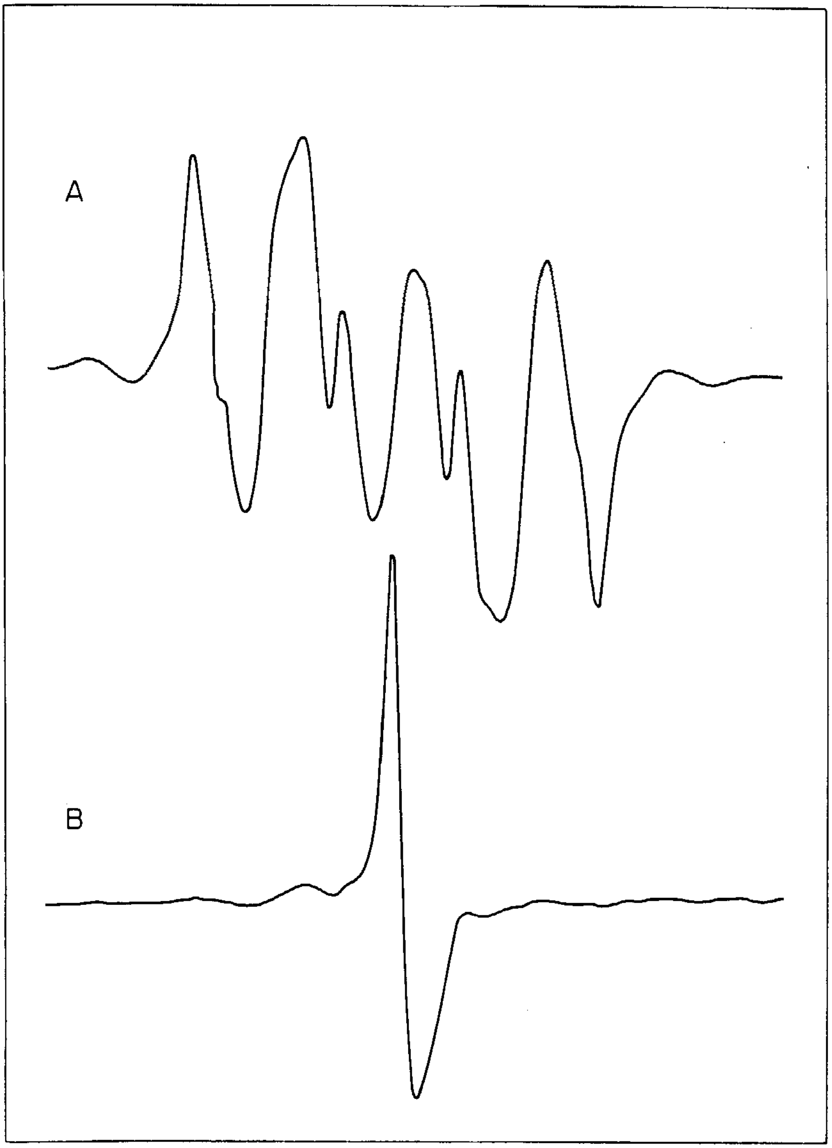


Figure 5. ESR spectrum of irradiated stearamide.
(a) Before admission of SO_2, Amplification factor 160: (b) 48 hours after admission of SO_2 Amplification factor 80.

