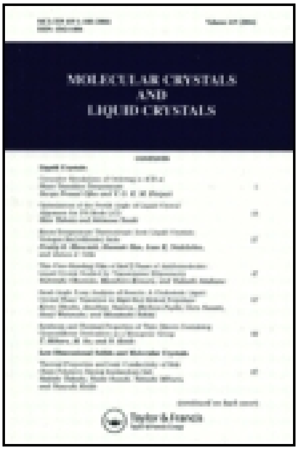

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Reactions of Gases with Irradiated Organic Solids

II. Reactions of Propionanmide, *n*-Butyramide, Isobutyramide, and Stearamide With Oxygen and Nitric Oxide‡

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Abstract—When organic solids are subjected to ionizing radiation free radicals which often persist for long periods of time are generated. It is shown here that the free radicals in irradiated crystalline propionamide, *n*-butyramide, isobutyramide, and stearamide can react rapidly with oxygen, nitric oxide, and similar gases. Evidence has been obtained from electron spin resonance, X-ray diffraction, gas absorption, and end-product analysis that the gases diffuse into the crystalline lattice of the amides reaching the radical sites and initiating chain reactions which are influenced by the diffusion rate. The layer type crystal structure which is found in these compounds is important in understanding these effects.

With oxygen, the first step in the reaction is the formation of peroxy radicals. The reaction is then propagated by a hydrogen abstraction mechanism with the formation of hydroperoxides and ketoamides.

With nitric oxide the picture is less clear. There is evidence from ESR spectra for the formation of iminoxy radicals whichreact further with nitric oxides.

It has been shown by Lingafelter and Turner[1] that the linear unsubstituted mono-amides, at least from proionamide to hexadecanamide, all crystallize in the same space group with two of the lattice para-

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meters roughly similar. The third lattice parameter varies systematically with the hydrocarbon chain length. The only exception was nonamide. Lingafelter and co-workers[2,3] then determined the crystal structure decanamide and tetradecanamide and found them to be almost identical except for the hydrocarbon chain length. This seems to indicate that with the exception of acetamide and possibly nonamide, the linear monoamides form a series all of whose members have a very similar crystal structure. This crystal structure can be described in the following terms. The molecules are hydrogen bonded through the amide group to form dimers. The dimers are further hydrogen bonded into sheets or layers. The amide groups form the core of each layer and the hydrocarbon groups the outside. The crystal structure is made up of stacks of these layers.

Acrylamide and propionamide[4] have been shown to have this same type of structure and there is some preliminary evidence that isobutyramide, the simplest of the branched chain amides fits this pattern also.[5] In addition, it has been demonstrated that when oxygen is admitted to irradiated propionamide or solutions of acrylamide in propionamide, the ESR spectrum is rapidly quenched and polymerization is inhibited.[4,6] This was explained in terms of the ability of the oxygen to diffuse between the layers of the crystal structure and react with the free radicals previously induced by radiation. This implied that a layer-like crystal structure with relatively large distances and weak forces between layers was the key to the reaction and suggests that the other amides with similar lattice structure should exhibit the similar phenomena and that it may be feasible to use other reactive gases. In a previous publication[7] we have shown that this, indeed, may be true. In this and the following communications, we extend and amplify these observations.

Experimental

Propionamide, *n*-butyramide, isobutyramide were twice recrystallized from acetone, and stearamide was recrystallized from ethanol. The powdered samples have been prepared by grinding and sieving. Only material passing 0.064 mm and retained by 0.044-mm mesh sieves were used in the attempt to get a relatively uniform particle size. The large crystals of isobutyramide and *n*-butyramide were prepared by slow cooling to room temperature of the solutions in acetone saturated at few degrees above room temperature. Research grade (Matheson) oxygen and nitric oxide were used.

All the experiments, except when otherwise specified, were done using the postirradiated technique. The samples were irradiated at – 78 °C under vacuum in the underwater Co^{60} radiation facility at Brookhaven National Laboratory,[8] at dose rates of 1 to 6 Mrads/hr. After irradiation, the samples were warmed to room temperature, re-evacuated for at least 15 min to remove radiolytic gases, and then allowed to react with the proper gas. Dosimetry was done by the Fricke method.[9]

All the gas absorption measurements were made at constant pressure using a conventional manostatic apparatus. The containers for the samples were equipped with break seals, ground glass joints, and narrow tubes (2.5-mm external diameters) so that they could be attached to the vacuum system for the absorption measurements, or to a 50-ml flask containing the gas for the ESR measurements during the reaction.

For the ESR measurements, an X-band Varian spectrometer with 100-kc modulation and a rectangular cavity was used. The radical concentrations were measured by double integration of the first derivative pattern and compared with a standard sample of strong pitch containing a known concentration of unpaired spins.

Where only relative values of the radical concentrations were needed, the height of the first derivative peaks was used, provided that no change of the shape of that part of the spectrum occurred during the reaction. Owing to the high reaction rate, the buildup of peroxy radicals under oxygen and the decay of the initial radicals under nitric oxide were measured by centering the magnetic field on a peak maximum of the first derivative of the proxy radical or of the initiating radical signals and following the peak height as a function of time.

After the reaction with oxygen, the hydroperoxide content was determined by conventional iodometric titration, under a nitrogen atmosphere, using 0.01 normal $Na_2S_2O_3$. The carbonyl compounds were determined quantitatively by reaction with 2, 4-dinitrophenyl hydrazine method, and have been identified as α-ketoamides by polarography and by IR. The polarograms were made in 0.1 N KCl with a Metrohm polarograph, using a dropping mercury electrode.

The infrared spectra were made using the KBr pellet technique.

The X-ray diffraction measurements were made on powdered samples before and after irradiation and reaction with the gases. A G.E. X-ray diffractometer and Cr$k\alpha$ radiation were used. NaCl was included with some of the samples to act as an internal standard for diffraction.

Results

A. The Nature of the Initiating Radicals

The ESR spectra of the radicals obtained by γ irradiation of propionamide, *n*-butyramide, and isobutyramide, at least after warm-up to room temperature, can best be interpreted in terms of the radicals being formed by the loss of the hydrogen α to the amide group.[7,10,11] In stearamide it seems necessary to invoke the presence of two radicals, one with the unpaired spin α to the amide group, which we shall call the α-radical, and the other one nearer the other end of the hydrocarbon chain which we shall call the x-radical. These seem to decay at different rates so that the over-all shape of the ESR spectrum changes with time. All these radicals decay with time even if the sample is kept under vacuum. As will be shown below, the rate of decay increases many fold on admission of the proper reactive gas. The ESR spectra are shown in ref. 12.

B. Reaction with Nitric Oxide

i. *Decay of the initiating radicals under nitric oxide.* Nitric oxide reacts with the radicals in γ-irradiated powdered propionamide, *n*-butyramide, and isobutyramide resulting in a very fast decay without change of the shape of the spectrum (Fig. 1).

