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Single Crystal EPR Studies of Radical Pairs in Dibenzoyl Peroxide

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Four different phenyl-benzoyloxy (PB) radical pairs and two different benzoyloxy-benzoyloxy (BB) pairs, each existing in four symmetry-related orientations, have been observed by epr in single crystals of dibenzoyl peroxide after brief uv irradiation at low temperature. At 5 K two PB pairs are formed; PBT disappears in less than 2 minutes at 5 K, but PB5K persists to 15 K, where it converts to PB15K in a process that involves 39° in-plane rotation of the benzoyloxy radical. Further warming to 24 K generates PB24K from an unidentified precursor which gives no epr spectrum and is destroyed by visible light. PB15K and PB24K persist to 65 K. Irradiation at 10 K forms a BB pair which converts cleanly to a second BB at 25 K. Stability of the pairs and distinguishability of PB pairs are discussed in light of a crystal packing analysis.

INTRODUCTION

In 1970 Box, Budzinski, and Freund reported observing pairs of phenyl radicals in crystals of dibenzoyl peroxide (BPO) which had undergone uv irradiation at 4.2 K.[2] More recently Barchuk, Dubinsky, Grinberg, and Lebedev observed phenyl-benzoyloxy pairs in crystals photolyzed at 62 K.[3] The Russian workers reported that photolysis with polarized light could lead to selective expulsion of either of the two chemically equivalent CO_2 fragments in a BPO molecule. On this basis they suggested that photoexcitation is localized in half of one molecule on the time scale of decarboxylation.

We began a detailed epr study of phenyl-benzoyloxy pairs in crystalline BPO hoping to discriminate between different assignments of the benzoyloxy radical's electronic configuration.[4–6] Although we have not yet resolved this question, we have identified five new radical pairs in irradiated BPO. This paper discusses the nature of the radical pairs and their interconversions. Our observations bear on the question of molecular mobility in a crystalline reaction site, and together with analysis of the molecular packing they permit some reinterpretation of the work of Barchuk, *et al.*

EXPERIMENTAL

Crystals of Dibenzoyl Peroxide were grown from benzene by evaporation at room temperature. Typically, a solution saturated by stirring without heating was gravity filtered, diluted with 10% excess benzene, proportional into 50 ml beakers, covered with paper and allowed to stand in the hood overnight. Crystals of variable sizes (2 × 2 × 1 to 1.5 mm for epr; 0.3 mm maximum for X-ray) were isolated by vacuum filtration and washed with hexane.

X-Ray measurements were made on a Nonius CAD-4 automatic diffractometer using Mo K_α radiation. The crystal data are; $C_{14}H_{10}O_4$, mol. wt. 242.23; orthorhombic, space group $P2_12_12_1$; $a = 8.992(2)$ Å, $b = 14.322(3)$ Å, $c = 9.446(2)$ Å, $V = 1216.2$ Å^3, d(calc) = 1.323 g/cm^3 for $Z = 4$. Unit cell parameters were obtained by least squares fitting to 23 reflections ($17.3° < 2\theta < 45.4°$). Data reduction and refinement were performed with the Enraf–Nonius SDP software (Jan. 1977). Full matrix least squares refinement of 163 parameters using 801 (3σ) observations converged at R(unweighted) = 4.4% and R(weighted) = 5.4%. Hydrogen atoms were placed at calculated positions and not refined. Positions were recalculated before the final two cycles. The largest peak in the final difference Fourier map was 0.183 e/Å^3.

The crystal structure determined previously by Sax and McMullan using film data is essentially correct.[7] Their atomic numbering scheme is shown in Figure 1. Most atomic coordinates are within two of the standard deviations they reported, although atom C(13) deviates by 0.043 Å. The new standard deviations are at most half as large as the old ones.[8]

EPR measurement techniques, fitting procedures and equipment were described previously.[4] Crystals were irradiated within the microwave cavity with an Osram HBO 200W/2 lamp focused with an f/1 quartz lens and filtered to pass 300–400 nm.[4] The temperature was controlled by Varian 4540 and Air Products Heli-tran LTD-3-110 cryostats and monitored with a gold-constantan thermocouple placed two centimeters below the crystal.