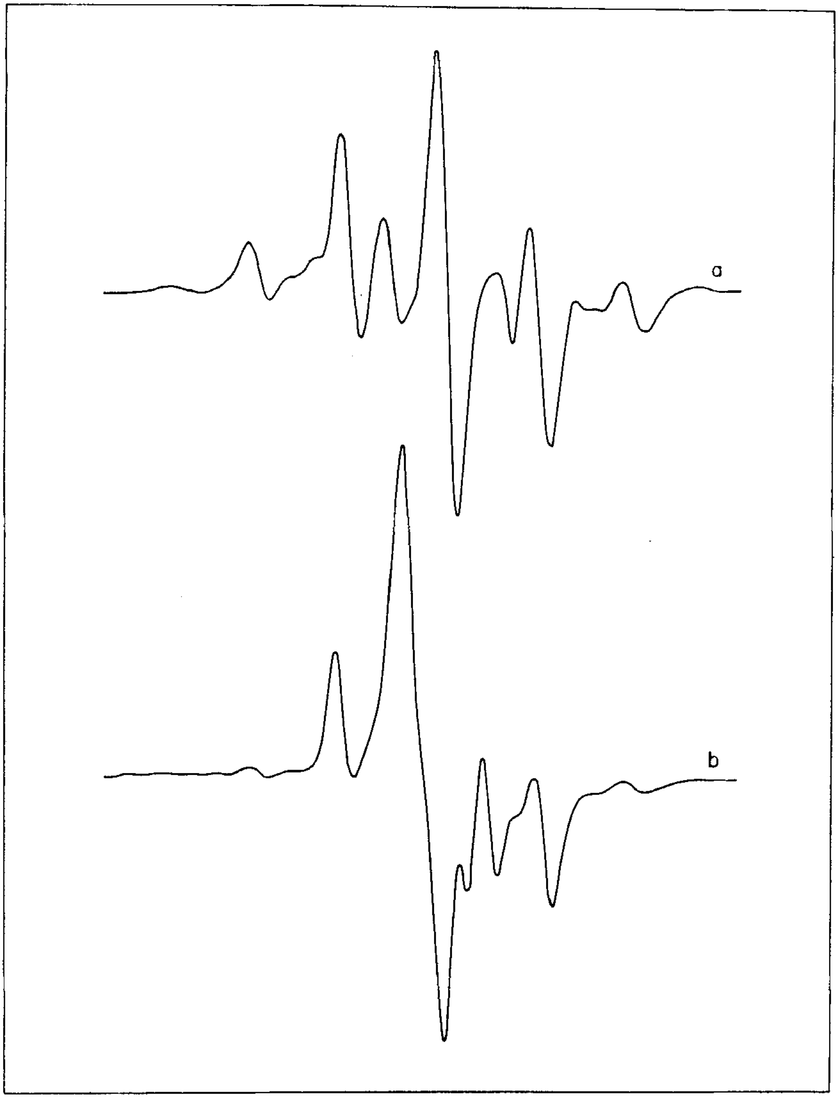


Figure 6. ESR spectrum of irradiated and polymerizing methacrylamide. (a) Before admission of SO_2, Amplification factor 32; (b) 80 hours after admission of SO_2, Amplification factor 80.

B. Reactions with Sulfur Dioxide

Sulfur dioxide at pressures ranging from 300 to 600 mm was admitted to the specimens at room temperature after irradiation. Except in the case of methacrylamide, there was a rapid change in the ESR spectra. The result was a spectrum having two components. One was apparently the original spectrum but diminished now by a large factor to some fraction of its original value. These radicals proceeded to decay at a rate related to but somewhat more rapid than normal. The other component was the appearance of an asymmetric singlet whose shape varied, depending on the starting amide. The absence of hyperfine structure and the asymmetry of this spectrum, which may be caused by an anisotropic *g*-factor associated with incomplete quenching of the orbital angular momentum,[14] indicates that sulfonyl radicals are formed. These have the unpaired spin presumably located on the sulfur or the oxygen atoms. The sulfonyl radicals, $RSO_2\cdot$, of the different amides have nearly the same average *g*-factors, about 2.0045 ± 0.0005. Since the decay rate of these radicals is considerably slower than that of the original radicals, the $RSO_2\cdot$ radicals are the only ones left after a prolonged period of time.

With powdered and sieved samples (particle size 0.04 to 0.06 mm) and a SO_2 pressure of about 500 mm, more than 90% of the remaining signal is $RSO_2\cdot$ after time periods ranging from 30 min to a few hours. The sulfonyl radical concentration builds up with time then a slow decay sets in. The half-times for the radical buildup are 1, 2, 4, 6, and 30 min for propionamide, isobutyramide, *n*-butyramide, valeramide, and stearamide, respectively. With methacrylamide the reaction is very much slower and, since there is no appreciable decay of the polymerizing radicals normally found in this substance during the time period of the experiment, the $RSO_2\cdot$ radical spectrum is always accompanied by that of the other radicals present (Fig. 6).

During the reaction the concentration of the $RSO_2\cdot$ radicals increases until a maximum is reached, then a definite decay is observed. The half-times of these decays are 20, 100, 200, and 240 min for propionamide-, isobutyramide-, *n*-butyramide-, and valeramide-sulfonyl radicals respectively. No appreciable decay has been observed for methacrylamide- and stearamide-sulfonyl radicals during a period of observation of more than 10 hr.

