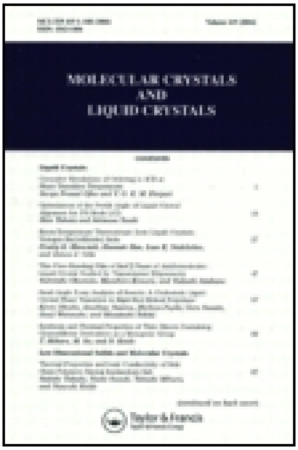

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Mark D. Hollingsworth [a] & J. Michael Mcbride [a]
[a] Department of Chemistry, Yale University New Haven, CT, 06511, U.S.A.

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INFRARED STUDIES OF LONG-RANGE STRESS IN SOLID-STATE PEROXIDE PHOTOREACTIONS

MARK D. HOLLINGSWORTH[1] AND J. MICHAEL MCBRIDE

Department of Chemistry, Yale University
New Haven, CT 06511, U.S.A.

ABSTRACT When crystals of di(undecanoyl) peroxide are photolyzed at low temperature to conversions greater than about 0.06%, *in situ* FTIR spectroscopy of the CO_2 product shows numerous ν_3 bands which are not observed after less extensive photolysis. The shift of these bands to high frequency suggests the influence of stress fields generated by distant reaction sites. The influence becomes more pronounced upon annealing to about 140K, but disappears after annealing above 280K. This behavior is discussed in terms of relaxation through both rapid elastic deformation and stepwise, thermally activated plastic deformation. Isotope labeling shows that the new CO_2 vibrations are not tightly coupled to one another. An analysis based on random decomposition shows that the perturbing defects lie well beyond the first coordination sphere of the probe CO_2 molecule and probably cooperate in influencing subsequent reactions. These results suggest caution in interpreting solid state product distributions, even at very low decomposition levels.

Much of our understanding of reaction paths in organic crystals comes from interpreting product distributions in terms of ideal crystal structures. Such interpretations are difficult because significant levels of conversion are needed for accurate product analysis, and, as decomposition proceeds, the crystal environment changes. At some point forces on reactant molecules should begin to differ substantially from those in a pristine crystal. The new forces could influence both the rates of competing processes and the packing structure of reaction intermediates. Depending on the amount of environmental distortion that accompanies reaction, and the degree to which the lattice can accommodate this distortion, the course of a solid-state reaction should change more or less dramatically during decomposition.[2]

During our FTIR investigation of solid-state diacyl peroxide photolysis,[3] it was important to establish the conversion limit beyond which reactioninduced changes in crystal properties would begin to complicate the chemical behavior. Results from preliminary studies of this question are discussed in the present paper. We find that reaction sites may interact significantly after less than 0.06% (600 ppm) decomposition. This indicates that reactivity in single crystals can be controlled by defects far beyond the first coordination sphere of the reaction center,[4] and that caution must be used when interpreting product ratios, even after low levels of decomposition.

LOCAL STRESS IN DI(UNDECANOYL) PEROXIDE DECOMPOSITION

Long molecules of di(undecanoyl) peroxide (UP) pack in a sheet-like structure, with efficient side-to-side contacts among alkyl chains within a layer, but with inefficient contacts at the interface between adjacent layers, where only methyl groups touch.[5]

Photolysis of crystalline UP at low temperature produces long-lived aggregates of two decyl radicals and two CO_2 molecules with well-defined packing structures. Segmuller and McBride, using single-crystal EPR spectroscopy to study successive motions of the radical pair upon warming from 20K, defined a reaction sequence involving three distinct radical pair intermediates, named A, B, and C, which differ only in the spatial arrangement of a common set of the molecular fragments - two decyl radicals and two CO_2 molecules.[6] The reaction sequence is "non-topochemical" in that the radicals in successive pairs are driven further and further apart before they come together to give eicosane and other products. The radicals are driven into the loosely packed interface between layers by repulsion among the four molecular fragments produced inside the cage that had held a single precursor molecule.

In studying the same process by FTIR, we have used the asymmetric stretching (ν_3) mode of CO_2 both as a gauge of the local stress generated by photochemical bond cleavage, and as a probe of the structure and dynamics of the reaction intermediates. Because this mode absorbs strongly in a spectral region with minimal background absorption, carefully measured spectra can show products from decomposition of a few molecules per million in a crystal 0.5 mm thick. This sensitivity has made it possible to study the effects of long-range stress by comparing spectra for very different amounts of photolysis.