Because of the radical nature of NO it is likely that the decay occurs according to the reaction.

$$R\cdot + NO \rightarrow RNO$$

which is diffusion controlled even when finely powdered samples are used. In fact, a linear relationship which holds up to a decay of 30 to 50% (Fig. 2) has been found between the fraction of radicals decayed and the square root of the reaction time, as might be expected from diffusion controlled processes.[13] The slopes of the curves reported in Fig. 2 should be proportional to the diffusion coefficients so that the

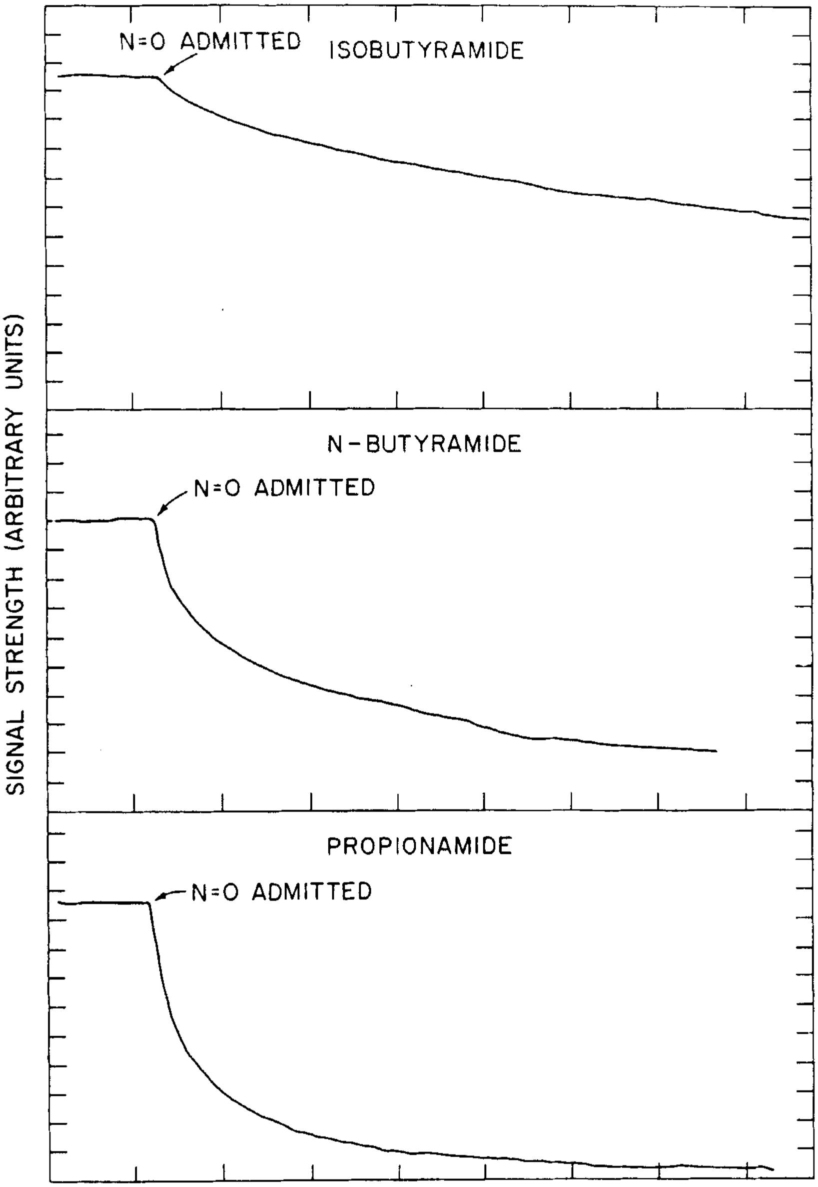


Figure 1. Decay of the initiating radicals under nitric oxide in γ-irradiated propionamide, *n*-butyramide and isobutyramide.

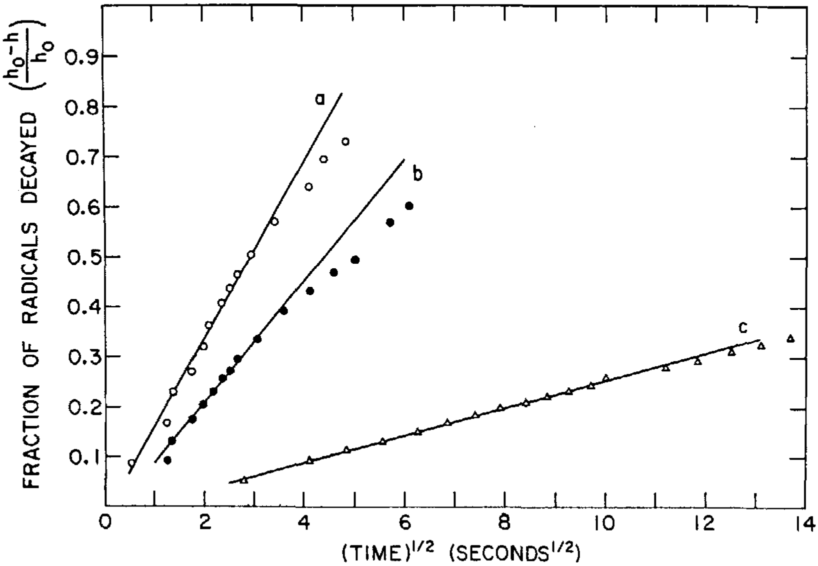


Figure 2. Kinetics of the decay of the initiatal radicals under nitric oxide in γ-irradiated propionamide, n-butyramide and isobutyramide.

approximate relative values for the three amides can be obtained, provided that the average particle size and shape do not change too much. Then we have:

$$D_{\text{propionamide}}:D_{n\text{-butyramide}}:D_{\text{isobutyramide}} = 6.4 : 4.4 : 1$$

Stearamide presents a more complex picture. Under nitric oxide one of the two radicals initially present, the x-radical, decays much more rapidly than the α-radical. As a consequence, the shape of the spectrum changes until only the α-radical spectrum is present near to the end of the reaction (Fig. 3). From that point on, the shape of the spectrum remains unchanged while the decay goes on at a slower rate.