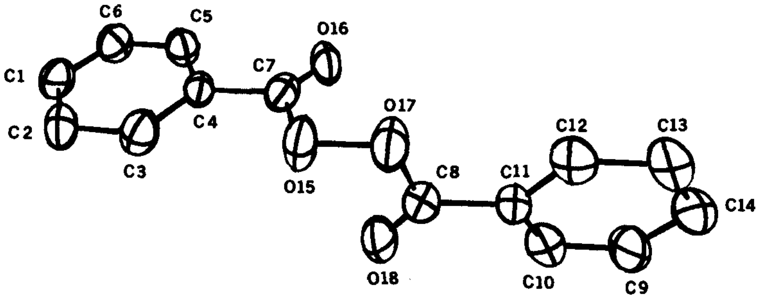


FIGURE 1 ORTEP view of BPO along the c-axis. Thermal ellipsoids at 33% probability.

The thick crystals were attached to a flat face on a spectrosil rod with silicone grease. Initially we had difficulty in maintaining the crystal mounting either because the crystals fractured due to thermal shock or because they were bumped on insertion into the EPR cavity. We avoided the first problem by cooling the mounted crystals in the cavity from room temperature to 5 K over 30 minutes.

We avoided the second problem by refining the crystal orientation on the basis of internal symmetry. For a general mounting of a $P2_12_12_1$ crystal the four radical pairs related by three orthogonal screw axes are magnetically inequivalent. On rotation about an axis perpendicular to the field, the fine structure splitting of each pair describes a cosine squared curve characterized by three parameters (minimum, maximum, and phase). These twelve observed parameters may be used to determine the five parameters of the traceless zero-field splitting tensor and three eulerian angles which determine the crystal mounting.[9] All fine structure splittings were initially fit to a zero-field splitting tensor, D, using the measured mounting angles. The resulting tensor was used to find a new orientation which would fit the twelve observed parameters better. This new orientation was used in a second least squares determination of D, which was used to find a new orientation. This iterative procedure converged to within the 2 G experimental error in determining peak positions. Most initial measurements of mounting angles proved accurate within 1.5°, but in a few cases crystals had apparently been bumped and reoriented as much as 8°. Bumping is uncommon with thinner crystals.

The $\{110\}$ and $\{011\}$ crystal faces were indexed by birefringence and crude optical goniometry.[10]

RESULTS AND DISCUSSION

Crystal packing

Since the halves of a BPO molecule are not related by space group symmetry, the phenyl-benzoyloxy radical pair formed by loss of the CO_2 from one end of the molecule would not be related by symmetry to that formed by loss of the other CO_2. Thus a crystal might contain two classes of pairs, which could appear and decay with different rates, and which could give distinguishable epr spectra. To appreciate how different these pairs should be, and to interpret the polarized photoselection results of Barchuk, *et al.*, one must consider the packing of crystalline BPO.

As in several diacyl peroxides, the atoms of BPO lie near two planes created by a fold of about 90° along the O-O bond.[11] This bond is parallel to