Each of the intermediate structures identified by EPR showed its own distinctive, clean IR spectrum of CO_2 with fwhm linewidths of about 0.5 cm^{-1}.[7]

During conversion of A to B, small additional peaks were observed and assigned to intermediates in the A to B transition that had not been detected by EPR. Each structure showed two ν_3 peaks corresponding to neighboring CO_2 molecules in an unsymmetrical environment. Usually the spatial proximity of the two CO_2s was apparent from vibrational coupling between them.[8] The various ν_3 absorptions span a range of some 20 cm^{-1} and shift in discrete steps from one intermediate to the next, generally to the red. We attribute most of this frequency shift to reduction of force along the long axis of CO_2 during relaxation of a highly anisotropic local stress field initially equivalent to a pressure of 20-30 kbar.[9] Annealing the photolyzed crystal at 124-130K, so that the radical pairs react, gives a species D that shows a single CO_2 stretching peak at relatively low frequency (2333.2 cm^{-1}). On the basis of our work with terminally halogenated analogues of UP,[10] we assign this peak to CO_2 that has been squeezed out of the molecular layers into the loosely packed interface.

A MODEL FOR LONG-RANGE STRESS

When a molecule breaks apart within a crystal, it generates high local stress that exerts strong influence on the behavior of its own fragments.[2,6] At high enough concentration of reacted sites the stress originating from one defect should influence the behavior of fragments in nearby defects. The very simplest linear elasticity theory for an isotropic continuum provides a qualitative picture of how this might occur. When a pressure **p** is generated in a spherical cavity of radius $\mathbf{r_0}$ in an infinite isotropic continuum, each portion of the solid undergoes a radial displacement (Δ), which is inversely proportional to the square of its distance (**r**) from the center of the cavity and directly proportional to the pressure and to the cube of the cavity radius:

$$\Delta = r_0^3 / r^2 \cdot p / 4\mu$$

where μ is the shear modulus of the solid.[11] To achieve a 10% radial expansion of the cavity ($\Delta = 0.1\, r_0$ at $r = r_0$) would require a pressure of 0.4 μ.[12] This would amount to 1100 kbar in diamond, 106 kbar in LiF, 12 kbar in KCl, and some 6 kbar in biphenyl at room temperature.[13]

In this idealized system strain dies away rapidly, since it is proportional to r^{-2}. If a group at a distance of one molecule from the defect were displaced by 1Å, a group ten molecules away would be displaced by only 0.01Å. Stress dies away still more rapidly. Since the state of strain is established by pr_0^3, effective pressure is proportional to the inverse cube of distance. A pressure of 30 kbar at a distance of one molecule from the defect would fall to 30 bar at a distance of ten molecules. This equilibrium gradient of elastic strain and stress should be established rapidly, according to the speed of sound in the medium.

There are two notable differences between this continuum model and our molecular crystals. One difference is that our crystals are discontinuous and very anisotropic. Most of the elastic "give" comes between molecules, not within them. Thus stress and strain could be transmitted over much longer distances along the chains of bonds than normal to them.

The second difference is that large strains near the defect should undergo thermally activated relaxation. When the sample is warmed after low-temperature photolysis, successive barriers should fall as their elastic limits are exceeded. This would reduce stress inside the former barrier but increase stress further out in the bulk. An analogue would be a nest of concentric balloons, with the stiffest, highest pressure balloon at the center. If the central balloon pops, pressure at the center falls, but pressure further out increases. The radical pairs of UP provide a specific example.[6] At 33K the CO_2s between the two decyl radicals of Species A force one radical to back up by a screw motion in which each CH_2 group in the zig-zag chain replaces its neighbor. This relaxation gives Species B. At 54K the other chain is forced back, converting Species B to Species C. In each process the overall strain energy is reduced, but stress increases at the remote end of the chains and probably further into the crystal as well. Since these irreversible plastic deformations are thermally activated, they can be negligibly slow at low temperature. After each plastic change, elastic equilibration is rapid at any temperature.

This analysis suggests that the stress measured at some distance from the reaction center should *increase* with each successive plastic deformation, until the boundary of plastic deformation passes the point of measurement.

TESTING THE MODEL

At very low levels of decomposition, the asymmetric stretching bands of CO_2 in photolyzed UP crystals are simple and well-characterized,[7] but increasing decomposition complicates the spectra. Except for a slight broadening of lines, spectra of Species A and B are not noticeably affected by somewhat longer photolysis, but spectra of C, and especially of D, show new bands at higher frequencies. We believe this represents spreading of the stress field about each defect until, in C and D, adjacent stress fields overlap and influence one another.

Below we discuss five questions related to this interpretation:

(1) How much decomposition is required to generate the new bands?
(2) Can one infer the range over which stress is influential by assuming random decomposition?
(3) Do several point defects cooperate in exerting stress influence?
(4) Might the new band positions reflect unusual vibrational coupling between neighboring CO_2 molecules as well as unusual stress?
(5) How easily can long range stress be reduced by annealing?