These results can be explained rather simply by a diffusion controlled reaction mechanism in which diffusion can be broken down into three components, diffusion down lattice defects such as dislocations, grain boundaries, etc., diffusion between the layers of the lattice, and diffusion orthogonal to these layers. Dislocation diffusion is the most rapid. It will de discussed in subsequent publications. Diffusion between the lattice layers is indicated by the fact that all the amides we have worked with having this type of layer structure show this reaction whereas amides such as acetamide,

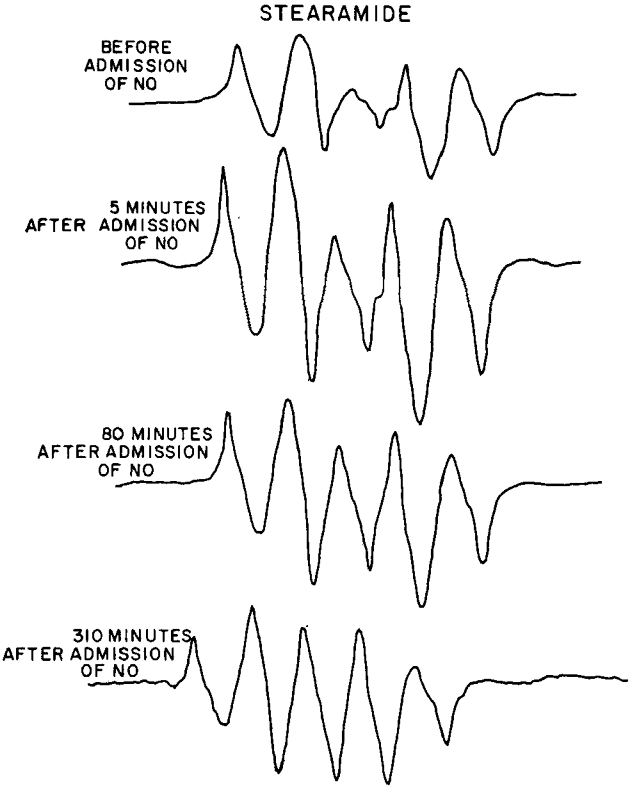


Figure 3. Changes in the ESR spectrum of γ-irradiated stearamide during the reaction with nitric oxide ($P_{NO} = 200$ mm Hg. The initial spectrum of the stearamide here has already shown appreciable decay of the X-radical. (Compare with Fig. 5 ref. 12).

succinamide, urea, and others having a different type of crystal structure do not.[5] Furthermore, the free radicals were generated in these crystals using high energy γ-radiation. Although a large fraction of the radicals may be in the vicinity of defects and surfaces, it is very unlikely that all are. Yet, the nitric oxide seems able to react with all the radicals. This, again, indicates penetration of the lattice by the gas.

The third component of diffusion is apparently the slowest. It should be remembered that the radicals we are considering are α to the amide group and are, therefore, separated from the plane in which the gas is presumed to diffuse by the rest of the hydrocarbon group. Thus, the longer and larger the hydrocarbon chain the greater the distance orthogonal to the layer the gas must diffuse in order to reach the reactive site. Therefore, the reaction should be slower in *n*-butyramide than in propionamide, as is observed. This pattern seems to hold for valeramide, hexamide, and other amides.[5] Isobutyramide has an extra methyl group which can sterically hinder diffusion both in the layer plane and orthogonal to it. It, therefore, shows a slower reaction note than the other two.

We can now explain the interesting case of stearamide. The x-radical is nearer the chain end than the α-radical and, therefore, closer to the layer plane in which the NO diffuses. It should react fairly rapidly. The α-radical is a relatively large distance from the plane and a longer diffusion path is required before the gas can react with it. Its reaction rate is, therefore, slower than that of the other compounds.

This pattern of reaction rate cannot easily be explained other than by diffusion of the gas in the lattice. If the radicals were all on the surface and in dislocations and grain boundaries, the radicals would probably all be more nearly equally accessible to the gas and it seems unlikely that this pattern of reaction rates would be found.

ii. *Nitric oxide absorption measurements.* The ratio of the number of molecules of nitric oxide absorbed to the number of radicals reacted is 22 for propionamide and *n*-butyramide and 9 for isobutyramide, judging from the estimate of the radical population before the admission of the gas (Table 1). This estimate may be off by as

TABLE 1 Postirradiation Reactions With Nitric Oxide

Compound[a]	N=O absorbed, moles/g[b]	Initial concentration[c] of radicals, No. of radicals/g	Moles of N=O absorbed / Moles of radicals reacted	Dose, megarads
Propionamide	0.833×10^{-5}	2.3×10^{17}	21.7	29
	0.690×10^{-5}	1.60×10^{17}	26	17
n-Butyramide	1.37×10^{-5}	30×10^{17}	26.5	14.5
Isobutyramide	0.42×10^{-5}	2.70×10^{17}	9.1	14.5

[a]. Powdered samples sieved between 0.04 and 0.06-mm mesh opening sieves.

[b]. Measurements made at constant pressure of nitric oxide. $P_{NO} = 30$ cm Hg.

[c]. Samples irradiated under vacuum at − 78 °C and then allowed to stand at roon temperature for 60 min before admission of the gas.

much as 50%, but this doesn't change the picture. The over-all reaction, therefore, seems to be a chain reaction propagated presumably by addition of NO to the nitroso compounds which are initially formed. This would accord with the mechanism postulated for the gas phase and liquid phase reaction of NO with radicals.[14,15] The possible occurrence of a chain reaction is also suggested by the fact that only 20% of the final amount of NO has been absorbed when 75% of the original radicals have already decayed as judged by the ESR spectra (Fig. 4). The shorter chain length observed for

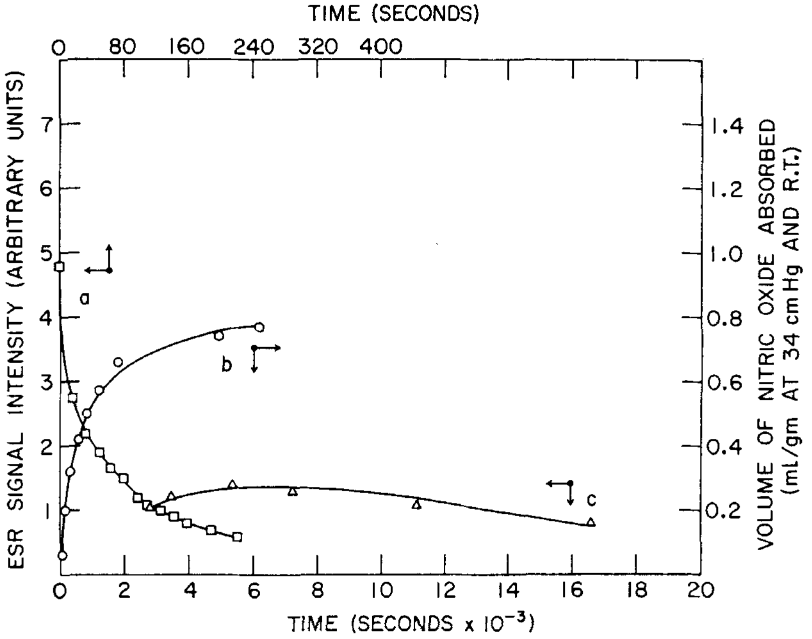


Figure 4. Reaction of γ-irradiated *n*-butyramide with nitric oxide (P_{NO} = 340 mm Hg; γ dose = 14.4 Mrad).
(a) decay of the initiating radicals, (b) nitric oxide uptake, (c) build up of the iminoxy-radical-nitric oxide adduct.

isobutyramide suggests that the pattern of the reaction may be different when tertiary nitroso compounds are involved. It is unlikely that absorption can account for more than a small fraction of the gas uptake, since no similar uptake was found for the unirradiated material.

iii. *Formation of iminoxyradicals.* After the decay of the original radicals under nitric oxide the propionamide and *n*-butyramide samples were put under vacuum (5×10^{-4} mm Hg). A new signal was observed in the ESR spectrum which corresponded to the formation of a new radical (Fig. 5). The spectrum was asymmetric and

