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Reactions of Gases with Irradiated Organic Solids IV. Reactions of Propionamide, *n*-Butyramide, Isobutyramide, Valeramide, and Stearamide with Ethylene‡

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Abstract—The reactions of gamma irradiated propionamide, isobutyramide, valeramide and stearamide with ethylene were studied by ESR spectroscopy, gas absorption, and X-ray diffraction. Some degree of polymerization of the ethylene apparently occurs in these systems. The results are discussed.

Introduction

A particular type of layerlike crystal structure appears to be common to the saturated linear monoamides.[1] Preliminary work suggests that isobutyramide, the simplest branched chain amide, also fits into this structural pattern.[2] Free radicals are generated in these compounds when they are irradiated. In previous communications we have shown that reactive gases will react with the free radicals present in these crystals[3,4,5] but not to any great extent with other amides, such as succinamide, having a different type of crystal structure.[2] Oxygen and nitric oxide seem to be capable of diffusing into the lattice between the layers of the

‡ This work was performed under the auspices of the U.S. Atomic Energy Commission.

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crystal structure.[3,4] These gases therefore can reach all the radicals present and react with them; the oxygen initiating a chain peroxidation. The larger molecules of sulfur dioxide appear to react only with the free radicals present near surfaces and crystal defects such as dislocations.[5] Evidence was found in these reactions which suggest that, at least in some circumstances, where annealing can take place, the radicals in these crystals tend to concentrate in the vicinity of defects.

In the course of this work it becomes of interest to see how other gases of different molecular size would behave, especially those capable of undergoing chain reaction. Ethylene and related compounds immediately come to mind. It was hoped that the use of these gases would give some additional information on these irradiated solid–gas reactions. In addition, if a chain reaction did indeed occur, they offered the possibility of a new type of solid state polymerization in which a monomer molecule which is foreign to the crystal diffuses in and becomes polymerized. This communication will present briefly some preliminary results on the reaction of these systems with ethylene.

Experimental

The purification and irradiation of the amides, the electron spin resonance, gas volumetric, and X-ray diffraction measurements were all made using the previously described techniques.[3,4,5] The concentration of free radicals was determined by comparison with a pitch standard and double integration. Matheson research grade ethylene was used. The radiation doses used ranged from 18–23 Mrad. A ^{60}Co source was the radiation source. The irradiations were performed at $-80\,^{\circ}$C and the measurements were made at $25\,^{\circ}$C.

Results and Discussion

When ethylene is admitted to the γ-irradiated powdered amides, a change occurs in the ESR spectra of all the observed

amides except isobutyramide. This is shown in Figs. 1 to 4. The spectrum of isobutyramide remains unchanged and is identical with that shown in Fig. 3a Ref. 5. There is a simultaneous absorption of ethylene in all cases, including isobutyramide (Fig. 5). The change in ESR spectrum is easily seen in *n*-butyramide, Fig. 1. The change begins on admission of the ethylene. At an intermediate stage the spectrum is that shown in Fig. 1b.

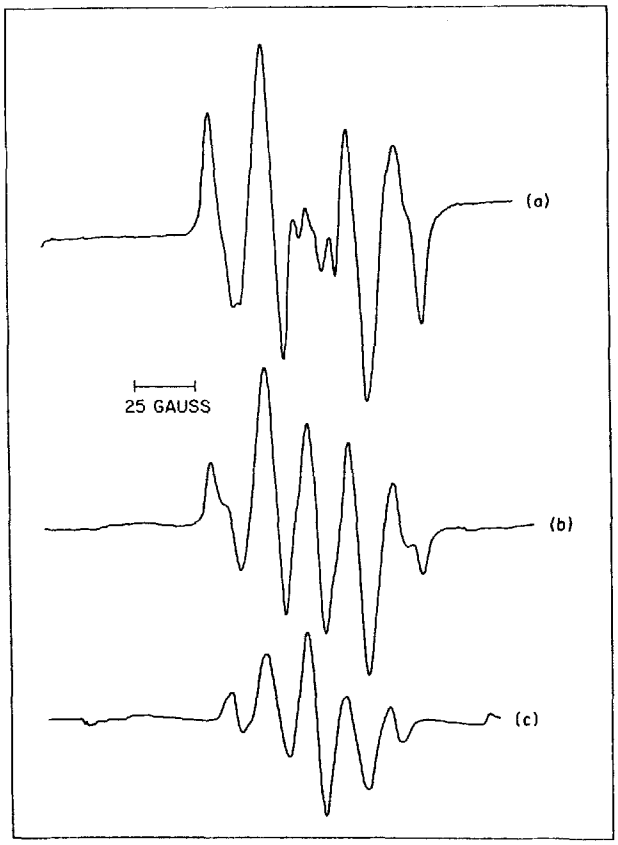
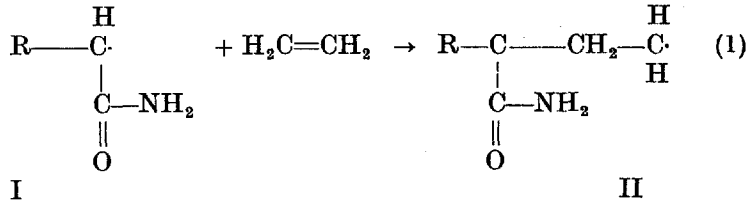