EXTENT OF DECOMPOSITION

In principle it is straightforward to use the IR absorbance of ν_3 to measure the extent of decomposition at which new bands begin to appear. The integrated absorption is easy enough to measure in our single crystal samples, but there are numerous difficulties related to estimating the extinction coefficient, because it depends on IR polarization and molecular orientation, on the molecular environment of the CO_2, and on the possibility of vibrational coupling between adjacent CO_2 molecules.[14] In the following discussion we err intentionally toward slightly overestimating the concentration of CO_2, so that we may be confident that long-range stress becomes important at even lower concentration than we estimate, and at even greater distance.

We have estimated the concentration of CO_2 using the absorption of Species C, the immediate precursor of the species which shows the most additional peaks at intermediate conversion. Species C was convenient because the pattern of two ν_3 peaks is relatively simple, because the orientation of its CO_2 molecules is known, and because the absorptions are identical, within 8%, for light polarized along the a and b crystal axes.[3] This made it possible to use unpolarized light without introducing undue error when absorption is high. For the amount of conversion involved in these experiments the relative intensity of the two ν_3 peaks is constant, suggesting that the CO_2 orientations do not change. At much higher conversion the spectrum of Species C becomes more complex, like that of Species D, and is unreliable for estimating concentration.

Compared with other CO_2 bands found in UP, the molar absorptivities in Species C are relatively high (1.5 times those in the species with the lowest absorptivity). We feel confident that by using Yamada and Person's value[15] for the molar absorptivity of polycrystalline CO_2 (45,900 cm $mmol^{-1}$, as against a gas phase value[16] of 60,400 cm $mmol^{-1}$) we have overestimated the concentration of CO_2, but by a factor less than 2.[17]

Given the thickness and orientation of the crystal, the components of the absorbance tensor for the two ν_3 bands from Species C, and the integrated intensities corrected for coupling, we used the following equation to estimate the mole fraction of defect sites:[18]

$$\chi_{\text{defects}} = \frac{n(CO_2)\,/\,2}{n(\text{Peroxide})} \approx \frac{\int \ln(I_0/I)\, d\upsilon}{3 \cdot \varepsilon \cdot t \cdot (A_a + A_b) \cdot D/MW}$$

Here, **n** is the concentration ($mmol/cm^3$)

ε is the absorptivity in darks (cm $mmol^{-1}$)

t is the thickness of the crystal along [001] (cm)

D is the density of the peroxide (1.02 g/cm^3 for UP)

MW is the molecular weight of the peroxide (g/mmol)

The integral is the spectral intensity (in cm^{-1}, corrected for coupling) of ν_3 in a crystal whose (001) face is perpendicular to the incident beam

A_a and A_b are direction cosines of the ν_3 transition dipole of CO_2 in crystal coordinates; a factor of 2 for an unpolarized light beam in the c direction cancels the 2 for stoichiometry of CO_2 production.

The factor 3 is used to adjust the molar absorptivity of a randomly oriented CO_2 to that of a CO_2 aligned with its long axis along the electric vector of the incoming beam.

Table 1 summarizes the results from four UP crystals of differing thickness. The last three rows concern successive experiments on the same crystal. The second and third columns show that the two ν_3 bands of Species C agree well in estimating the amount of decomposition. The fourth and fifth columns show that extra stretching and bending peaks of CO_2 become important for Species D beyond a threshhold of about 600 ppm decomposition. The spectra of Species C at this level of decomposition are much cleaner than those of D. Figure 1 shows the most complicated spectrum of C, corresponding to the last row of Table 1, and Figure 2 shows spectra of D for the last three rows of Table 1.

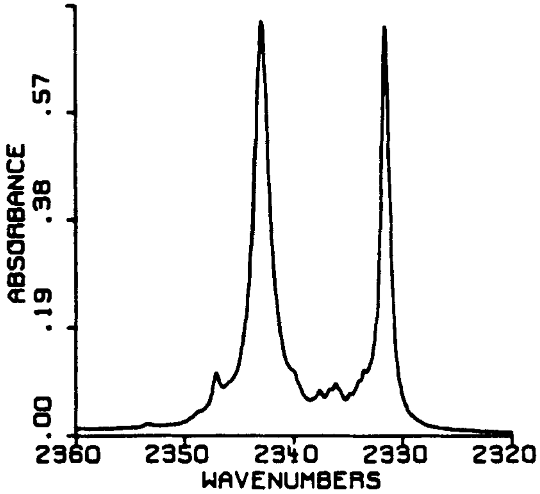

FIGURE 1. CO_2 stretching of Species C for the last entry in Table 1 (photolysis to 0.1% conversion of a UP crystal, which was previously 0.13% photolyzed). Spectra of Species C for the other entries in Table 1 show much cleaner doublets. The corresponding spectrum of Species D (Fig. 2f) shows a higher fraction of extra peaks.