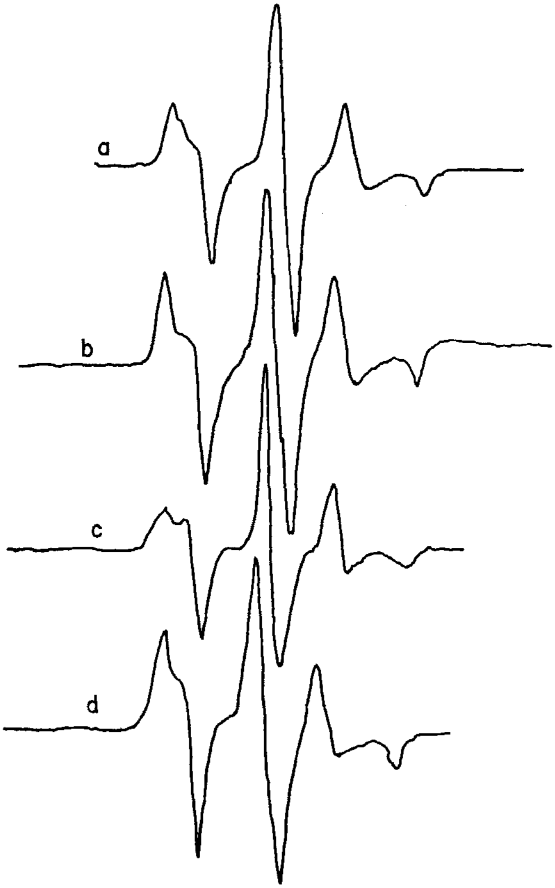
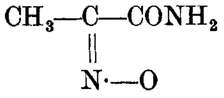


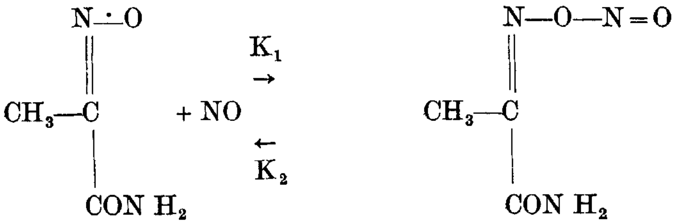
Figure 5. ESR spectra of the radicals formed in propionamide and *n*-butyramide after the postirradiation reaction with nitric oxide followed by re-evacuation of the samples.
(a) propionamide: γ dose 25 Mrad, $P_{NO} = 260$ mm Hg put under vacuum after 6 hrs 40 min. under NO. Spectrum recorded at room temperature. (b) propionamide: spectrum recorded at − 196 °C, (c) *n*-butyramide: γ dose 15 Mrad, $P_{NO} = 250$ mm Hg, put under vacuum at − 78 °C; spectrum recorded at 25 °C, (d) pyruvamidoxime: γ dose 4 Mrad under vacuum at − 78°; spectrum recorded at 25 °C.

seemed to be constituted of three main lines (splitting 28 to 30 gauss), each line showing evidence of a smaller splitting. This suggests that we were dealing with iminoxy radical of the type:



$$CH_3\text{—}\underset{\substack{\| \\ N^{\cdot}\text{—}O}}{C}\text{—}CONH_2$$

This class of radicals is characterized by a large hyperfine splitting due to the nitrogen ($a_N = 30$ gauss) and a much smaller splitting (1 to 15 gauss) due to α and β coupling and which shows angular dependence.[16,17] The spectra obtained in this way for propionamide and *n*-butyramide are practically identical to the one obtained by γ-irradiation of solid powdered pyruvamidoxime under vacuum (Fig. 5d). This supports the view that the observed radicals are iminoxy radicals since the oximes show selective hydrogen abstraction from the =N—OH group under γ-irradiation.[18,19] Nitric oxide adds immediately to the iminoxyradicals resulting in the elimination of the unpaired spins. The process can be reversed. This suggests the existence of the following equilibrium:



$$CH_3\text{—}\underset{\substack{| \\ CON\,H_2}}{\overset{\substack{N\cdot\text{—}O \\ \|}}{C}} + NO \underset{K_2}{\overset{K_1}{\rightleftarrows}} CH_3\text{—}\underset{\substack{| \\ CON\,H_2}}{\overset{\substack{N\text{—}O\text{—}N=O \\ \|}}{C}} \qquad (1)$$

The rate of the forward reaction seems several hundred times faster than the rate of the reverse (Fig. 6) and the equilibrium is practically completely shifted on the right side when external pressures of NO around 30 cm Hg and powdered samples are used. Under these conditions it is unlikely that the iminoxy radicals undergo other reactions besides the reaction with nitric oxide.

The rate of decay of iminoxy radicals under a constant pressure of nitric oxide is considerably faster than the rate of decay of the initiating radicals and follows first order kinetics (Fig. 7). This implies that the rate diffusion of the NO molecules to the sites of the iminoxy radicals has increased to such an extent that diffusion is no

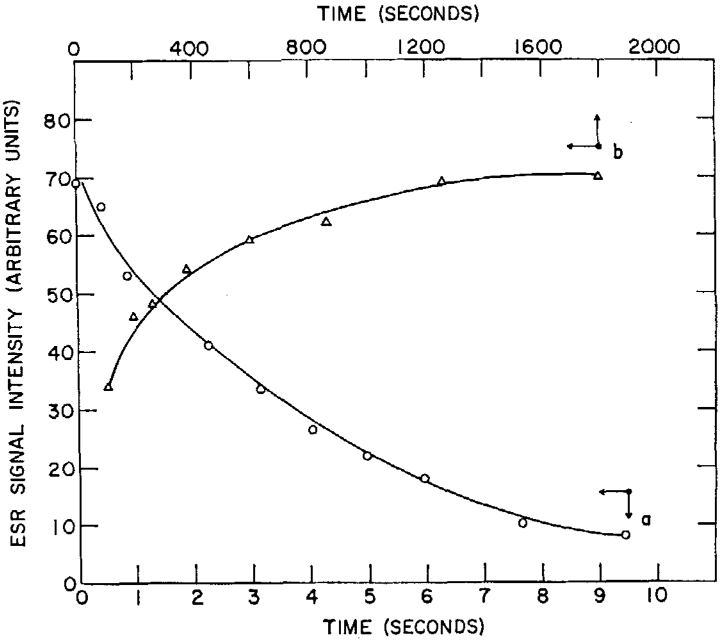


Figure 6 (a) decay of iminoxyradicals derived from propionamide nitric oxide ($P_{NO} = 250$ mm Hg), (b) build up of iminoxyradicals under vacuum.

more the rate determining step. To explain this effect we suggest that the formation of iminoxy radicals is accompanied by some reorientation and misalignment of the molecules with respect to the lattice, so that a more favorable position of the $=\mathrm{N}\overset{\cdot}{-}\mathrm{O}$ group, carrying the unpaired spin, is reached in respect to the direction of diffusion of the gas. This is due to the bulk of the NO group. We might also expect a buildup of products within the lattice. A small concomitant increase in lattice spacing which this would cause should have a large effect in increasing diffusion rate. An increase in lattice spacing can indeed be seen in some circumstances.