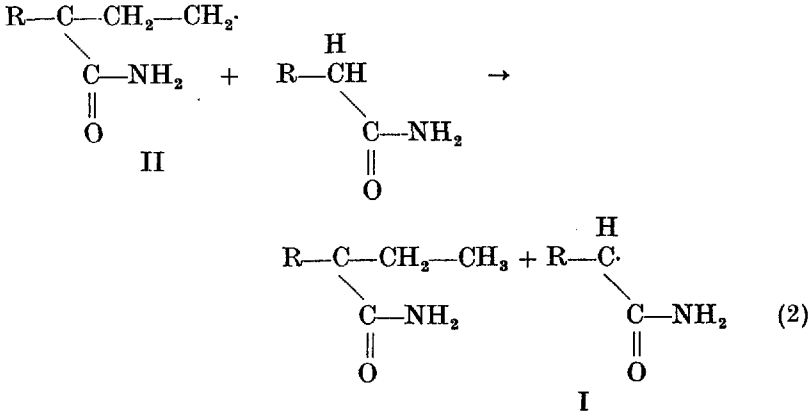
Figure 1. ESR Spectra of *n*-butyramide. Radiation dose 20 MR. (a) before admission of ethylene. Gain 125; (b) 7 minutes after admission of ethylene. Gain 125; (c) 245 minutes after admission of ethylene. Gain 125. Ethylene pressure 471 mm.

When the change in spectrum is complete, it has the form shown in Fig. 1c. There is simultaneously some decay in the number of free radicals. The resultant spectrum has five peaks with an almost binomial distribution in peak height. From this point on the spectrum appears to have a reasonably stable form remaining unchanged in shape for long periods of time. Even putting the sample under vacuum again will not change it. This suggests a radical of the type $R—CH_2—CH_2^{\cdot}$, where the dot stands for the unpaired electron of the free radical. This would be accounted for by the following reactions:



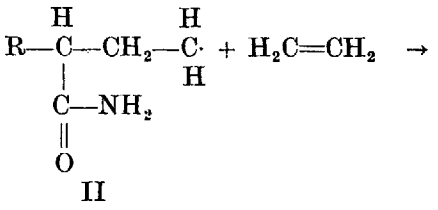
(1)

where R stands for $CH_3—CH_2—$ in the case of *n*-butyramide. Ethylene adds to the radical already present (radical I) to form radical II. One of two things can now happen. Radical II can abstract a hydrogen atom from a neighboring butyramide molecule resulting in a 6 carbon amide and regenerating radical I as shown:

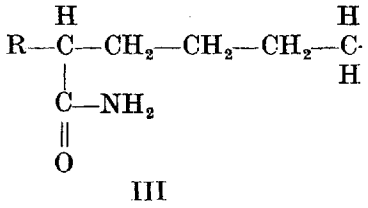


(2)

The combination of reactions 1 and 2 would result in the spectrum observed provided reaction 1 is much faster than reaction 2. The alternative is that additional ethylene adds to radical II as shown in reaction 3:



II



III (3)

Radical III could add more ethylene to give a growing polymer molecule. This would also account for the five line spectrum.

In the case of *n*-butyramide and the other linear amides the evidence seems to suggest the latter mechanism (Eq. (3)) for the reasons given below.