TABLE 1. Relation of Extent of Conversion, Measured by the Doublet of Species C, to Appearance of Extra Peaks for Species D.

t (mm)	[C1]*	[C2]*	$\chi_{\mathrm{def}} \cdot 10^6$	Extra D?	Figure
0.77	0.25	0.22	86	no	-
0.12	0.53	0.51	188	no	-
0.22	0.63	0.58	222	no	-
0.32	1.53	1.47	546	no	2d
"	2.00	1.95	716	yes	1 , 2a
"	2.76	2.90	1022	yes	2f

* Concentration ($mmol/cm^3$) inferred from each of the two peaks of Species C

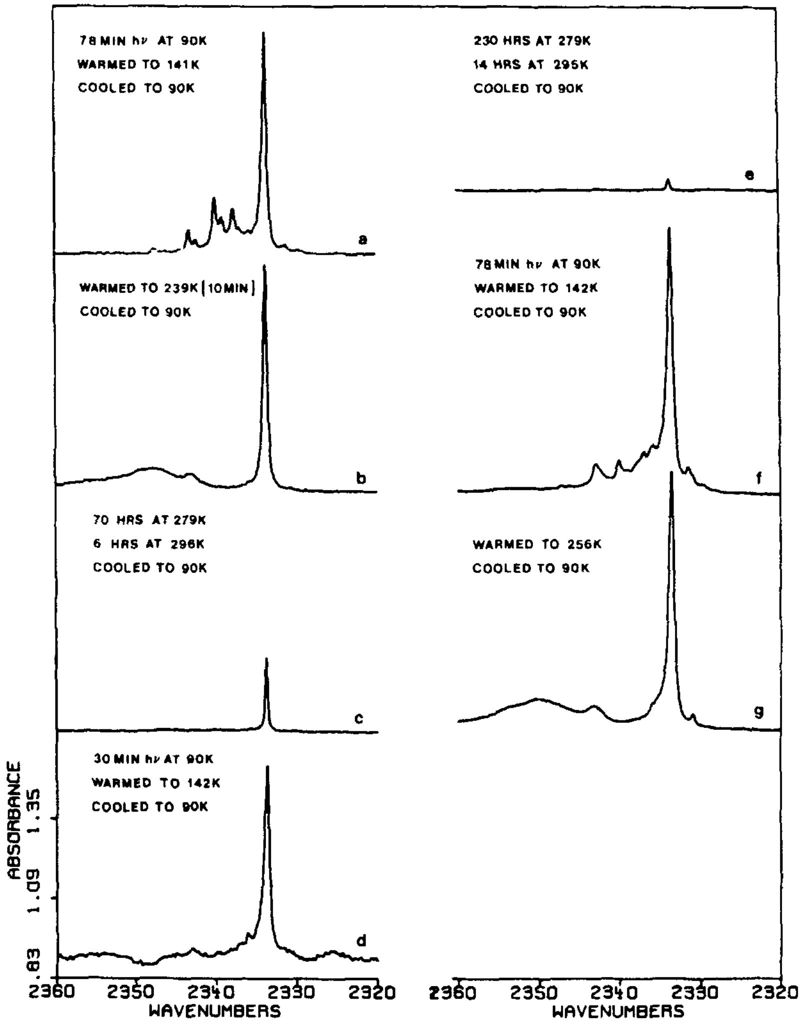

FIGURE 2. CO_2 stretching during three successive cycles of photolyzing and annealing a single UP crystal. All spectra have the same scale and were measured at the photolysis temperataure of 90K. After the first and third 78-min. photolyses (a and f) many extra bands accompany the Species D singlet. After the second 30-min. photolysis (d) they do not appear, although the singlet is nearly as large. The broad bands from annealing at 239K (b and g) disappear at 295K (c and e).