The mechanism of the over-all process seems to be more complicated than the expected from the simple scheme:

$$R\cdot + SO_2 \longrightarrow RSO_2\cdot \longrightarrow \text{molecular products} \qquad (1)$$

which has been applied for analogous reactions in irradiated polymers.[15] The gas absorption measurements of sulfur dioxide indicate that some sort of limited chain reaction probably occurs. The ratio of moles of SO_2 absorbed to the moles of radicals reacted is approximately 27, 34, 7, and 17 for propionamide, *n*-butyramide, isobutyramide, and valeramide, respectively. This is based on an estimate of the number of the R· radicals present before the reaction. This estimate may be off by as much as 50% and a limited amount of gas adsorption may be involved, but this does not change the picture. The first step is likely to be the addition of SO_2 to the primary radicals. Most of the gas absorption occurs when the asymmetric singlets are the major fraction of the ESR spectra. The $RSO_2\cdot$ radicals could therefore be considered at least one of the propagating species of the reaction. In this case there should be a correlation between SO_2 uptake and $RSO_2\cdot$, SO_2 being absorbed as long as sulfonyl radicals are present in the system. This is approximately true for propionamide. For *n*-butyramide, isobutyramide, valeramide, and stearamide the SO_2 uptake is practically over while there is still an appreciable concentration of $RSO_2\cdot$ left (Fig. 7). In stearamide the $RSO_2\cdot$ seems to increase even after gas absorption has ceased.

A chain reaction has been observed also in methacrylamide. The propagation does not seem to be based on the addition of $RSO_2\cdot$ radicals to the double bond of the monomer, since under vacuum no regeneration of the growing polymer chain radicals has been observed. The inability of the $RSO_2\cdot$ radicals to add to the double bond under the experimental condition employed has been observed also in another case. The *n*-butyramide radicals were allowed to react with SO_2 and the system was put under vacuum so that both R· and $RSO_2\cdot$ radicals were present. Ethylene, at a pressure of 500 mm Hg, was added. No change or decay of the asymmetric singlet of the $RSO_2\cdot$ radicals was observed, although the ability of ethylene to reach the radical sites was indicated[16] by the fact that the ESR spectrum of the R· radicals changed into the one corresponding to the growing polyethylene radical.

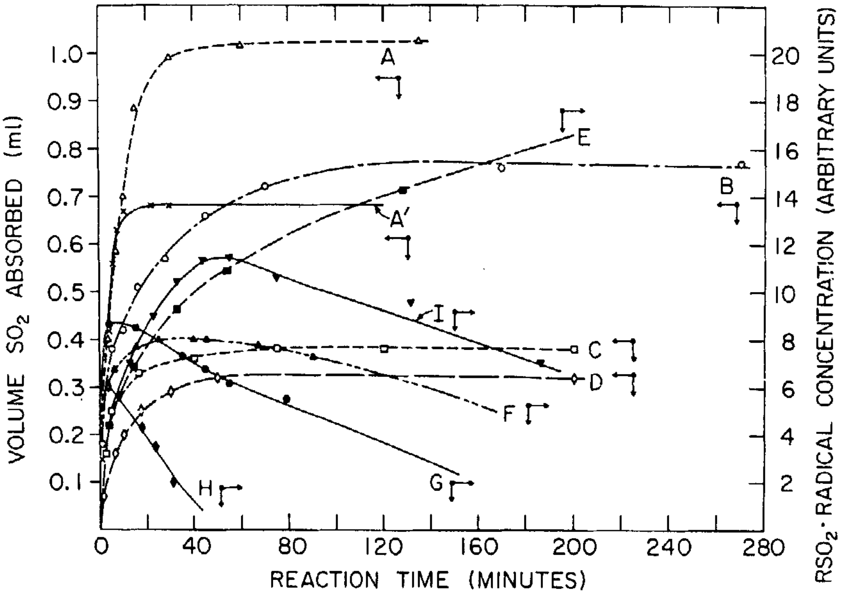


Figure 7. Post irradiation reaction with SO_2.

I SO_2 absorption curves
A, propionamide; B, valeramide; C, stearamide; D, isobutyramide; A^1, *n*-butyramide
II Sulfonyl radical buildup curves.
E, stearamide; F, *n*-butyramide; G, isobutyramide; H, propionamide; I, valeramide.