When the number of moles of ethylene absorbed in the reaction is compared with the concentration of free radicals originally present (Table 1) it becomes evident that a chain reaction is

TABLE 1

Compound	Moles of ethylene adsorbed per mole of free radicals
propionamide	87
n-butyramide	276
isobutyramide	131
valeramide	111
stearamide	300

involved. This is consistent with both the mechanism of Eq. (2) and Eq. (3). It was shown in Ref. 4 that when oxygen is added to these systems, a relatively rapid reaction occurs. The reaction involved is similar to Eq. (2) except that oxygen, which cannot polymerize, is involved instead of ethylene. The reaction is reflected in a very rapid decrease in the ESR signal. A similar decrease would be expected in this case if reaction 2 were important. It does not occur. This is consistent with the polymerization reaction, Eq. (3).

We have been able to isolate a small amount of material, insoluble in methanol from the dissolved sample. The amount was too small to characterize adequately but its behavior was consistent with polymer, probably of relatively low molecular weight. Finally, some crystals were washed or partially sublimed to remove or clean the surface. When these were observed by optical and scanning electron microscopy, small masses of material were seen whose appearance was consistent with polymer.

Stearamide seems to behave similarly to *n*-butyramide. It has been shown that there are two free radicals in irradiated stearamide, one less accessible to the diffusing gas than the other.[3] The final ESR spectrum, Fig. 2, can be accounted for by the superposition of the same five line pattern seen on addition of ethylene to butyramide and some amount of the free radical in stearamide which would be less accessible to the gas.

The behavior of valeramide and propionamide is somewhat different. Figure 3b shows an intermediate stage in propionamide. The spectrum can apparently be explained by an admixture of the original five line pattern with a new one possibly having four lines. Figures 4b and c show the intermediate and final stage of the spectrum of valeramide. A four line pattern with an almost binomial peak height distribution is apparent. In addition, shoulders can be seen on the outer lines in 4c which may indicate a second radical, possibly a trace of the original one. The four line spectrum presents some difficulty. It seems probable that the radicals here are similar to the ones in *n*-butyramide and stearamide. Perhaps the difference lies in the conformation of

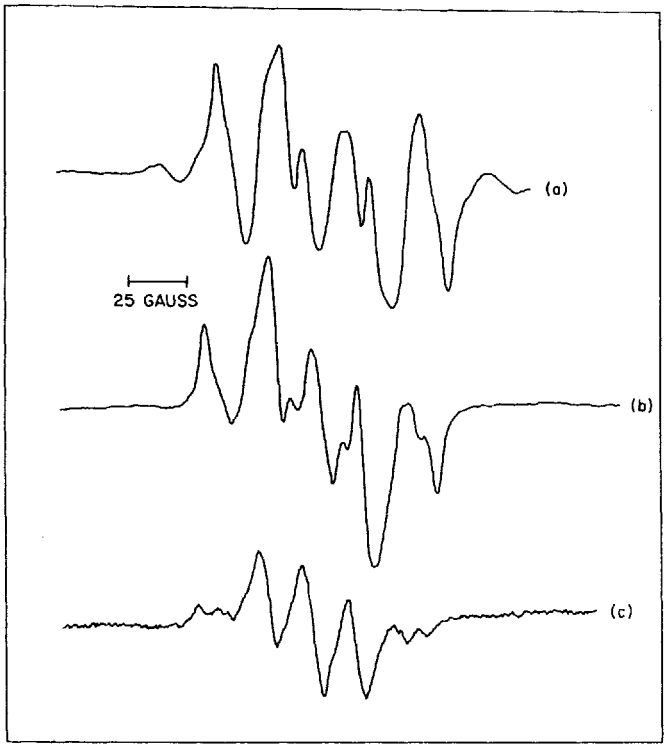


Figure 2. ESR Spectra of Stearamide. Radiation dose 24 MR. (a) before admission of ethylene. Gain 160; (b) 53 hr after admission of ethylene. Gain 400; (c) 168 hr after admission of ethylene, Gain 800. Ethylene pressure 489 mm.

the growing radical. If the methylene group at or next to the chain end could not rotate freely and one of the protons was at such an angle so as to be almost in the plane of the radical, its coupling constant might be less than the line width. In that case only the other three protons would given rise to a detectable hyperfine splitting, accounting for the four line pattern. It is at present difficult to see why there should be less rotational freedom and a difference in conformation when compared with *n*-butyramide and stearamide. It is interesting to note, however, that