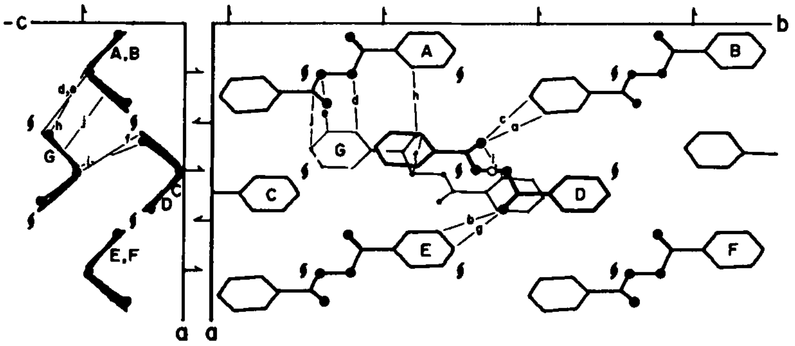


FIGURE 2 Orthogonal projections of a pleated sheet of BPO molecules and one molecule (G) from an adjacent sheet. The origin of axes in both projections is (−0.5, −0.8, −0.5). Molecules are lettered in the ring containing C(9)-C(14) and are related as: (A) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (B) $-x, y + \frac{1}{2}, \frac{1}{2} - z$; (C) $x, y - 1, z$; (D) x, y, z; (E) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (F) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (G) $\frac{1}{2} - x, -y, z - \frac{1}{2}$. The ten shortest non-hydrogen intermolecular contacts are lettered a-j and have distances of 3.27, 3.30, 3.34, 3.42, 3.43, 3.46, 3.47, 3.47, and 3.50 Å, respectively. The open circle near the center of molecule (D) denotes the pseudo dyad for molecules A-F.

the *b* axis within 1°. The left panel of Figure 2 shows the projection of molecules on the *ac* plane, and the right panel shows their projection on the *ab* plane.

Screw axes parallel to *b* carry the central molecule (D) of the *ab* projection into the molecules (A, B, E, F) in the four corners of that panel. This family of molecules forms a pleated sheet, as may be seen in the zig-zag pattern on the right of the *ac* projection. Within the pleated sheet intermolecular contacts between carbonyl oxygens and meta and para phenyl positions determine the *b* spacing. These four O-C distances range from 3.27 to 3.46 Å and include the three shortest non-hydrogen contacts in the crystal. They are indicated in Figure 2 by a, b, c, and g. The entire sheet displays approximate two-fold symmetry for rotation about an axis parallel to *c* near the midpoint of the O-O bond. Rotation about the point indicated by an open circle in the *ab* projection ($x = 0.2500$, $y = 0.1048$) superimposes carbon atoms in the sheet with an average deviation of 0.14 Å (maximum deviation 0.23 Å). Peroxy oxygens deviate by 0.11 Å. The carbonyl oxygens deviate by 0.49 Å because of differing torsional angles about the C(4)-C(7) and the C(8)-C(11) bonds (3.6 and 9.0°, respectively). It is no accident that the peroxy oxygens lie near $x = 1/4$, since that position balances the intermolecular interactions across the different screw axes parallel to *b*.

The pleated sheets stack along *c* with adjacent sheets being related by the screw axes parallel to *c* and *a*. The position of these screw axes is determined by the offset in the *b* direction between adjacent sheets (see molecule G in

Figure 2). Sliding the lower sheet by 3.00 Å in the *b* direction would make molecule G fall under molecule D. This would shift the screw axis to the open circle. Modest readjustment of the atomic positions would then convert the screw axis to a two-fold axis within the molecule, and the space group to $P2_12_12$. Since adjacent sheets would now be related by translation, the unit cell would be halved along *c*. In this space group the radical pairs formed by loss of either CO_2 in a molecule would be related by the two-fold axis. Thus understanding the difference between the two pairs is closely related to understanding what determines the offset between adjacent sheets.

The *ac* projection of Figure 2 shows that most short contacts between adjacent sheets involve faces of molecules related by screw axes parallel to *a*. Shifting to the $P2_12_12$ geometry does not increase the number of short (<3.5 Å) non-hydrogen contacts between the sheets, so it is unlikely that the offset is determined solely by van der Waals repulsions. The offset is just sufficient to bring the lettered phenyl group of molecule G under the carbonylperoxy group of the unlettered half of molecule A. Because of the screw axis parallel to *a*, this also brings the unlettered carbonylperoxy group of G under the lettered phenyl group of E. Contacts d and e between peroxy oxygens and phenyl carbons are the shortest intersheet distances. This suggests an attractive interaction between the carbonylperoxy and phenyl groups.