In all of the amides the rate of $RSO_2\cdot$ formation increases with decreasing particle size and increasing the partial pressure of SO_2. With large crystals the rate of the reaction is so slow that no change in the ESR spectra can be observed within a reasonable time.

When irradiated with a Tesla-coil discharge, the rates of conversion of the R· radicals into the corresponding $RSO_2\cdot$ radicals is about two times higher than with γ-radiation. This suggests that the kinetics of the reactions is influenced by the rate of diffusion of the SO_2 molecules towards the reaction sites. In the case of stearamide, a linear relationship between the number of radicals R· transformed and the square root of the time has been found (Fig. 8) as might be expected in a reaction in which diffusion plays an important role.

Under vacuum (10^{-5} mm Hg), and at room temperature, the $RSO_2\cdot$ radicals decompose regenerating the initial radicals R·

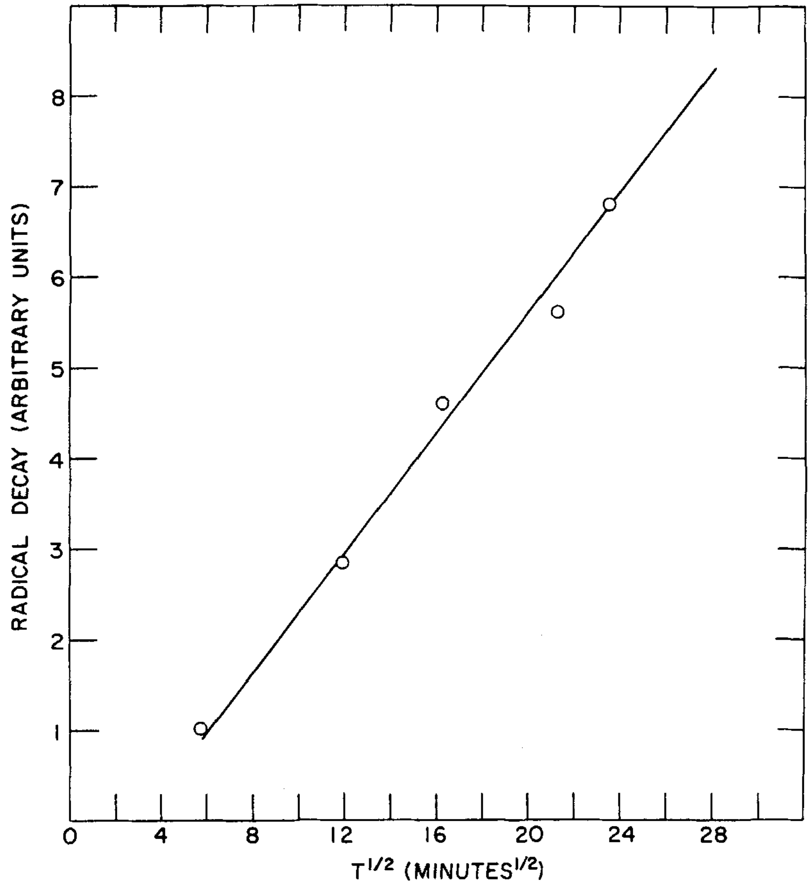


Figure 8. Kinetics of the decay of the initial stearmide radical in the presence of SO_2.

(Fig. 9). The half-time of this process is 2, 12, and 8 min for propionamide-, isobutyramide-, and *n*-butyramide-sulfonyl radicals, respectively. No regeneration of R· radicals has been observed from methacrylamide-, valeramide-, and stearamide-sulfonyl radicals.

This process seems to be related either to the reversibility of the reaction:

$$R\cdot + SO_2 \rightleftarrows RSO_2\cdot \tag{2}$$

or a hydrogen abstraction reaction

$$R - SO_2\cdot + RH \rightarrow RSO_2H + R\cdot \tag{3}$$

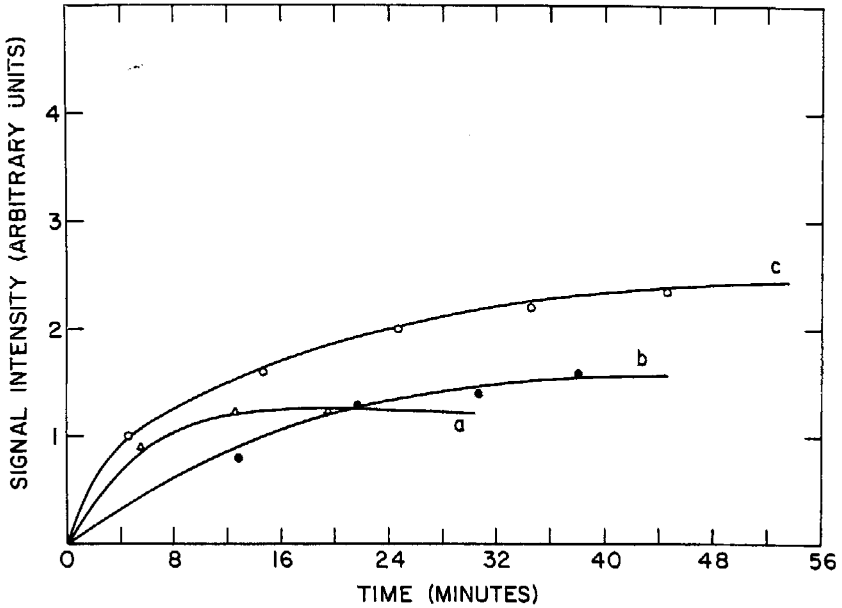


Figure 9. Regeneration of the initial R· radical from RSO_2· under vacuum. (a) propionamide, (b) *n*-butyramide, (c) isobutyramide.

which may also take part in the chain reaction. That reaction (2) plays a part is indicated by the fact that the rate of SO_2 absorption, immediately before the system was put under vacuum, was practically negligible, that is, when the chain reactions were no longer occurring. A loss of about 30% of the radicals present was observed during this process. This could be accounted for by decay of both RSO_2· and R· radicals during the time needed for the experiments. A small amount of sulfonyl radical, less than 5 to 10%, remains undecomposed in the case of *n*-butyramide, even after 24 hr under vacuum.

The readmission of SO_2 into the system results in the re-formation of RSO_2· radicals. The rate of conversion is faster than the one observed during the first conversion and increases still further on additional cycles of evacuation and readmission of SO_2. This effect is accompanied by a change in the shape of the RSO_2· radical ESR spectra. These become more nearly symmetrical (Fig. 10). They finally resemble the signals obtained in the samples irradiated with Tesla-coil discharge, a technique which leads to the formation of

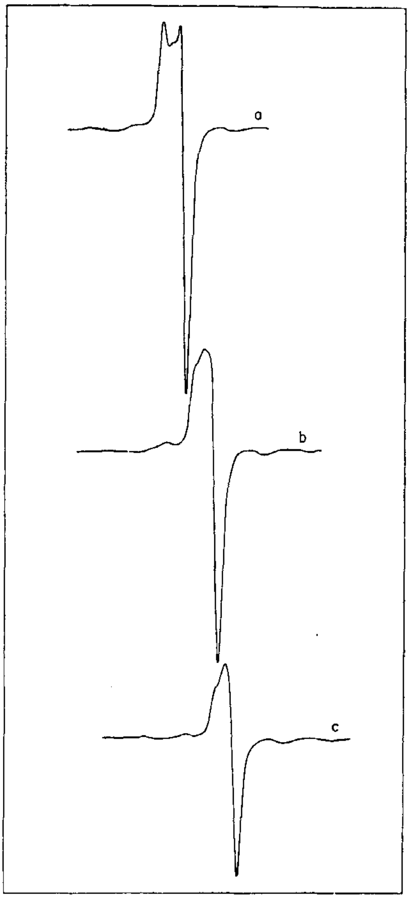


Figure 10. Effect of repeated admission and re-evacuation of SO_2 on the shape of the ESR spectrum of the *n*-butyramide sulfonyl radical.
(a) first admission of SO_2, (b) second admission of SO_2, (c) third admission of SO_2.

radicals at the surface (Fig. 11) where freedom of reorientation of the molecular groups is somewhat greater. The changes in the ESR spectra are probably related to the enhancement of the reorientation freedom of the group carrying the unpaired spin on repeated reaction. This results in a better averaging of the *g* anisotropy and therefore in a more symmetrical signal. Both irreversible changes occurring within the lattice during the reaction and migration of the radicals toward the surface and defect sites may occur and facilitate these effects.

