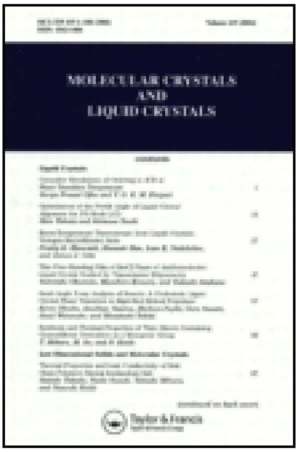

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The Molecular Dynamics of Peroxy Radicals in Irradiated Crystalline Aliphatic Amides

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THE MOLECULAR DYNAMICS OF PEROXY RADICALS IN IRRADIATED CRYSTALLINE ALIPHATIC AMIDES

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Abstract The molecular dynamics of peroxy radicals generated from several amides have been investigated as a function of temperature by ESR using a modified Bloch formalism. Rotation about the C-O bond was found to be a mode of motion common to the peroxy radicals in the amides studied thus far. In the linear amides, we have also obtained preliminary evidence for rotation about the chain axis leading to inversion of the parallel and perpendicular principal g values. The frequence of motion at a given temperature decreases with increasing molecular size and with branching. The mobility parameters correlate reasonably well with the previously reported kinetics of post irradiation oxidation in the amides.

INTRODUCTION

The linear aliphatic amides have a layer-like structure which, for the purposes of this comunication, may be described in the following manner[1]; the molecules are hydrogen bonded through the amide group in a head to head configuration thus forming dimers. The dimers are further hydrogen bonded to form bilayers with one amide of the dimer in each half of the bilayer. The crystal structure is made up of stacks of these bilayers. All the linear amides, at least from the three carbon to the 18 carbon amide, seem to conform to this pattern and crystallize in the same or a similar space group[1a]. For the purposes of the arguments presented here, the amide groups can be considered as forming the core of the bilayer whereas the aliphatic chains form the outside.

In previous work[2,3,4,5], reviewed in[6],it was shown that oxygen and various other low molecular weight molecules (e. g. nitric oxide, nitrogen dioxide, sulfur dioxide, ethylene and other small molecular weight olefins) were capable of diffusing into these crystals and reacting with any free radicals that happened to be present. Especially interesting was the unusually high efficiency of hydroperoxide formation when oxygen was used as the diffusing gas. These suggested that the study of gas-solid reactions employing free radicals generated by radiation in these amides might shed light on some interesting solid state processes as well as on the mechanism of peroxide formation in lipids upon exposure of biological systems to radiation.

The oxidation we observed in these systems showed some interesting features, such as large differences in reaction rate as a function of aliphatic chain length and branching, unusually large kinetic chain length as compared to oxidations in liquid or polymer systems and high selectivity in peroxide formation[2,4,5].

These characteristics suggested that some solid state peculiarities related to crystal packing and geometry were playing a significant role in these processes. This was further suggested by some preliminary work on longer chain amides and fatty acids[7]. One aim of the work reported here is to investigate some of these solid state effects with particular reference to the molecular dynamics of peroxy radicals in these crystals. These dynamics are expected to be of crucial importance in determining the rate of free valence migration and the frequency of bimolecular encounters within these bilayer type amide lattices.

EXPERIMENTAL

The aliphatic amides propionamide, valeramide (n-pentanamide) and isobutyramide (obtained from Fluka) were purified by recrystallization from acetone. The amide samples were then exposed to ^{60}Co gamma radiation, under vacuum at a temperature of 77 K and a dose rate of 0.03

Mrad/h to a total radiation dose of 1-1.5 Mrad. The material was then brought to the experimental temperature. It has previously been shown that, in these and similar amides, over the range of temperature studied, the free radical most prominent in ESR spectra is the one formed by loss of a hydrogen atom alpha to the amide group[2,3,8]. After identification of these radicals from their spectra, the peroxy radicals were prepared by allowing oxygen at a presure of about 50 cm.Hg to diffuse into the material (at the experimental temperatures of -10°C ÷ 0°C).

$$RR'CHCONH_2 \xrightarrow{\gamma} RR'\dot{C}CONH_2 \quad (1)$$
$$RR'\dot{C}CONH_2 + O_2 \longrightarrow RR'C(O\dot{O})CONH_2$$

R = CH_3-, R'= H-, propionamide; R,R'= CH_3-, isobutyramide; R'= H, R = $CH_3CH_2CH_2$-, valeramide

The behaviour of the peroxy radicals thus formed were observed by ESR using a Varian X-band E-109 spectrometer equipped with a variable temperature probe.