Whatever the source of the offset between sheets, the ends of a BPO molecule are distinguished in that the phenyl group at one end, and the carbonylperoxy group at the other, contact the complementary groups in adjacent molecules. This distinction has two implications:

1) One type of CO_2 may be lost preferentially in photolysis, either for physical reasons (excitation could be selectively trapped by the lettered, or the unlettered, end of molecules), or for chemical reasons (one of the radicals in an excited[17] intermediate benzoyloxy-benzoyloxy pair could be stabilized against decarboxylation by complexing with a neighboring phenyl group); and

2) The phenyl-benzoyloxy pairs formed by loss of different CO_2 groups should deviate from a two-fold symmetry relationship about *c* by at least 0.1–0.2 Å. Only one type of pair may be formed, but if both are formed, they should be distinguishable in the present epr spectra which show hyperfine features with linewidths of 2 G.[18] Since the fractional change in dipolar splitting is three times as large as the fractional change in dipole-dipole distance, and the dipolar splittings of phenyl-benzoyloxy pairs are as large as 471 G, radical pairs with distances differing by 0.3% or about 0.02 Å should give distinct spectra.

Phenyl-benzoyloxy pairs

Irradiation at 5 K produces two different kinds of phenyl-benzoyloxy radical pairs. The first, PB5K (phenyl-benzoyloxy 5 K) was readily identified by its sensitivity to visible light, its anisotropic *g* factor, and its distinctive phenyl hyperfine splittings (hfs), half as large as those of free phenyl (Figures 3; 4a,b). In most orientations the phenyl pattern can be described as a triplet of triplets with unresolved splitting by the para hydrogen. The distance between the outer components of the larger triplet splitting is the sum of the ortho coupling constants. To gain information about the orientation of the phenyl radical we fit a tensor to this splitting. The T_0 to T_1 and T_{-1} to T_0 patterns (49 of each) were treated independently, as the latter is more first order. The eigenvalues in Table I agree with those reported by Kasai.[19] The eigenvector associated with a positive anisotropic contribution to the hfs is reliable in direction. It lies within 10° of the ortho-ortho vector (C2-C6) in one phenyl ring of BPO and within 12° of the ortho-ortho vector (C10-C12) in the other, when crystal symmetry is applied. While this result does not establish which phenyl was decarboxylated, it does show that the phenyl group underwent only modest reorientation during PB5K formation.

We also determined *D* and *g* tensors for PB5K pairs.[20] The strong deviation from axial symmetry of the *D* tensor for PB5K ($D = 0.0220$; $E = 0.0039\ \text{cm}^{-1}$) is inconsistent with spin localization on one atom of the benzoyloxy radical and tends to support the assignment of a spin-delocalized π electronic state.

The other phenyl-benzoyloxy radical pair formed at 5 K is PBT (phenyl-benzoyloxy transient). Although its fine structure splitting is similar to that of PB5K, PBT shows broad hyperfine patterns indicative of disorder and decays with a half-life of less than two minutes at 5 K (Figure 4a,b). We have not studied this pair in detail because of its instability.

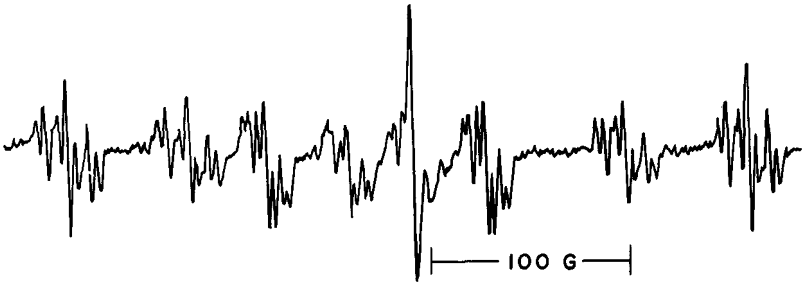


FIGURE 3 Four symmetry-related PB5K doublets with clearly resolved hfs, generated by brief photolysis of a BPO crystal in a general orientation. The DPPH reference near the center of the spectrum (× 0.1) overlaps one of the PB5K signals.