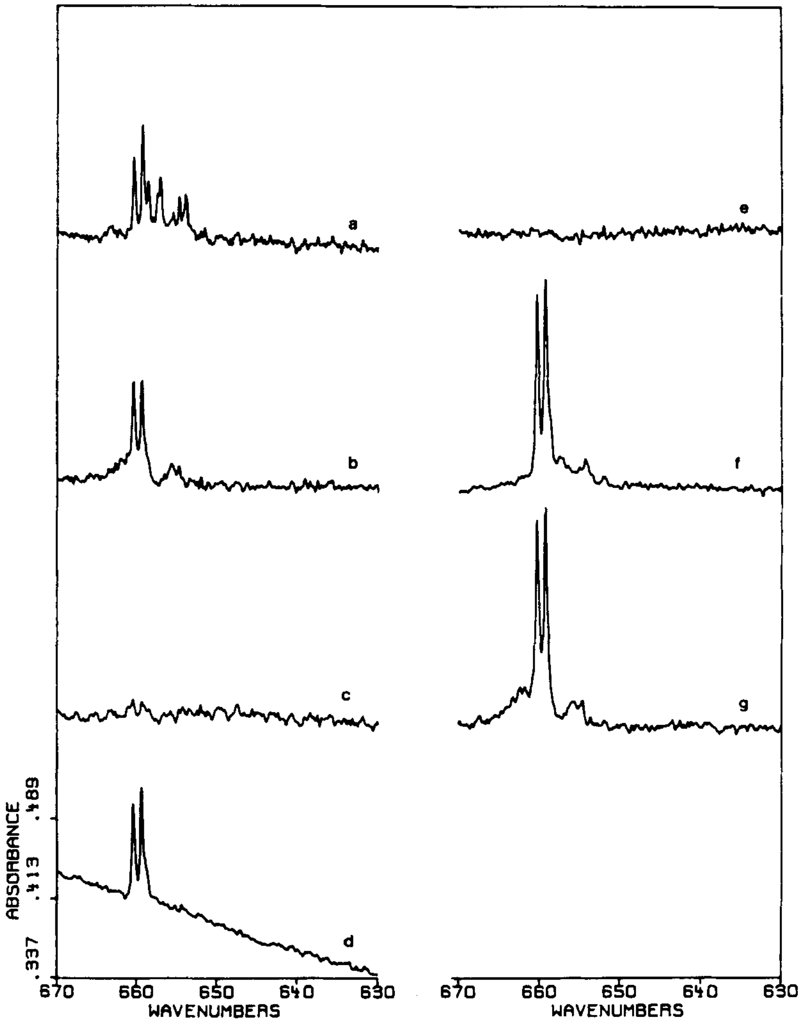

FIGURE 3. CO_2 bending under the same conditions as for the spectra of Figure 2. The solid environment lifts the degeneracy of the two bending modes to give a doublet. Note the purity after shorter photolysis (d) as compared to after longer photolysis (a and f). Again the extra peaks are significantly broader from the third photolysis (f) than from the first (a).

THE RANGE AND COOPERATIVITY OF STRESS INFLUENCE

Naive use of the 600 ppm decomposition threshhold to estimate the distance over which local stress is influential requires assuming that decomposition is random and that its influence is isotropic. Decomposition is probably random, because the light intensity is uniform throughout the crystal,[19] and yields in the primary photochemical events of photon absorption and bond cleavage are probably not strongly stress dependent.[20] However, local stress fields are certainly not isotropic; in fact their influence is probably qualitatively different in different directions, as suggested by the variety of the extra peaks. Some of this anisotropy is due to molecular shape. Since intramolecular potentials are much stiffer than intermolecular ones, stress should be transmitted further in the direction of a molecule's long axis. For purposes of this crude discussion we take anisotropy into account by measuring distance in "molecules" rather than in angstrom units. This assigns primary importance to the number of intermolecular gaps between the source of stress and the position where its influence is to be measured.

A "sphere" with a radius equivalent to r molecular spacings would contain $M = 4/3\,\pi\, r^3$ molecules. Suppose a small fraction, **f**, of the molecules in the sample have decomposed at random. The probability, ρ_n', that exactly a small number **n** of the **M** molecules within the sphere have decomposed can be approximated[21] by the following relationship:

$$\rho_n' \approx \frac{1}{n!} M^n f^n (1-f)^M$$

And the probability, ρ_n, that *at least* n of the molecules have decomposed can be approximated by:[22]

$$\rho_n \approx 1-(1-f)^M \sum_{k=0}^{n-1} \frac{1}{k!} M^k f^k$$

In Spectrum 2a perhaps 40% of the CO_2 ν_3 intensity occurs in abnormal peaks. At the threshhold conversion of f = 600 ppm, to achieve a 40% probability of at least one decomposition would require a sphere containing 851 molecules (radius = 5.9 molecules). A 40% probability of at least two decompositions would require a sphere of 2295 molecules (radius = 8.2 molecules). A 40% probability of at least three decompositions would require a sphere of 3806 molecules (radius = 9.7 molecules).

Previous damage in the neighborhood causes Species C and D to show extra peaks, but it is not certain at what point in the reaction scheme this influence is exerted. Since Species A and B show no spectral changes at this level of decomposition, we infer that the influence is only felt when the photolyzed crystal is warmed and the stress field of each defect expands during plastic deformation. If so, all sets of fragments throughout the crystal make the decision to become normal or abnormal at the same level of overall decomposition. It is possible, however, that long range stress determines the choice of paths *during* photolysis, and the choice becomes observable only upon subsequent warming. The latter case would be more difficult to model because choices would have been made continuously at varying levels of overall decomposition.