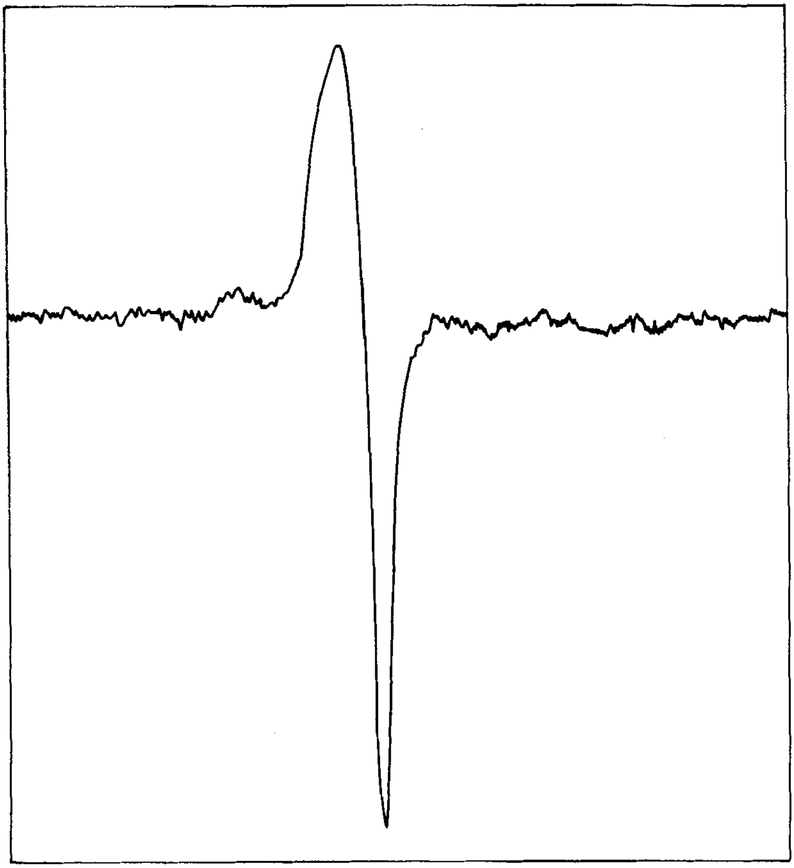


Figure 11. ESR spectrum of the sulfonyl radical generated from Tesla-coil irradiated *n*-butyramide.

The X-ray powder diagrams of the samples which were allowed to react with sulfur dioxide do not show any appreciable shift of the diffraction lines such as was seen upon the addition of oxygen.[5] No lattice expansion can be measured during the reaction, within the limit of the sensitivity of the technique employed. Neither are new lines seen which would indicate the formation of new phases. It should be remembered, however, that these effects might be too weak to be detected, owing to the very low concentration of the reaction products in the system ($\simeq 0.1\%$).

Discussion

As has been shown previously[5] oxygen and nitric oxide are capable of diffusing into the lattice of crystalline amides having a certain type of layer structure and reacting with the free radicals present. In this communication we are dealing with sulfur dioxide, a gas molecule of larger molecular dimensions and weight. In this case too, the reaction is probably not confined to the surface of the crystalline particles. Several observations suggest this. First of all, except in the case of methacrylamide which we shall discuss later, a large fraction of the radicals present do react fairly rapidly with the sulfur dioxide, too large a fraction to be accounted for by reaction at the surface. The rate of reaction of the γ-irradiated samples is more than twice as fast as for the Tesla-coil irradiated material. In the latter case the radicals are all generated at the surface and therefore directly accessible to the gas. Also, for stearamide at least, the linear relationship between the square root of time and the radical decay (Fig. 8) is suggestive of a diffusion controlled reaction.

In contrast to the situation with nitric oxide and oxygen[5] an appreciable fraction of the free radicals does not react rapidly with the sulfur dioxide but seem to decay by some other mechanism. This suggests that many of the radicals are relatively inaccessible to the larger gas molecules. Furthermore, the lack of observable change in the lattice parameters suggests that the sulfur dioxide does not react within the lattice, though this may possibly also be explained by the small amount of product expected to be present.

We would like to suggest that in this case the gas-free radical reaction is confined principally to the radicals present at edged islocations, grain boundaries, surfaces, and similar defects present throughout the crystalline particles. This could explain the lack of change of lattice parameters. It would also explain the large fraction of radicals that seem to decay independently of the sulfur dioxide. These are simply the radicals that are too far from the defects to be accessible. It is also consistent with the reaction of radicals located beyond the surfaces accessible to Tesla-coil irradiation.