ANALYSIS OF RADICAL MOTION BY THE MODIFIED BLOCH METHOD

The Bloch technique is based on a phenomenological set of differential equations describing the relaxation of the bulk of the magnetism. This employs as a frame of reference a set of axes rotating at an angular frequency ω about an axis in the direction of the static magnetic field [9,10]. If the motion is approximated as a sequence of jumps between N different sites, the differential equation describing the change in the complex transverse magnetization at a specific site under the influence of motion, G_s, can be written as:

$$\frac{dG_s}{dT} + \left[\frac{1}{T_{2s}} - i(\omega_{o,s} - \omega)\right] G_s = -i\gamma H_1 M_{o,s} + \sum_{x=1}^{N} (K_x G_x - K_s G_s) \qquad (2)$$

where the summation contains all the kinetic terms describing the build up and decay of G_s as a consequence of the interchange between sites with an equal probability of occupancy. $K_x = 1/\tau_x$, where τ_x is the correlation time in seconds, H_1 the oscillating magnetic field, ω the sweep frequency, and $\omega_{o,x}$ is the resonance frequency for site x. The imaginary part of the total complex magnetization, $G = \sum_{X=1}^{N} G_i$ is given by

$$G = \frac{i \cdot \gamma \cdot H_1 \cdot M_o \cdot \tau \sum_{X=1}^{N} f_x}{N\left[1 - \sum_{X=1}^{N} f_x\right]} \qquad f_x = (N + \alpha_x \tau)^{-1} \qquad \alpha_x = \frac{1}{T_{2x}} - i\,(\omega_{o,x} - \omega) \tag{3}$$

where T_2 is the transverse relaxation time and M_o is the total magnetization along the external fixed magnetic field. The resonance frequency $\omega_{o,s}$ at a given orientation with respect to the external magnetic field defined by the direction cosines l_1, l_2, l_3 is given by:

$$\omega_s = \left(\frac{\beta H_o}{\hbar}\right)\left(\left[l_1, l_2, l_3\right] \cdot \tilde{g}_{(s)} \cdot \begin{bmatrix} l_1 \\ l_2 \\ l_3 \end{bmatrix}\right) \qquad \begin{array}{l} l_1 = \sin\vartheta\cos\varphi \\ l_2 = \sin\vartheta\sin\varphi \\ l_3 = \cos\vartheta \end{array} \tag{4}$$

g(s) is the tensor for the specific site. It is obtained from the following equation:

$$\tilde{g}_{(s)} = L\,\tilde{g}\,(s-1)\,.\,L^{-1} \tag{5}$$

where L is the rotation matrix connecting site s-1 to site s. Specific rotation matrices for the different rotational models adopted were derived following the procedure outlined by Kevan[10]. Three types of motion were considered (Fig.1); rotation about the Z' "chain" axis, rotation about the C-O bond and the "cubic jump" model. The effect of rotation about the C-O bond on ESR line shape depends on the magnitude of the O-O-C bond angle. The observed effects were reproduced by assuming a bond angle of 104 degrees[11].

Rotation about the Z' axis is not strongly influenced by the geometry of the radical. Neither is the cubic jump motion which interchanges the principal g values by a motion equivalent to rotation about the body diagonal of a cube. The orientation of the principal values of the g tensor with respect to the molecular reference axis system of the peroxy radicals are shown in Fig.1.