Whenever partitioning between normal and abnormal products occurs, the abnormal/normal ratio should depend on the overall extent of decomposition as of that time. If only one neighboring defect suffices to cause formation of abnormal product, the ratio should depend linearly on the fractional decomposition, but if cooperative influence from n nearby defects is required, the ratio might approximate n*th* order dependance on f :

$$\frac{\text{abnormal}}{\text{normal}} \propto f^n$$

$$\log\left(\frac{\text{abnormal}}{\text{normal}}\right) = n \log(f) + \text{const}$$

From the fourth and fifth rows of Table 1 and frames d and a of Figure 2 it appears that increasing f from 546 to 716 ppm causes the ratio of abnormal to normal product to increase from perhaps 0.3 to 0.7; that is, $\Delta \log f = 0.27$, $\Delta \log(\text{abnormal/normal}) = 0.84$, and $n \sim 3$ to 4. The cooperative influence of three or four neighboring defects could explain the sharp onset of abnormal products at a threshhold extent of photolysis.

Both the data and the level of analysis are inadequate for such a complicated system, but they suggest that the range of stress influence extends over distances of at least 6 to 10 molecules, and that stress fields from several distant defects may well cooperate in influencing the reaction path.

VERY LONG RANGE INFLUENCE

Such long range influence may seem inconsistent with the rapid decrease in stress and strain predicted above from continuum mechanics. Although the stress from an individual defect falls off with the cube of distance, the number of random defects in a spherical shell at a given distance from the point of sampling is proportional to the square of the distance. Thus, assuming additivity of the stress contributions from separate defects,[23] the net stress from a spherical shell should be inversely proportional to its radius. Integration of 1/r dr suggests that the total contribution out to a distance r is proportional to log(r). This means that on average there should be equal contributions from defects within 10 molecular distances, from defects between 10 and 100 distances, from defects between 100 and 1000 distances, and so on. The upper limit would be set by the dimensions of crystal blocks, probably less than 1000 molecules on a side for cooled crystals with ideal mosaic structure. Of course the influence of very near neighbors would be too specific and anisotropic to fit this model.

ABSENCE OF COUPLING FOR ABNORMAL BANDS OF SPECIES C

Studies of long photolysis were carried out with a UP crystal that was randomly labeled with ^{13}C in the carbonyl position. With 24.7% ^{13}C in the peroxide, 37.2% of the CO_2 pairs contained one ^{13}C, and 6.1% contained two. In CO_2 pairs containing both carbon isotopes (heteronuclear pairs), the near-resonant interactions between CO_2s are disrupted, and the frequencies of the bands shift toward their intrinsic, uncoupled values.[24]

Figure 4 shows the result of photolyzing this crystal long enough to perturb the spectrum of Species C. Note that the $^{13}CO_2$ and $^{12}CO_2$ patterns are very similar, and that the abnormal bands grow relative to the normal C1-C2 doublet as photolysis continues. In Figure 5, the $^{13}CO_2$ bands have been shifted and scaled so that peaks of equal force constant are displaced vertically. Although resonant coupling is evident in the band labeled 2 (see dashed line and arrow), the observed frequency shifts are due primarily to a change in environment which does not concern coupling.

The absence of pronounced vibrational coupling argues against the view that the abnormal bands are due to local pockets containing several decomposed molecules formed by some non-random decomposition process.

Since the polarization and coupling for the abnormal CO_2 bands are not necessarily the same as for the bands observed at low conversion, it is not possible to be certain that all of the frequency shifts are directly due to stress. However, it is suggestive that long photolysis produces blue shifts. Our current hypothesis is that the abnormal peaks correspond to CO_2s which, because