It must be pointed out, however, that this effect can also be explained by assuming that migration of the radical sites to the surface or defects connected to the surface occurs during the reaction. This seems unlikely, however, in view of the other data.

Under vacuum the iminoxy radicals show a very slow decay which follows first order kinetics. The stability of the iminoxy radicals made it possible to determine the curve of buildup of the nitric

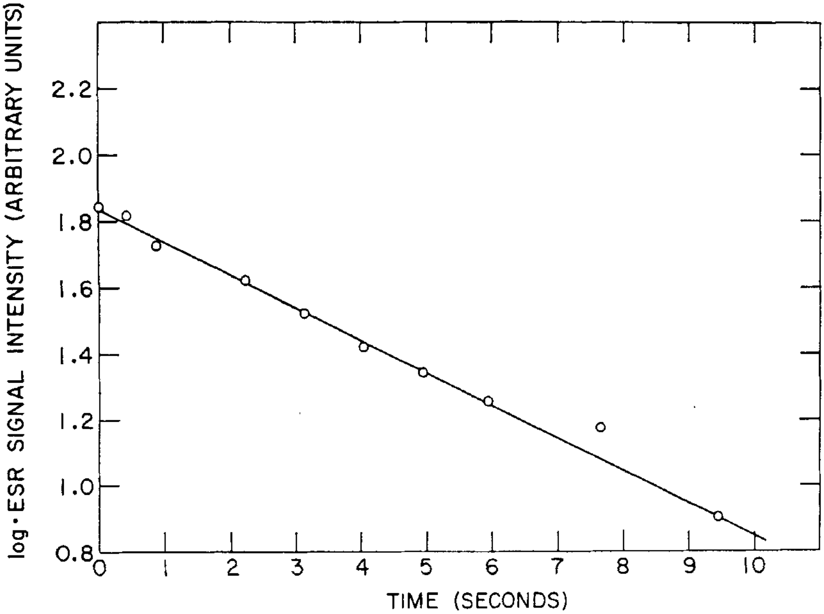


Figure 7. Kinetics of the decay of propionamide iminoxyradicals under nitric oxide (P_{NO} = 250 mm Hg).

oxide-iminoxy radical adduct simply by putting the sample temporarily under vacuum at regular intervals of time, and measuring the intensity of the ESR signal obtained.

Comparing the curve of buildup of the nitric oxide adduct, decay of initiating radicals and of nitric oxide absorption for propionamide (Fig. 8), the following observations can be made. The curve of buildup passes through a maximum, which indicates that the adduct is formed as an intermediate in a consecutive reaction scheme. Most of the initiating radicals have already decayed and more than 90% of the over-all amount of nitric oxide has already been absorbed when the concentration of the adduct in the system is only 20% of the maximum concentration reached.

This suggests that the adduct is formed in a reaction which is slower than the main propagation step. The behavior of *n*-butyramide is similar to propionamide (Fig. 4), whereas no formation of the nitric oxide adduct is observed in isobutyramide, which gives tertiary nitroso compounds in the first step of the reaction. We are, therefore, tempted to suggest that the formation of the adduct occurs

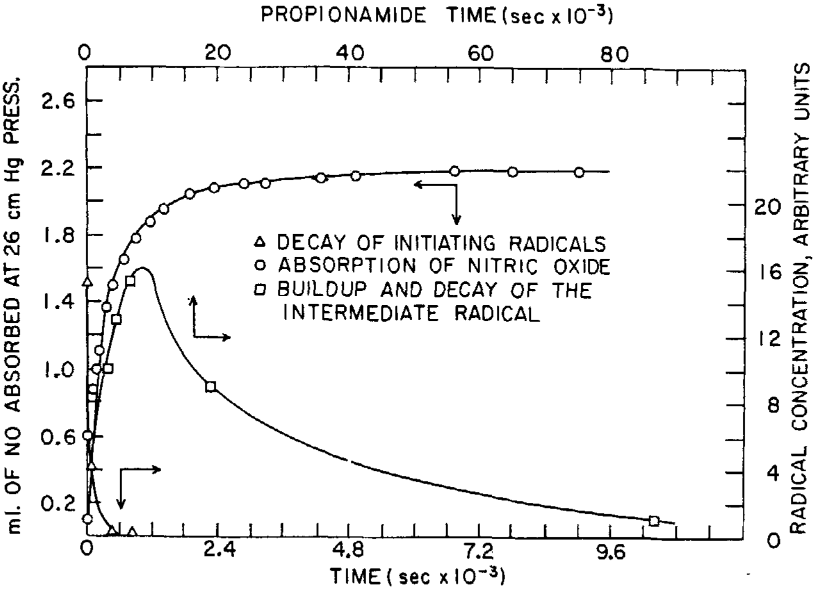


Figure 8. Reaction of γ-irradiated propionamide with nitric oxide (P_{NO} = 260 mm Hg; γ dose = 29 Mrad)

△ decay of the initiating radicals

○ absorption of nitric oxide

□ build up and decay of the intermediate radical

through the isomerization of the nitroso compounds to oxime which then undergoes oxidative hydrogen abstraction from the oxime group by some active species arising from the main propagation steps, or by nitric oxide itself.

C. Reaction with Oxygen

i. *ESR measurements.* Oxygen reacts with the radicals in γ-irradiated powdered propionamide, *n*-butyramide, and isobutyramide resulting in a decay much faster than under vacuum.[7] The formation of peroxyradicals can be simultaneously observed from their characteristic asymmetric singlets superimposed to the ESR spectra of the initiating radicals. The intensity of the peroxyradical signals increases relatively fast in the beginning, until a maximum concentration is reached, then a decay is observed (Fig. 9, curve *a*). For a given amide the rate of the peroxy radical buildup,

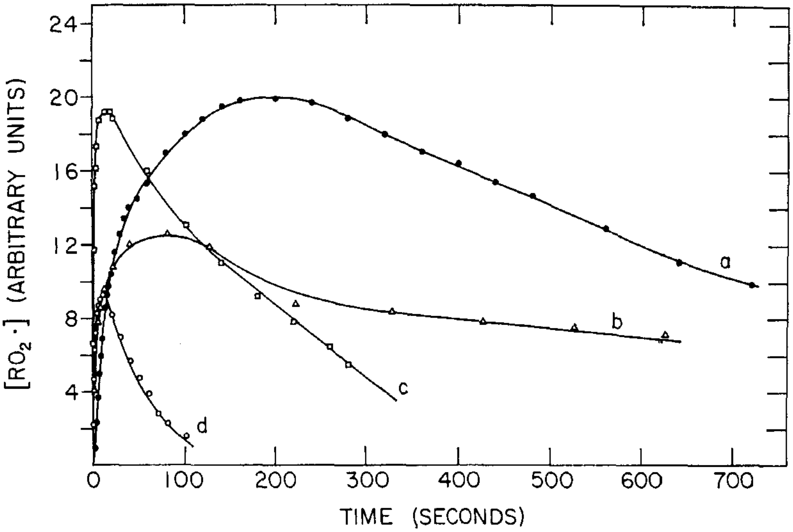


Figure 9. Build up and decay of peroxyradicals during the postirradiation reactions of propionamide, in *n*-butyramide and isobutyramide with oxygen. (a) *n*-butyramide: γ dose = 15 Mrad; air, atmospheric press, (b) isobutyramide, Tesla-coil irr. air, atmospheric press, (c) *n*-butyramide Tesla-coil irr. air, atmospheric press, (d) propionamide Tesla-coil irr. air, atmospheric press.