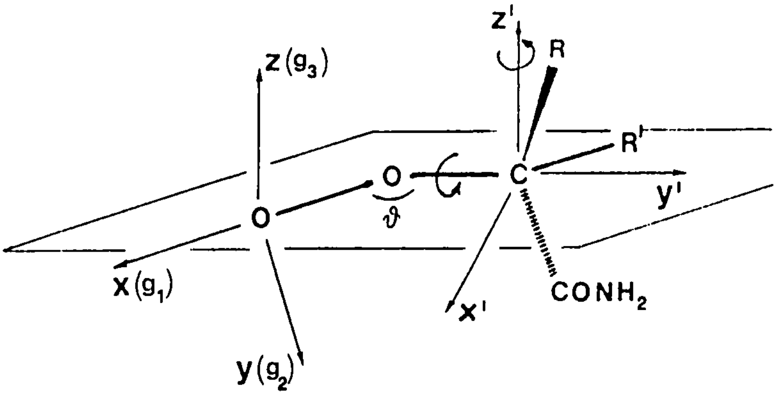


FIGURE 1 Reference axis system for the g tensor and the motion models.

The polycrystalline line shapes are obtained by convolution of the spectra obtained at all orientations and using the equation:

$$Y(N,\tau) = \sum_{\vartheta=0}^{\pi/2} \sum_{\varphi=0}^{\pi} G(\vartheta, \varphi, \tau, N) \sin\vartheta \qquad (6)$$

The computer simulations of the peroxy radical spectra were done for the three states of motion and the results are shown in Figures 2,3 and 4.

ANALYSIS OF THE ESR LINE PROFILES

Propionamide Peroxy Radical $CH_3CH(O\dot{O})CONH_2$

At 77 K the peroxy radical obtained from irradiated propionamide produced a rigid limit type of spectrum which showed the anisotropy typical of an axial g tensor with $g_{//} = 2.044$, $g_{\perp} = 2.000$ and $g_{iso} = 2.016$ (Fig.5).

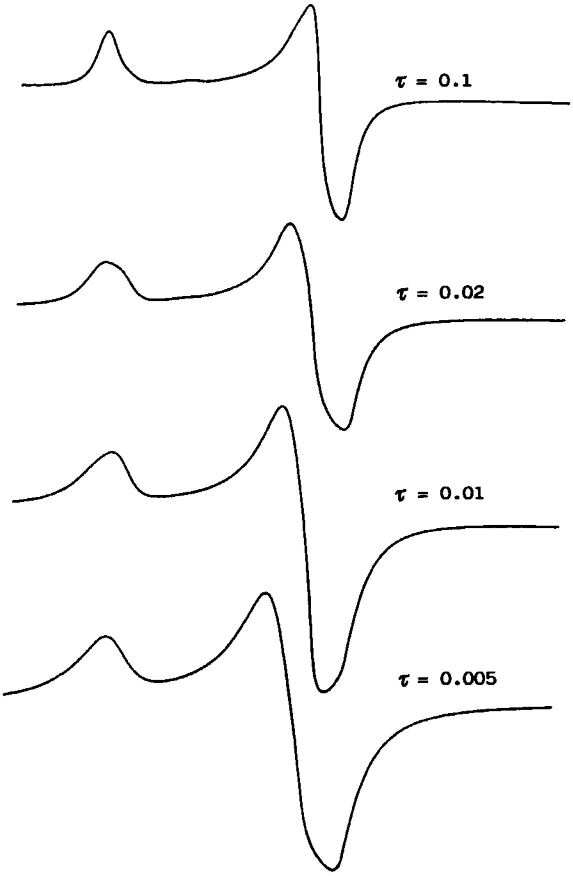


FIGURE 2 Computer simulation of the peroxyradical line shape performed according to the model of rotation about the C-O bond. $C\hat{O}O = 104°$, τ in microseconds

Upon warming above 77 K, large changes in the line shape were observed, apparently due to modulation of the g tensor by a specific type of motion. As the temperature was raised above about 112 K, a progressive decrease in the $g_{//}$ to $g_{\perp}$ separation was noted. This specific effect is similar to the one seen in polypropylene[11]. The analogous shift shown in the computer simulations,(Fig.2), suggests that it is due to the progressive rotation about the C-O bond with a constant C-$\hat{O}$-O bond angle of 104 degrees being maintained.