TABLE I

Hyperfine splitting by *o*-phenyl protons in PB5K[a]

Transition[b]	*x*	*y*	*z*	iso
$T_0 \rightarrow T_1$	5.1	−2.4	−2.7	18.1
$T_{-1} \rightarrow T_0$	4.0[c]	−1.6	−2.3	17.1
[d]	4.5[e]	−2.0	−2.5	17.4

[a] Line separations are given in gauss as anisotropic eigenvalues and an isotropic value. The first two rows show the sums of splitting by protons in the 2 and 6 positions in the radical-pair spectrum, which are appropriately compared with their average in isolated phenyl radicals.[4,6]

[b] See text.

[c] The direction of this eigenvector is (0.5730, ±0.2069, ±0.7930) in a cartesian frame based on the crystallographic *abc*.

[d] Literature values for phenyl.[19]

[e] This value was assigned to the direction connecting the ortho positions.[19]

When a crystal irradiated at 5 K is warmed to 15 K, PB5K converts irreversibly to PB15K (Figure 4c). Because the signals differ in saturation behavior, we are still uncertain whether this conversion is quantitative. The transformation must involve motion of at least one of the radicals in the pair, and the change in g tensor orientation (Figure 5) suggests that the benzoyloxy radical rotates in its plane by about 39°. A change in the electronic state of the benzoyloxy radical would also reorient the g tensor, but it would have been expected to change the eigenvalues as well.

Continued warming of the same crystal generates new signals at 24 K (Figure 4d,e). They are weaker than those of PB15K but give similar fine structure and hyperfine splittings in many orientations. This new pair, PB24K, appears after all traces of PB5K have vanished and PB15K has stopped growing. PB24K does not grow at the expense of PB15K, and both species are indefinitely stable below 50 K. The precursor of PB24K must be spectroscopically invisible. Certain phenyl-phenyl radical pairs might form a new type of phenyl-benzoyloxy pair by recapturing the CO_2 which is lost in forming PB5K and PB15K, and they might have been invisible at low temperature because of saturation. However, when crystals containing the precursor of PB24K are irradiated with visible light at 5 K, no PB24K appears on warming. Phenyl radicals are insensitive to visible light, although benzoyloxy radicals are decarboxylated. We have no reasonable suggestion for the identity of the precursor.

When the crystal containing PB15K and PB24K is warmed slowly, the two signals decay between 62 K and 67 K with rates which differ by less than 10%.