as well as the maximum concentration reached, increases with increasing oxygen pressure and decreasing the particle size. For a given particle size and oxygen pressure, it apparently increases with increasing diffusion coefficient and the stability of the peroxyradicals. This points to the peroxyradicals being formed as intermediates in a series of consecutive reactions, where the first two steps are diffusion of O_2 into the lattice followed by reaction of the oxygen with the radical according to the following scheme:

$$R\cdot + O_2 \xrightarrow{K_1} RO_2\cdot \qquad (2)$$

In the initial stage of the reaction the rate of decay of peroxyradicals is small, so that a linear relationship between the number of $RO_2\cdot$ radicals formed and the square root of the reaction time should be found provided that the diffusion rate is rapid compared with K_1. This is indeed what has been observed for *n*-butyramide (Fig. 10).

The rate of diffusion is slow enough so that when large crystals

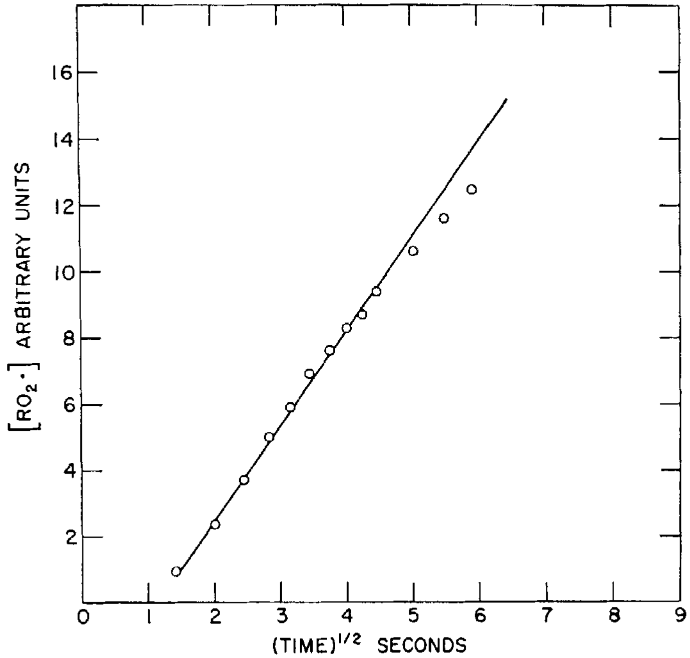


Figure 10. Kinetics of the buildup of peroxyradicals in γ-irradiated n-butyramide under oxygen.

are used instead of powdered specimens the concentration of peroxyradicals in the system does not reach the limit of sensitivity of the spectrometer. This is because the diffusion paths are now long enough so that a much longer time is necessary for the gas to reach the bulk of the radicals. It must be remembered that the radicals are decaying at the same time. When the discharge from a Tesla-coil is used as a radiation source, it generates radicals to a depth of only 10 to 20 Å below the surface.[20] A complete transformation of the initiating radicals into peroxyradicals is obtained in times ranging from 10 to 20 sec for propionamide and n-butyramide, to 60 sec for isobutyramide (Fig. 9, curves b, c, and d). In all three of the amides the decay of the peroxyradicals follows first order kinetics,[7] the rate constants being $0.85 \times 10^{-2}\,\mathrm{sec}^{-1}$, $0.41 \times 10^{-2}\,\mathrm{sec}^{-1}$, and $0.17 \times 10^{-2}\,\mathrm{sec}^{-1}$ for propionamide, n-butyramide, and isobutyramide, respectively.

ii. *Oxygen uptake and product analysis.* The curves of oxygen absorption on the samples of powdered propionamide given different γ doses are shown in Fig. 11. Similar curves were obtained for the other two amides. The rate of absorption increases with increased radiation dose, and oxygen pressure and decreases with particle size (Fig. 12). No simple kinetics have been found for the oxygen uptake for powdered samples, but when large crystals, about 0.2 mm thick, were used, a linear relationship with the square root of the time has been observed. The reactions are chain reactions with the ratios of oxygen absorbed to the moles of radicals reacted ranging from 30 to 50 for propionamide and *n*-butyramide, to more than 250 for isobutyramide.

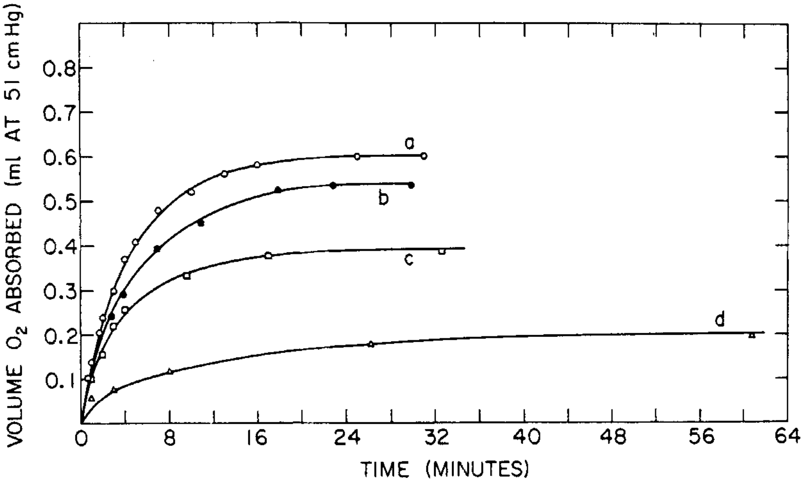


Figure 11. Oxygen uptake in the post-irradiation reaction of propionamide, γ dose:
(a) 28.5 Mr, (b) 14.2 Mr, (c) 7.1 Mr, (d) 2.3 Mr.