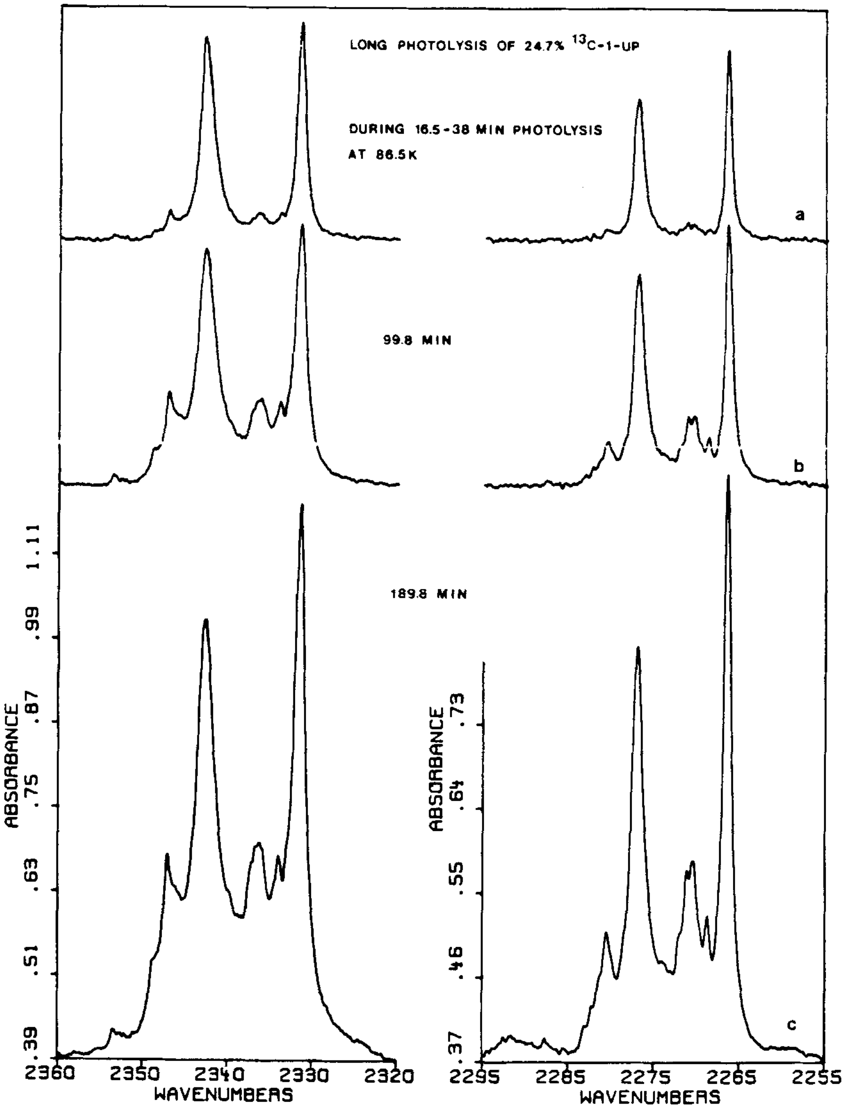

FIGURE 4. Comparison of stretching patterns for Species C during very long photolysis of a UP crystal with 24.7% ^{13}C distributed randomly in the carbonyl carbon position. The left column in the $^{12}CO_2$ range is mostly from homonuclear pairs; the right column, $^{13}CO_2$, mostly from heteronuclear pairs.

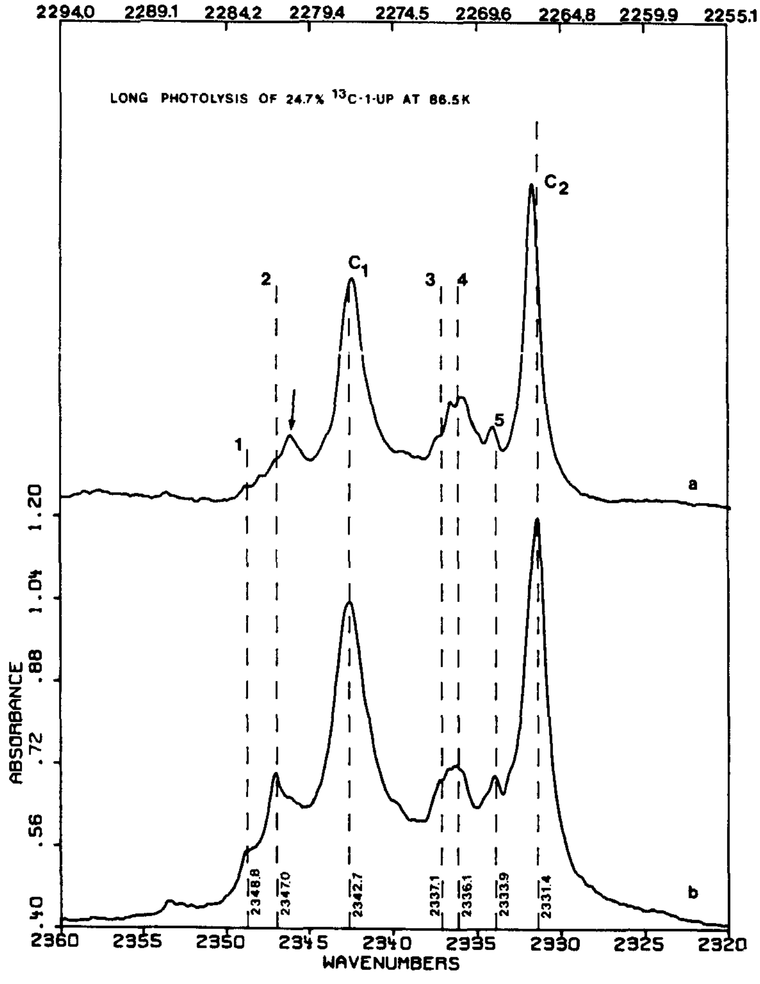

FIGURE 5. Spectra from the bottom frames of Figure 4 with $^{12}CO_2$ below and $^{13}CO_2$ above, its scale expanded and shifted by a factor of 1.02876 to correct for the difference in reduced mass (original scale at top). The homonuclear spectrum below shows that vibrational coupling is significant only for the extra peak labeled 2, and even in this case accounts for a modest portion of the shift from C1 and C2.