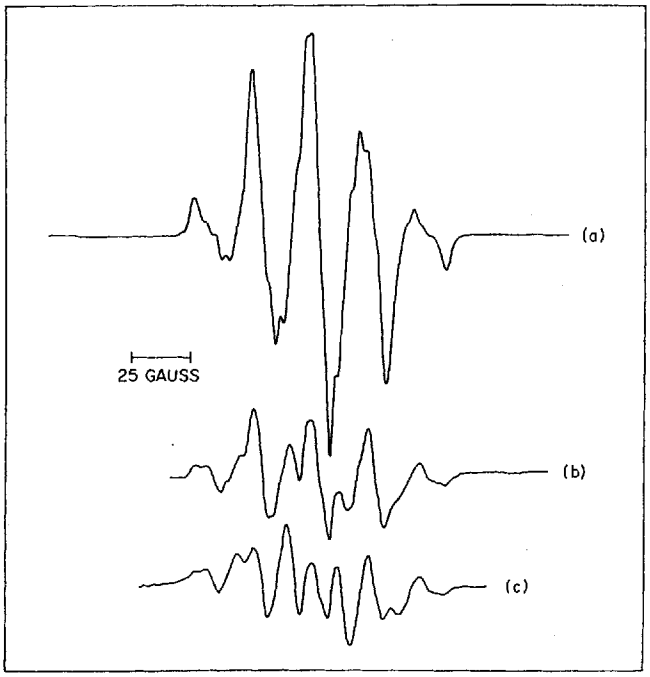


Figure 3. ESR Spectra of Propionamide. Radiation dose 22 MR. (a) before admission of ethylene. Gain 160; (b) 5 minutes after admission of ethylene. Gain 160; (c) 66 minutes after admission of ethylene. Gain 400; Ethylene pressure 590 mm.

butyramide and stearamide have an even number of carbon atoms whereas propionamide and valeramide have an odd number. Davies *et al.*[6] have shown that odd carbon amides show a different sequence of lattice energy dependence on the carbon number than the even carbon amides and that the even carbon amides break up into two series depending on the number of carbon atoms. It may also be significant that the kinetic chain length of the reaction, as reflected in the ethylene uptake, is a factor of two or three greater in stearamide and *n*-butyramide than it is in propionamide and valeramide (see Table 1).

Isobutyramide is the simplest of the branched chain amides and

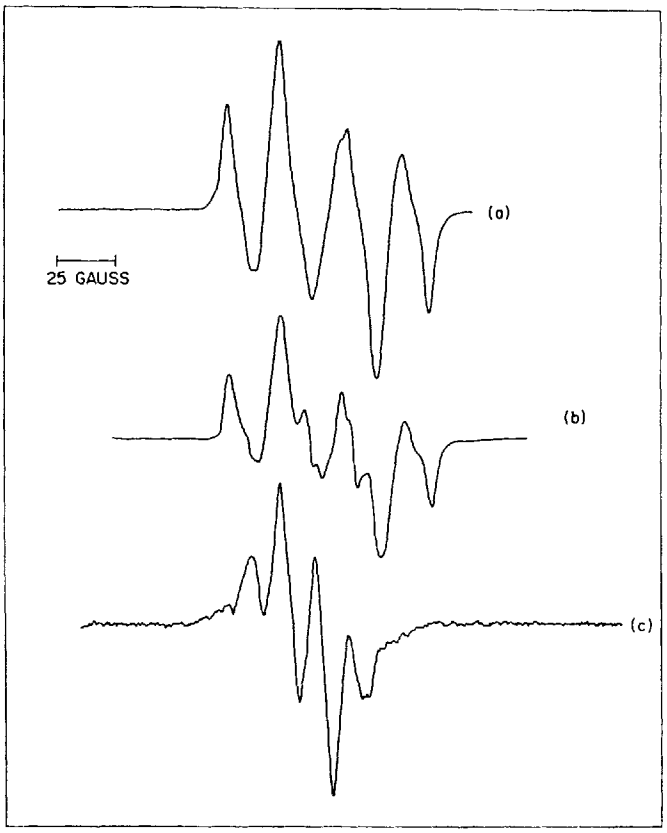
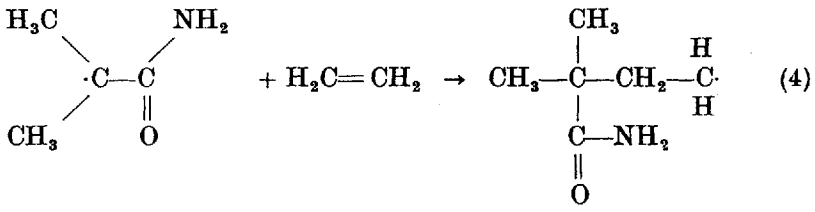


Figure 4. ESR Spectra of Valeramide. Radiation dose 20 MR. (a) before admission of ethylene. Gain 60; (b) 3 hrs after admission of ethylene. Gain 200; (c) 408 hrs after admission of ethylene. Gain 800; Ethylene pressure 549 mm.