The reaction products in *n*-butyramide and propionamide give identical polarograms with two distinct waves, the half-wave potential being − 0.1 and − 1.15 V versus S.C.E. The first wave is completely suppressed by SO_2 and Fe^{+2} ions and was, therefore, attributed to easily reducible hydroperoxides. The presence of the hydroperoxide has been confirmed by the iodometric test reaction. The second wave was attributed to α-ketoamides, since the half-wave potential is identical to the one observed for α-ketopropionamide

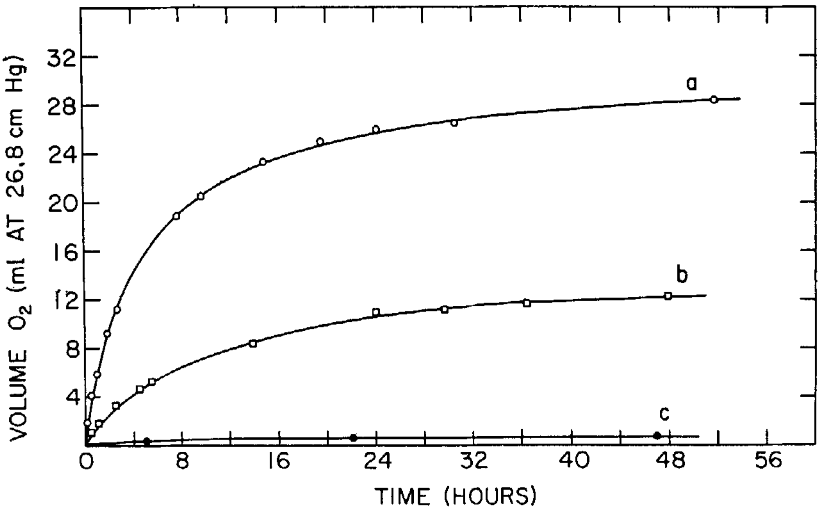


Figure 12. Effect of the particle size on the rate of oxygen uptake in γ-irradiated isobutyramide
(a) sample ground, (b) sample unground, (c) large crystals (0.2 mm thickness)

(pyruvamide). This is confirmed by the fact that 2, 4-dinitrophenylhydrazones of the pyruvamide and of the carbonyl compounds isolated from propionamide give identical infrared spectra.

With isobutyramide only the hydroperoxide wave has been found. No wave corresponding to H_2O_2 has been observed and the addition of catalase B, an enzyme specific for the decomposition of H_2O_2, did not change the shape of the polarograms appreciably.

In propionamide and *n*-butyramide 50 to 60% of the oxygen absorbed is converted in hydroperoxides (moles of hydroperoxide/moles of radicals reacted $\cong$ 20) and about 20% to α-ketoamides (moles of α-ketoamides/moles of radicals reacted $\cong$ 10). In isobutyramide practically the whole amount of oxygen absorbed (more than 95%) is converted to hydroperoxides (Table 2).

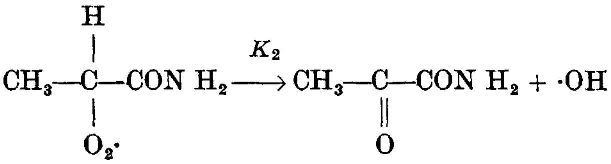
These results indicate that a chain reaction is involved with the chain propagation occurring mainly by hydrogen abstraction:

$$RO_2\cdot + RH \xrightarrow{K_2} RO_2H + R\cdot \qquad (3)$$

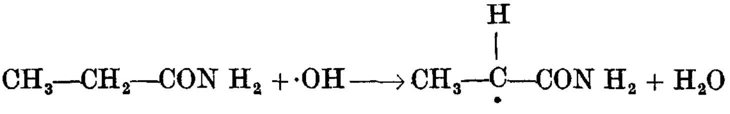
apparently leading to the specific formation of α-hydroperoxides.

This is indicated by the fact that the peroxyradicals present during the reaction, regenerate the primary radicals having the unpaired spin on the carbon α to the amide group when put under vacuum.

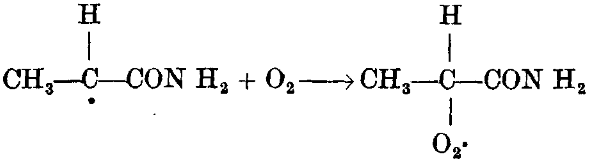
In propionamide and *n*-butyramide the yield of α-ketoamides, which is higher than would be expected for products formed in a chain termination step, implies that either thermal decomposition of hydroperoxides occurs during the reaction or that another propagation cycle, besides hydroperoxidation, exists. A chain process leading to the formation of α-ketoamides might arise from the monomolecular decomposition of the peroxyradicals, according to a mechanism which has been proposed to explain the formation of carbonyl compounds as main products in the high temperature oxidation of hydrocarbons.[21]



$$CH_3-\overset{H}{\underset{O_2\cdot}{C}}-CONH_2 \xrightarrow{K_2} CH_3-\underset{O}{\overset{\|}{C}}-CONH_2 + \cdot OH \tag{4}$$



$$CH_3-CH_2-CONH_2 + \cdot OH \longrightarrow CH_3-\overset{H}{\underset{\bullet}{C}}-CONH_2 + H_2O \tag{5}$$



$$CH_3-\overset{H}{\underset{\bullet}{C}}-CONH_2 + O_2 \longrightarrow CH_3-\overset{H}{\underset{O_2\cdot}{C}}-CONH_2 \tag{6}$$

The monomolecular decomposition of the peroxyradicals would probably involve an activation energy of the order of 20 kcal-mol^{-1}.[22] Decomposition of peroxyradicals will result in the formation of the low molecular weight OH radicals, which are probably able to diffuse within the lattice and to undergo recombination or disproportionation reactions with themselves or other radicals present in the system[23]:

$$RO_2\cdot + \cdot OH \longrightarrow ROH + O_2 \tag{7}$$

$$R\cdot + \cdot OH \longrightarrow ROH \tag{8}$$

$$\cdot OH + \cdot OH \longrightarrow H_2O_2 \tag{9}$$

This type of termination may occur in competition with the other type of termination based on the spin migration by hydrogen abstraction, originally proposed by Bresler.[24] The kinetics of decay of the peroxyradicals in the Tesla-coil irradiated samples gives an indication of the relative importance of these two mechanisms of termination.

As already reported, when Tesla-coil irradiation is used most of the radicals are confined to domains up to 10 to 20 Å below the surface. As a consequence, they are easily accessible to the diffusing gas and all the primary radicals are transformed in a few seconds into the peroxyradicals, which then decay following first order kinetics. During the decay the only R· radicals present in the system are the ones coming from the hydrogen abstraction steps. Their concentration as well as the concentration of the OH radicals is much smaller than the concentration of $RO_2\cdot$ radicals as long as the rate of hydrogen abstraction is slow compared with the oxygen addition.

iii. *Formation of hydroperoxides in large crystals.* In an attempt to get more direct evidence of the diffusion of oxygen within the crystalline lattice of the amides, 1 g of large crystals of isobutyramide (0.2 mm thick, 90 cm^2 total surface area) have been irradiated to a dose of 15 Mrads under vacuum and then allowed to react with oxygen ($P_{O_2} = 540$ mm Hg). At the end of the reaction 76% of the hydroperoxides was found in the outer parts of the crystals, while the remaining 24% was found in the interior part. The external part, about 40% of the over-all weight, was washed out with water and titration of the hydroperoxides was made for the external and internal parts of the crystals.