In a previous publication (5) we suggested that the diffusion which accompanys the reaction of O_2 and NO with the irradiated amides can be broken down into three components, diffusion down defects such as dislocations, diffusion between the layers of the lattice, and diffusion orthogonal to the layers. Of the three, the first is relatively facile while the third is the slowest, most difficult, and probably would be the most sensitive to the size of the diffusing gas molecules. It should be remembered that radicals α to the amide group would require this last type of diffusion before reaction can occur in the intact lattice.[5] If this type of diffusion were considerably more hindered for the larger SO_2 molecules than for the O_2, than the only radical sites accessible to the diffusing gas would be the ones present at edge dislocations and similar defects. Reaction at these sites would also explain the ease with which the $RSO_2\cdot$ radicals can reorient upon repeated reaction. It may also be true that even at these defects the radical site on the molecule becomes less accessible the longer the hydrocarbon chain length, and the greater the steric hindrance due to chain branching. This would explain the relative rates of reaction between the different compounds.

The picture then emerges of reaction of SO_2 at defects with very slow or negligible reaction at the other sites, except possibly in the case of the more rapidly reacting propionamide. This requires relatively rapid diffusion at defects and very little or negligible diffusion orthogonal to the layer planes of the lattice. This says nothing about the third component, diffusion between the lattice layers. At present we are inclined to believe this kind of diffusion does occur in this case as well as with O_2 and NO. As was noted above, a large fraction of the radical sites do in fact react fairly rapidly. The fraction is large enough to suggest that reaction occurs at all the dislocation sites. It is difficult to believe that all the edge dislocations are connected to the surface. To reach them, diffusion between the lattice layers would be necessary. In considering this possibility for a molecule as large as sulfur dioxide it should be remembered that the lattice spacing in the required direction is quite large and the forces between the layers are the weakest in the crystal.[5] It will be demonstrated subsequently[16] that even ethylene is capable of diffusing between the layers.

The amides so far considered all have the same type of layer structure. This structure was shown to be important in explaining the sensitivity of these materials to oxygen and nitric oxide.[5] The crystal structure of methacrylamide is at present unknown but it does have a different type of structure than the other amides considered in this paper. Its behavior with respect to sulfur dioxide is also different. It reacts more slowly and the extent of conversion to sulfonyl radicals is more limited. Here the process responsible for the reaction must be somewhat different.

Methacrylamide polymerizes in the solid state when irradiated. The free radicals we see at room temperature are those of the polymerizing material.[17] The polymer is amorphous and nucleates as a second phase. This polymerization and the nucleation of polymer phase is a relatively slow process. In this case we believe the sulfur dioxide difuses at the interface between the monomer and polymer phases and reacts with the limited number of free radicals present at the interface. Diffusion in the lattice and down dislocations is probably much more restricted in the case due to the different crystal structure. This would explain why the reaction with sulfur dioxide is so slow and limited in extent. This hypothesis can be supported by another observation. Acetamide, sucinamide, urea, *n*-butyl urea and other amides that do not have the same type of layer structure as the amides considered earlier in this communication, have been shown to be unreactive in the presence of NO and O_2.[18] Methacrylamide[6] and sorbamide,[18] which similarly do not have this type of layer structure, both show a slow and limited reaction with oxygen in the solid phase when irradiated. Both methacrylamide and sorbamide show a reaction in the solid state upon irradiation with the product probably nucleating as a second phase.

Conclusions

It has been shown that propionamide, *n*-butyramide, isobutramide and valeramide, all of which have the same type of layerlike crystal structure, show a relatively rapid reaction with sulfur dioxide. Apparently not all of the radicals react with the gas. It was suggested that the sulfur dioxide can only diffuse relatively freely down defects such as edge dislocations and possibly between the layers of the lattice structure. As a result only the radicals present at defect sites react with the gas.

Methacrylamide has a different type of lattice structure and behaves differently in the presence of sulfur dioxide. Here the reaction with the gas is explained in terms of diffusion of the gas at the interface between the monomer and the polymer phase that arises as a result of a radiation induced polymerization reaction which occurs in this solid. These problems and problems related to the presence of a large number of radicals at defect sites will be explored in subsequent publications.

Acknowledgments

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