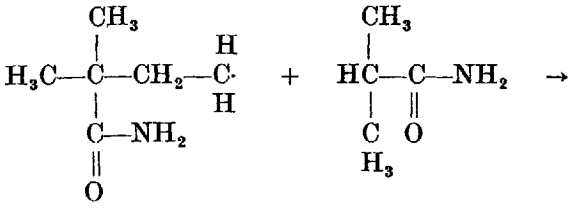
is apparently similar in crystal structure to the others. As noted above, its ESR spectrum does not appear to change on addition of ethylene. However, the absorption of ethylene seems to indicate that extensive reaction is occurring.

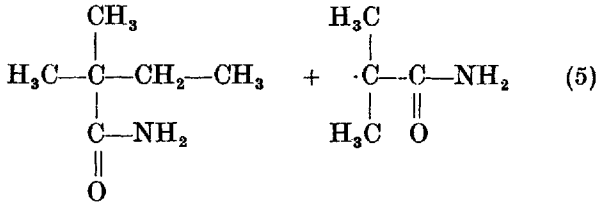
Isobutyramide has only a single tertiary hydrogen atom β to the amide group. Tertiary hydrogen is more reactive than the secondary hydrogens in the other amides and therefore would be

more easily abstracted in a reaction analogous to that in Eq. (2). The sequence of reactions would in this case be:



(4)





(5)

Reaction 5 is the analog of reaction 2. If it were much more rapid than reaction 4, then only a spectrum like that of the original radical can be seen. The amount of growing chain radical would then be relatively small due to the ease of abstraction of the tertiary hydrogen. Little polymer would be formed.

During the course of the reaction in these compounds, the concentration of chain radicals (radicals of type III) appears to increase at first then slowly decreases. This indicates a chain termination step. The rate of decay of the polymer radials depends on the system considered. The ESR spectra can be recorded several days after the beginning of the reaction in stearamide and *n*-butyramide. In propionamide the spectrum decreased below the level of detectability in about seven hours.

If the X-ray powder spectra of these materials before irradiation are compared with that after irradiation, some differences become apparent. Some of the lines become broader and a few of the lines, probably those reflecting the layer spacing of the crystal lattice, shift to greater *d* spacing (smaller angle). The change in *d* spacing for the most intense reflection is shown in Table 2, This shift is

TABLE 2

Compound	Radiation dose, MR	*d* spacing Å‡ before irradiation§	After reaction with ethylene
n-butyramide	20	10.02	10.13
isobutyramide	24	9.79	9.83
propionamide	24	8.30	8.38
valeramide	24	10.88	10.99
stearamide	23	12.05	12.37

‡ Cr Ka radiation used for diffraction.

§ Most intense reflection. There is no observable difference in *d* spacing between unirradiated and irradiated samples at these doses before reaction with ethylene.

reasonably evident in all cases except one. The small shift and broadening of the line in isobutyramide makes it a little less clearcut here. In the reaction of these amides with oxygen, the expansion of the lattice was considered as one among several pieces of evidence taken to indicate that reaction took place within the lattice and not just at surfaces and dislocations.[3,4] However, in that instance the free radical spectrum changed and decayed rapidly. With ethylene the spectrum changes more slowly and for much of the time shows the simultaneous presence of both the ethylene addition radical and the radical originally present. In this respect, the behavior is similar to that which occurs on addition of sulfur dioxide. However, when sulfur dioxide is added there is no apparent change in lattice parameters.[5] This was taken to indicate that the reaction with the larger sulfur dioxide molecule is confined to surfaces and dislocations. Ethylene is intermediate in molecular size between oxygen and sulfur

dioxide and seems to be intermediate in behavior. Probably the initial reaction is at defects but, due to its size, the product molecule distorts the lattice around it sufficiently so that the ethylene can begin to diffuse into it slowly.