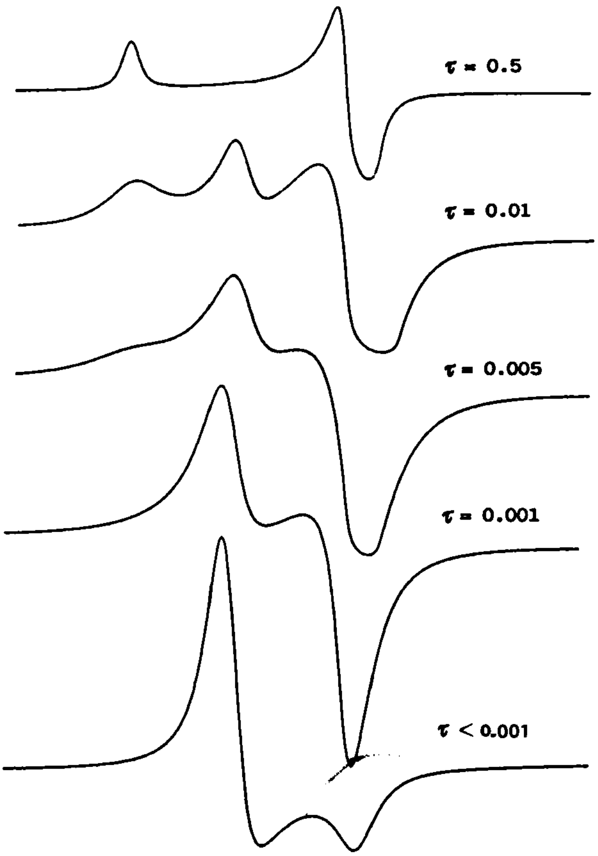


FIGURE 3 Computer simulation of the peroxyradical line shapes performed according to the model or rotation about the z' axis. **E** is the simulation of the pattern predicted for the fast interconversion of g_1 and g_2 principal values ($g_{\perp} = 2.025$, $g_{//} = 2.002$); τ in μseconds

Above about 152 K, an additional spectral feature begins to appear between $g_{//}$ and $g_{\perp}$. As suggested by the continuing evolution of the spectra, this may be associated with a progressive increase in a radical population having inverted principal g values, with $g_{\perp}$ greater than $g_{//}$.

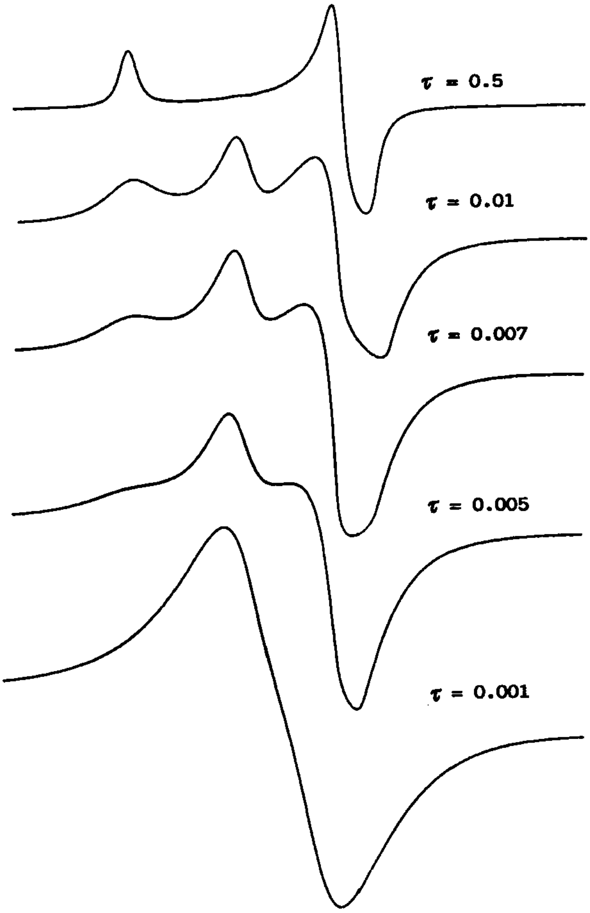


FIGURE 4 Computer simulation of the peroxyradical line shapes performed according to the model of cubic jump. τ in μseconds.