of stress from surrounding defects, remain trapped within the molecular layers, while the normal peaks of Species D come from CO_2 in the interlamellar space. This suggests a much more profound structural perturbation than in Whitsel's radical pair studies of acetyl benzoyl peroxide, where long-range stress changed the inter-radical separations by less than 0.03 Å.[2]

ANNEALING THE STRESS GENERATED BY LONG PHOTOLYSIS

Figures 2 and 3 show the effects of different lengths of photolysis and annealing on the stretching and bending spectra of Species D in a crystal of UP that was used in three successive experiments.[25] The sequence of events and observations was as follows:

(a) Long photolysis (716 ppm conversion); extra peaks observed
(b) Short annealing at 239K; broadening and shift of extra peaks[26]
(c) Long annealing at 296K; disappearance of extra peaks
(d) Slightly shorter photolysis (546 ppm); no extra peaks
(e) Long annealing at 295K; loss of most of the CO_2
(f) Long photolysis (1022 ppm); extra peaks observed
(g) Short annealing at 256K; broadening and shift of extra peaks

Figure 2d is particularly revealing, because it shows that annealing not only removed the abnormal CO_2 peaks, but also removed the crystal defects which caused them to occur, so that subsequent shorter photolysis generates only normal peaks. It is curious that the main peak in Figure 2d is almost as high as that in Figure 2a, since integrated spectra of their precursors (Species C) showed 30% more decomposition for Figure 2a. This shows that beyond 600 ppm conversion a large fraction of the reaction gives abnormal product.

CONCLUSIONS

Although the current work has not given definitive, quantitative answers to many of the questions about the influence of distant crystal defects on solid state reactions, it seems clear that defects can be influential at concentrations below 0.1%. The most likely source of this influence is mechanical stress generated by reaction and communicated over distances that are surprisingly large when viewed by continuum elasticity theory. Analogous influence might be expected from any process that changes the size or shape of the reaction cavity. These results show that caution must be exercised when interpreting product distributions from solid state reactions in terms of ideal crystal packing, even at low decomposition levels, except for the rare reactions that give negligible change in molecular shape.

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[18] Concentrations can be measured accurately only with polarized absorbances. This is especially important when absorption is high or when A_a and A_b are very different from each other. In the case of Species C, particularly with the low frequency peak for which $A_a/A_b = 1.04$, this is a reasonable approximation for all but the largest absorbances, as indicated by internal checks on corrected intensities (Columns 2 and 3 of Table 1). These points are discussed in more detail in Reference 3.

[19] A crystal 0.3 mm thick transmits 81.7% of incident 313 nm radiation, so that intensity is nearly uniform through the thickness of the crystal. The IR beam is some 8 mm in diameter, smaller than the photolysis beam which is carried to the crystal by a fiber optic light pipe, so intensity is uniform across the width of the sampled region as well.

[20] If molecules adjacent to a previously decomposed molecule showed increased photolability, the proportion of extra peaks should increase with increasing decomposition, but not with a threshhold as sharp as we observe. Decomposition of immediately adjacent molecules might also give vibrational coupling of CO_2s, which we do not observe in the extra peaks. If several adjacent molecules were decomposed by a single photon, the effect should be evident at low as well as high conversion.

[21] This approximation assumes that M is large, n is small, and f is very small. Under our conditions the error is certainly negligible compared to the assumption that all defects within the sphere exert the same influence at its center. The equation is based on the following expression:

$$\rho_n' = Mf \cdot 2^{-1}(M-1)f \cdot ... \cdot n^{-1}(M-n+1)f \cdot (1-f)^{(M-n)}$$

[22] The probability that none have decomposed is $(1-f)^M$; the probability that at least one has decomposed is $1 - (1-f)^M$. Successive members of the series are obtained by subtracting successive ρ_n' terms.

[23] The stress should not be perfectly additive, because with a uniform distribution of defects the macroscopic sample can expand to reduce its internal stress. For example, during a photodimerization which ultimately leads to shrinkage of all unit cell dimensions, there is an initial expansion of one side (by almost 1%) and of the cell volume. H. Nakanishi, W. Jones, J. M. Thomas, M. B. Hursthouse, and M. Motevalli, *J. Chem. Soc. Chem. Comm.*, **1980**, 611.

[24] M. D. Hollingsworth and J. M. McBride, *Chem. Phys. Lett.*, **1986**, *130*, 259.

[25] Although bending bands are shifted to the red by pressure,[9] it is not possible to attribute the shifts in Figure 3 to long range stress, since not enough is understood about the influence of environment on bending frequencies.

[26] We do not understand the reason for the very broad absorption.