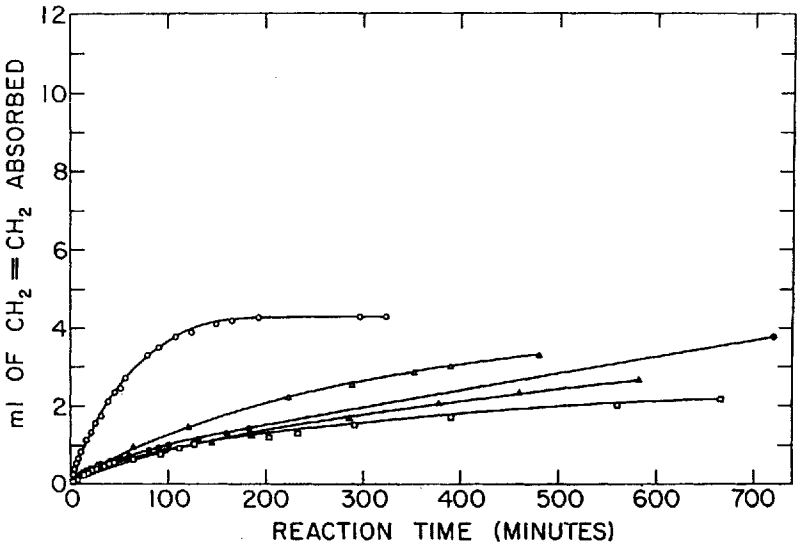


Figure 5. Ethylene absorption in γ-irradiated amides. Radiation dose 24 MR.

○ = propionamide, ethylene pressure 580 mm
△ = isobutyramide, ethylene pressure 580 mm
● = stearamide, ethylene pressure 580 mm
▲ = *n*-butyramide, ethylene pressure 356 mm
□ = valeramide, ethylene pressure 580 mm

The result of the reaction is a solid solution of the product and the amide. The lattice parameters must then change in accordance with Vegard's law. The change is not as big as might be expected probably because much of the reaction is confined to dislocations and surfaces. Isobutyramide shows a smaller change than the others since the product molecule, in this case, a six carbon amide, is smaller than the polymer molecule resulting from the other amides. The reflections become broader after reaction probably for two reasons. The strain induced in the lattice by the reaction

may cause breakup into smaller, more disoriented mosaic structures. In addition the reaction, as described above, may not take place uniformly throughout the lattice, being greatest near defects. The result would be a spread in lattice parameters.

Conclusions

It seems fairly probable that when ethylene is added to γ-irradiated powdered *n*-butyramide and stearamide, polymerization occurs. In the case of valeramide and propionamide polymerization is somewhat less probable. However, a chain reaction still occurs but the kinetic chain length is somewhat smaller. In isobutyramide, ethylene apparently adds to the free radical but then a tertiary hydrogen atom is probably abstracted from a neighboring molecule. This reaction is analogous to the chain transfer reaction fairly common in polymerization. The lack of change in the ESR spectrum in this case can be explained if the hydrogen abstraction step is much faster than the ethylene addition. This is likely especially if the diffusion of ethylene to the reaction site is slow. It is possible that some amount of chain transfer occurs in all these reactions. The resulting polymer then would not have a particularly large molecular weight.

It was previously shown that oxygen and nitric oxide diffuse fairly readily into the lattice and react rapidly with all free radicals present.[3,4] On the other hand, sulfur dioxide, being a larger and heavier molecule, appears to react only with the more accessible radicals present at surfaces and defects.[5] The ethylene reaction is intermediate between the two. The ESR spectra indicate that the free radicals are less accessible to ethylene than they are to oxygen and that diffusion to the reaction site is slower, On the other hand, the change in lattice parameters suggests that the gas does react within the lattice. It should be borne in mind that the radiation induced free radicals form a dilute solid solution throughout the host lattice though there probably is some degree of concentration near defects. It seems, therefore, consistent with the results obtained with other gases, that the reaction with ethylene is diffusion controlled. It occurs first at the sites most

readily accessible to the diffusing gas, such as surfaces and dislocations, but reactions within the lattice eventually occurs.

Preliminary evidence seems to indicate that propylene, which is a larger molecule, results in less lattice expansion than ethylene and butadiene, which is even larger, produces negligible lattice change in lattice spacing of the crystal though it is capable of reacting with the accessible free radicals. Evidently, in these gas–solid reactions, the size and shape of the diffusing molecule as well as the structure of the host lattice is an important parameter.

Acknowledgements

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