Comparison with the computed spectra, (Fig.3), suggests that this effect is related to the interchange of the $g_{x,x}$

and $g_{y,y}$ components initiated by a fast limit rotation about the Z' axis with $\tau<0.001$ μs. Above 202 K this type of motion involves the total peroxy radical population. Near room temperature the ESR spectra become nearly isotropic as a consequence of the initiation of more complicated modes of motion. Within the formalism of the modified Bloch method, this final change can be approximated by a cubic jump model with $\tau<0.003$ μs. (Fig.4).

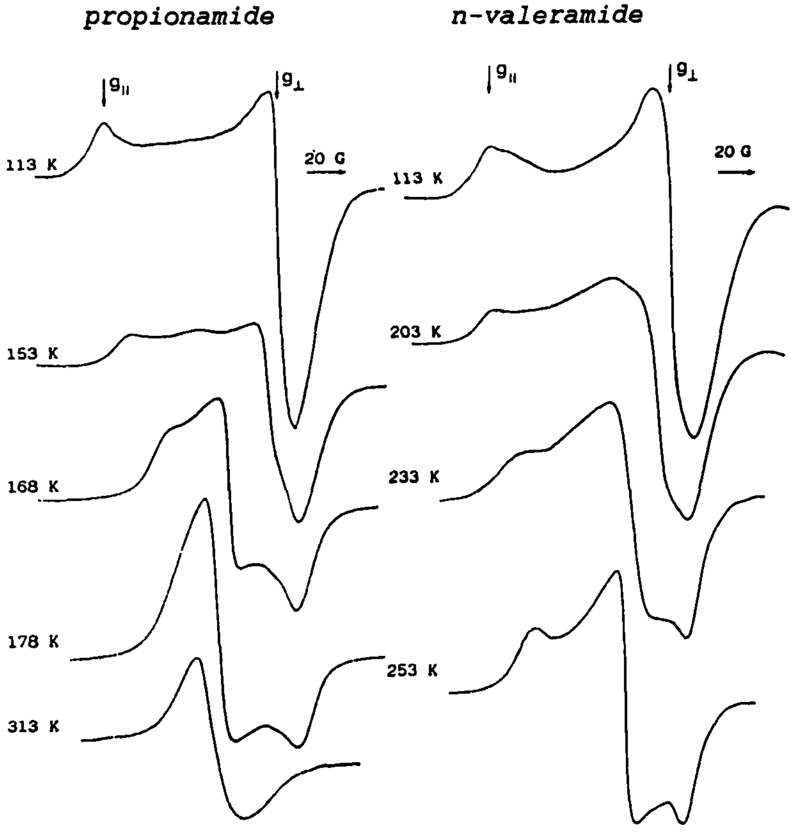


FIGURE 5 ESR line shapes of peroxyradicals from propionamide $CH_3CH(O\dot{O})CONH_2$ and n-valeramide $CH_3(CH_2)_2CH(O\dot{O})CONH_2$ recorded as a function of the temperature.

Valeramide Peroxy Radicals $CH_3(CH_2)_2CH(O\dot{O})CONH_2$
The peroxy radical changes observed by ESR as a function of temperature in this five carbon linear amide resemble those of the propionamide peroxy radical (Fig.5). Both the $g_{//}$ shift towards the high field and the inversion of the $g_{//}$ and $g_{\perp}$ principal values are observed with increasing temperature. However, at a given temperature, both types of motion are slower than in propionamide and their fast limits are reached at considerably higher temperatures. Thus the state of motion in valeramide at 252 K resembles that of propionamide at 152 K (Fig.5). It is most readily described in terms of two major radical populations undergoing rotation about the C-O bond and a limited rotation or large amplitude oscillation about the Z' axis with τ close to the fast limit. This may be analogous to the high temperature phase transition that has been observed in some compounds such as stearic acid where the high temperature phase has been attributed to rotation about the chain axis. We have not as yet explored the possibility of a phase change in this compound at higher temperatures. No similar phase change is known to occur in propionamide. However in both valeramide and in propionamide, such rotation may still be possible without an observable phase change because the peroxy radicals form only a small minority of the molecules in the crystal and they probably perturb the surrounding lattice by their bulk. Another possibility is that the majority of the radicals exhibiting this type of motion are located at such defects as properly oriented edge dislocations or surfaces.