This fact together with the observed linear dependence of the oxygen uptake with the square root of the reaction time suggests that O_2 molecules are able to diffuse into the lattice of isobutyramide. The ratio moles of O_2 absorbed to the moles of radicals present has been found considerably smaller than when powdered samples are used (Table 2); this decrease is believed to be due to the fact that, owing to the very low rate of diffusion, a large portion of the radicals decays before being reached by the oxygen molecules.

iv. *X-ray diffraction measurements.* The diffraction diagrams were taken on powdered samples of *n*-butyramide and isobutyramide irradiated under vacuum and under 600 mm of oxygen. The samples

TABLE 2 Postirradiation Oxidation of Proponamide, *n*-Butyramide, and Isobutyramide

Compound	Oxygen absorbed, moles/g × 10^5 (P_{O_2} – 500 mm Hg)	Initial concentration of radicals, No. of radicals/g × 10^{17}	Moles O_2 absorbed / Moles of radicals reacted	O_2 converted to hydroperoxides, %
Isobutyramide	5.55^a	0.686	598	97.8
	10.5^a	2.74	239	93.8
	2.53^{a,c}	3.0	52.8	92.4
Propionamide	1.16^b	1.36	51.30	64
	1.68^b	2.30	43.16	53.9
	1.35^b	1.57	51.7	64
-Butyramide	1.247^b	1.788	41.7	50.8
	1.65^b	3.00	32.6	52
	2.1^b	3.04	41.4	53.7
	0.6034^c	3.00	12.1	45.2

After 24 hr.
After decay of all radicals present as measured by ESR. Approximately 1 hr after admission of O_2.
Samples made of large flat crystals. 0.20 mm thick.

were allowed to stand for two days before use to allow for decay of the radicals. It was expected that there would be an expansion of the lattice if the peroxide was generated by diffusion through the lattice. Furthermore, this expansion would be most evident in an increase in the 001 spacing. If the reaction took place only at the surface and at defects there is not likely to be a similar expansion although there might be evidence of the formation of a new peroxide phase.

The expected expansion was indeed found. For example, *n*-butyramide after a dose of 170 Mrads gave a peak (probably 001) with a *d*-spacing of 10.04 Å. If irradiated in the presence of oxygen, the spacing was 10.10 Å. Isobutyramide showed a peak at 9.83 Å under vacuum and 9.93 Å in oxygen. These results did not have high reproducibility. The above figures are by no means the largest shifts observed but they are typical. In any case, the sample irradiated in the presence of oxygen invariably showed a significantly higher *d*-spacing than the corresponding vacuum sample. Isobutyramide seemed to show some decrease in spacing when irradiated under vacuum but in the presence of oxygen, the *d*-spacing always increased.

The diffraction peaks did not seem to differ much in broadness when the oxygen and vacuum irradiated samples were compared. The peaks in both cases remained comparatively sharp. Since it takes a number of equally spaced lattice planes to produce a relatively sharp diffraction peak, there seems to be good reason to believe that whatever was causing the increased spacing had been able to penetrate the lattice.

In a way, we were a bit disappointed that the lattice shifts have not been larger or more reproducible. This may be due to several factors. One is that the peroxide (and ketone) are generated in a chain reaction of the radicals with the oxygen. This would tend to produce small clusters of peroxide molecules around the site of each radical leading to a nonuniform concentration distribution except at high radiation doses and this could lead to a smaller observed average *d*-spacing.

Another important factor is that the distribution of radicals in the lattice may not be uniform in spite of the use of Co^{60} γ rays as a radiation source. There is some evidence that a relatively large fraction of the radicals are present at defects, grain boundaries, and similar locations. This may be due to both an exciton mechanism and a process involving a kind of radical migration through the lattice.[5] The result would be less lattice expansion observable by diffraction techniques than would otherwise occur. We have occasionally seen some new peaks in the isobutyramide samples which may be due to the presence of new product phases. This suggests that the lack of reproducibility may be due to variations in defect population, minute amount of impurities, and other experimental parameters which are very difficult to control. It should also be noted that unless we have more precise information about the peroxide molecules, their size, shape, orientation, and location within the lattice, we do not know *a priori* how much expansion to expect from a given amount of peroxide.

Conclusions

It seems fairly evident that we are dealing here with a solid-state diffusion-controlled reaction where the mechanism involves diffusion of reactive gas within the crystal. The evidence, briefly, rests on the following points. When the samples are irradiated with a Tesla coil so that all the radicals are generated at or near the surface of the crystals, the reaction rate with gases is considerably more rapid than when the radicals are generated by the more penetrating γ radiation. However, if the gas molecules are small enough, all the radicals do react in both cases. This suggests that even the radicals within the crystal are accessible to the gas. Since all the radicals are probably not located at defects, this suggests that the lattice itself is penetrated by the gas. This is most strongly borne out by expansion of the lattice upon reaction as evidenced by X-ray diffraction. Furthermore, it will be demonstrated in subsequent publications that when a gas is chosen with molecules too large to diffuse within the lattice but still capable of entering defects, a large fraction of the radicals do not react with the gas.[12]

Another line of evidence is that the kinetics of the initial stages of the reaction fits a linear plot when the radical population is plotted against the square root of time (e.g., Fig. 2). This suggests a diffusion-controlled reaction. Furthermore, it was shown with large crystals that the peroxide yield in the central part of the crystal is less than that of the outer parts but that there is still a definite yield.

The gas diffusion can be broken down into three parts, diffusion down defects being most rapid, diffusion between the layers of the lattice, and diffusion orthogonal to the layers. This last component is the slowest and accounts for the relative rates of reaction of the different amides. Since the product molecules are larger than the initiating ones, the reaction seems to spread apart the lattice so that subsequent diffusion is more rapid. At present, we cannot rule out the possibility that the reaction initiates at a defect and the distortion this produces in the surrounding crystal enables the initial stages of diffusion to begin. In some cases, this seems likely. The diffusion between the lattice layers is apparently possible because the distance between layers is relatively large and the forces between the layers are the weakest in the crystal. This is suggested by the fact that amides with a different type of layer structure do not show the effect and by the fact that acrylamide, which has the same type of structure but has a slightly smaller lattice spacing and stronger interlayer forces than propionamide, is insensitive to oxygen.[25]

Oxygen reacts with the irradiated solids by a chain mechanism so that a number of molecules of reaction product are formed for each initiating radical. Most of the oxygen consumed can be accounted for by the formation of peroxides and ketones. With nitric oxide, several molecules of gas seem to react, as measured by gas absorption, for each initial radical. Part of this can probably be accounted for by addition of nitric oxide to the initially formed iminoxy compounds. Part of the nitric oxide may be simply adsorbed on the solid.

The reactions we have discussed seem to be an unusual solid-state reaction in that the diffusing gas is capable of reacting with only a small fraction of the molecules it encounters. For example, in the oxidation of a metal, the oxygen can react with every metal atom present in the lattice. In our case, the reactive species, free radicals, form a very dilute solid solution within a relatively inert matrix. This makes gas diffusion into and within the solid necessary if extensive reaction is to occur. We will explore various aspects of these reactions in subsequent publications.

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