Isobutyramide Peroxy Radical $(CH_3)_2C(O\dot{O})CONH_2$
The isobutyramide peroxy radical is formed by the loss of the tertiary hydrogen at the branch point of the molecule followed by the addition of oxygen. The line shape changes of the signals belonging to the peroxy radicals, monitored as a function of temperature, are shown in Fig.6A. The decrease in $g_{//}$ to $g_{\perp}$ separation observed upon warming above

172 K, up to 242 K, suggests that rotations about the C-O bond takes place at a frequency greater than $5x10^7 sec^{-1}$.

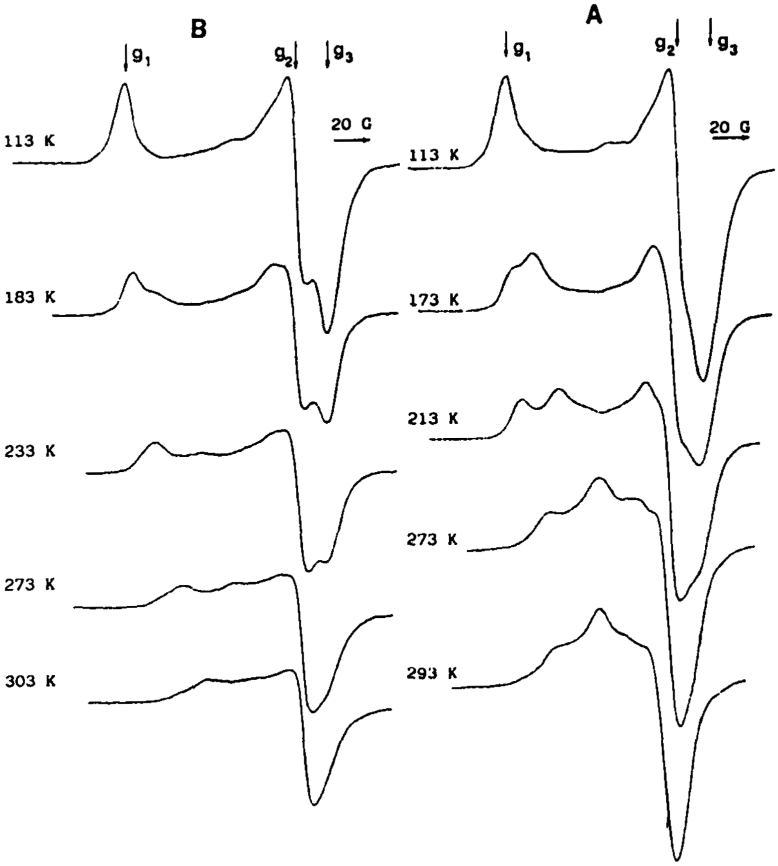


FIGURE 6 ESR line shapes of the isobutyramide peroxyradicals $(CH_3)_2C(O\dot{O})CONH_2$ recorded as a function of the temperature. **A**: first decay after the irradiation; **B**: second decay after 1 hr annealing to room temperature.

The presence of two peaks in the $g_{//}$ region, both of which progressively shift towards the high field region with increasing temperature, is suggestive of the presence of two major radical populations undergoing C-O bond rotation at different rates. Above 272 K, modification of the line shape is observed in the intermediate region between the

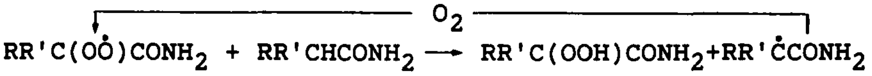
$g_{//}$ and $g_{\perp}$ features which relate to the fast C-O bond rotation. This may indicate that part of the radicals now undergo a more complex type of motion, either a slow cubic jump or, less probably because of the bulk of the peroxy and the two methyl groups, a Z' axis rotation or oscillation. On storing at room temperature these more mobile radicals decay more rapidly than the bulk of the radical population. This again suggests that there probably is more than one type of radical site present. The ESR line shape of the residual peroxy radicals, reexamined as a function of temperature, show more homogeneous states of motion (Fig.6B). In fact, the only observable effect shown by the residual radicals is a contraction of the $g_{//}$ to $g_{\perp}$ separation, with increasing temperature, due to rotation about the C-O bond with decreasing correlation time.

DISCUSSION

The experimental data suggest that there are two major types of motion possible below room temperature for the peroxy radicals of the linear aliphatic amides studied: rotation about the C-O bond and rotation or, more probably, oscillation about the Z' axis. The latter motion is activated at higher temperatures and, for a given temperature, is slower for the longer the hydrocarbon chain. Near room temperature complete averaging of the g tensor anisotropy takes place in propionamide, possibly due to the effects of a fast "cubic jump" motion. The methyl branching in isobutyramide almost completely dampens the rotation about the Z' axis. This is most likely due to the bulk of the methyl and peroxy groups, which are at the hydrocarbon end of the molecule and probably are close to the dimethyl group of a neighboring molecule. In this compound the dominant type of motion up until room temperature appears to be simple rotation about the C-O bond. Evidence was obtained for the distribution of peroxy radicals among different states of mobility reflecting the existence of a variety of trapping sites with differing trapping efficiencies, probably reflecting variations in the configuration of lattice surrounding the radical site. Thus, for example, a radical located at certain sites such as dislocations, stacking faults, vacancies, or possibly even impurities, would experience a somewhat different local environment than a radical within the intact lattice and this would be reflected in their ESR signature.

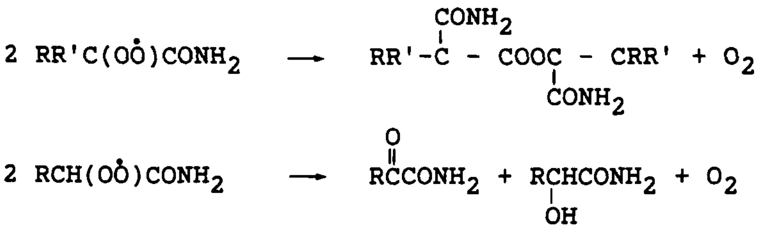
QUALITATIVE RELATIONSHIPS BETWEEN THE MOBILITY PARAMETERS OF PEROXY RADICALS AND THE KINETICS OF POST IRRADIATION KINETICS.

Peroxy radicals are the major intermediates in the propagation of the post irradiation chain oxidation. This results in hydroperoxides as the principal reaction product. Thus approximately 95% of the oxygen absorbed by isobutyramide, and 60-70% of the oxygen absorbed by the linear amides goes into the production of the hydroperoxide.



$$RR'C(O\dot{O})CONH_2 + RR'CHCONH_2 \longrightarrow RR'C(OOH)CONH_2 + RR'\dot{C}CONH_2 \quad (7)$$

By analogy with similar hydrocarbon peroxy radicals[12], termination of the kinetic chain by coupling is expected to occur by two principal mechanisms which apply to secondary and tertiary peroxy radicals respectively.



$$2\ RR'C(O\dot{O})CONH_2 \longrightarrow RR'-\overset{CONH_2}{\overset{|}{C}} - COO\underset{CONH_2}{\underset{|}{C}} - CRR' + O_2 \quad (8)$$

$$2\ RCH(O\dot{O})CONH_2 \longrightarrow R\overset{O}{\overset{\|}{C}}CONH_2 + R\underset{OH}{\underset{|}{C}}HCONH_2 + O_2$$

It is commonly accepted[13] that bimolecular encounters in the solid state in the presence of oxygen, are frequently made possible by a free valence migration mechanism based on the hydroperoxide cycle (equation 7). For such a model the rate constant for termination is given by a modified Smoluchowski equation[14]

$$K_e = 4\pi a\ D\cdot N/1000\ (LM^{-1}sec^{-1}) \qquad D = \lambda^2 .\ K\ [RH].\ 1/6 \qquad (9)$$

where **a** is the effective distance over which radicals can interact chemically, λ is the jump length and K[RH] is the rate of hydrogen abstraction corresponding to the jump frequency. The state of motion of the peroxy radicals is expected to influence K_e by affecting the amplitude of motion, which affects λ , and through the frequency of motion, probably also affects the jump frequency and thus, the rate of hydrogen abstraction. This is probable provided the latter is diffusion controlled. The effect on λ would seem to be that, the higher the amplitude, the faster the peroxy radical decay rate and the shorter the kinetic chain length for hydroperoxidation. On the other hand, an increase in jump frequency should increase the rate constants for both propagation and termination. Its overall effects are not easily predictable.

Among the kinds of motion observed, rotation or oscillation about the Z' axis and the cubic jump mechanism have the greatest amplitude. Therefore the systems in which they were observed, e.g. the linear amides, should have the most rapid decay rate for the peroxy radicals and the shortest kinetic chain length. This agrees with the experimental results since the peroxy radical decay rate runs in the following order [2] :

propionamide> n-butyramide> isobutyramide

The kinetic chain length for hydroperoxidation in isobutyramide, where the dominant mode of motion is rotation about the C-O bond, is almost an order of magnitude greater than the others. The unusual order of efficiency of the hydroperoxidation reactions we observed in the solid state oxidations of the amides, especially that of isobutyramide, may therefore be a consequence of a decrease of the diffusion rate and, therefore, its contribution to the frequency of bimolecular encounters. This seems to be particularly efficient in isobutyramide.

The above work can only be considered preliminary in nature and raises a number of questions. The peroxy radical is a relatively bulky group and it is present in a "foreign" lattice tied to a carbon atom attached to a tightly hydrogen bonded amide group. How can the postulated modes of motion occur within the crystal? At this point we can only speculate. Propionamide is the only one of the compounds studied whose structure we know in some detail[1d]. Diffraction data suggests that, in this compound, the alpha carbon has comparatively the largest thermal parameters, which suggests that it has the largest amplitude of motion. The loss of a hydrogen at this site should permit even higher amplitudes at least until the peroxy radical is formed. One possibility is that the peroxy radicals are initially generated at defect sites. Perhaps, because of the bulk of the group, it perturbs its surrounding lattice sufficiently to allow larger amplitudes of motion. This would also lead to more facile formation of additional peroxy radicals in the vicinity through the chain reaction mechanism. Such a mechanism would suggest "clustering" of the radicals. It should be kept in mind that, in these experiments, the peroxy radicals are a very small minority population within the crystal.

There are other important questions which arise. The linear amides discussed in this comunication, propionamide and valeramide, contain an odd number of carbons. It is known that there tends to be an alternation of physical properties between odd and even numbered amides. For example, the heats of sublimation of odd numbered amides forms a different series than even numbered amides[15]. There is an alternation in cross section area of the chain between odd and even amides[1a]. Is there also an alternation in the reaction and motion parameters of the radicals and is this related to differences in lattice packing efficiencies between odd and even compounds? To our knowledge, propionamide is the only odd carbon linear amide whose structure has been determined. Though it fits into the same series as even amides with respect to lattice parameters and space group, in one respect it seems to differ in crystal structure from even amides. It seems to have rotated 180 degrees about the chain axis when compared to the even amides. This, if true for the other amides, would seem to provide a basis for the alternation of properties.

Other questions suggest themselves. In isobutyramide the radical is present at the branch point of the molecule. In a longer molecule, a branch point in the middle would tend to interfere with efficient packing of the hydrocarbon chains. If the peroxy radical was at a position one or two carbon atoms removed from the branch point, would it have greater freedom of motion than the compounds studied here? That this seems likely is suggested by an observation made on oleamide. This compound has a cis double bond which interferes with the efficient packing of the hydrocarbon chains. In this compound the diffusion of gasses was found to be much more rapid than in the linear saturated amides[7].

One other question seems suggested from this work. The comparison between propionamide and valeramide suggests that the Z' axis motion is more hindered the longer the chain length. With a long enough chain length, will this motion be completely eliminated or will it reach a limiting value? These question of some importance in understanding solid state reaction mechanisms and because some of the processes occurring in these crystals may bear some resemblance to similar processes in cell membranes, which also have a bilayer type of structure.

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