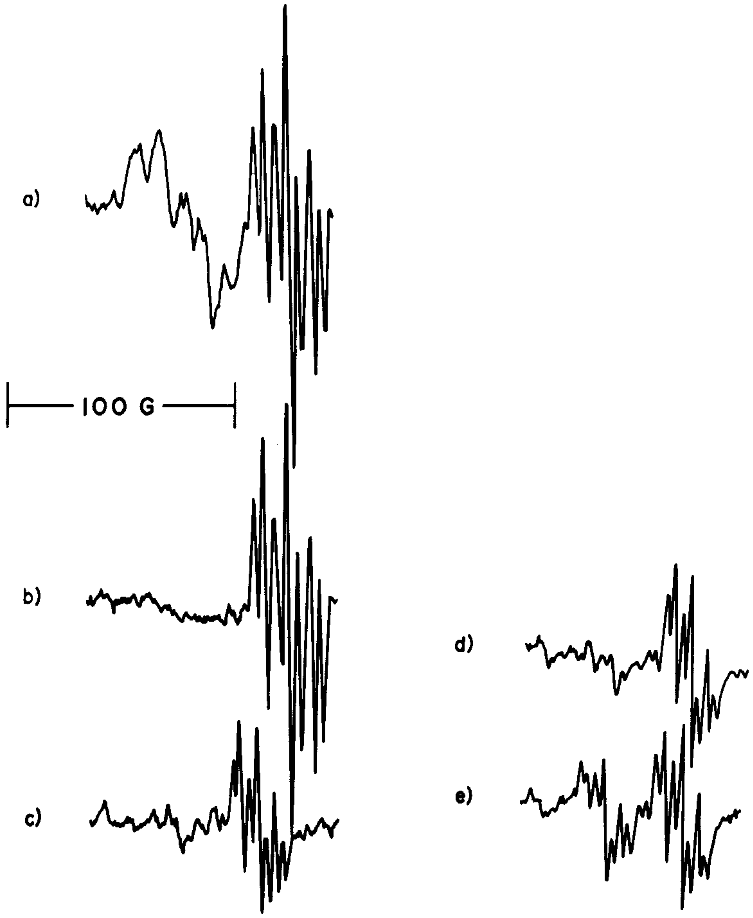


FIGURE 4 Repeated scans (3080–3180 G) after irradiation of a BPO crystal at 5 K. (a) immediately after irradiation, PBT and PB5K. (b) After 4 min at 5 K, PB5K. (c) After warming to 15 K, PB15K. Note absence of PB5K. (d) During warming from 20 to 24 K, PB15K. (e) After 1 min at 24 K, PB24K and PB15K.

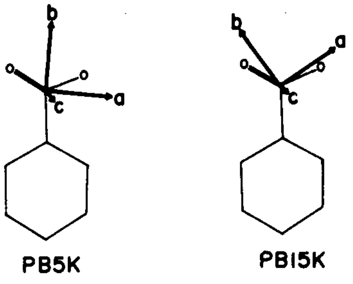
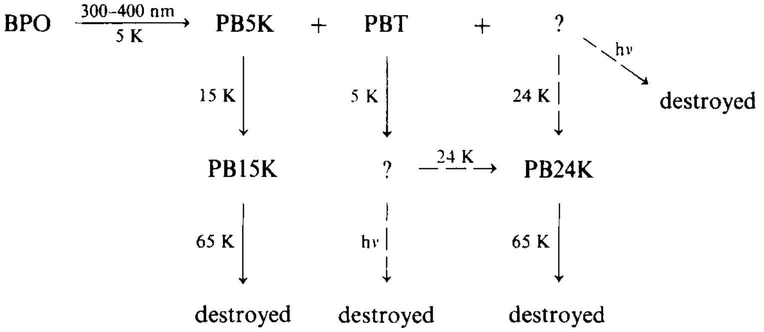


FIGURE 5 Projections of g tensor eigenvectors of PB5K and PB15K on a benzoyloxy group in BPO. the g values for PB5K are $a = 2.0246$, $b = 2.0020$, $c = 2.0060$; for PB15K they are 2.0244, 2.0038, and 2.0084. The eigenvectors labelled c are parallel within 3.2°, the others diverge by 39.3°.

This kinetic similarity and the similarity in fine structure may result from the similarity in surroundings that would result if the same CO_2 were lost in forming both pairs. If so, the same end of BPO must lose CO_2 in forming all the phenyl-benzoyloxy pairs we have observed, with the possible exception of PBT. It may be that the radical which moves most during pair collapse has identical environments in PB15K and PB24K.



Scheme 1

Our observations on phenyl-benzoyloxy pairs are summarized in Scheme 1, where alternative locations for the epr-invisible species are denoted by " ? ".

Benzoyloxy-benzoyloxy pairs

UV irradiation of BPO between 20 K and 25 K forms not only the PB15K and PB24K pairs discussed above, but also two new radical pairs (Figures 6, 7) which show no hyperfine structure, have larger *g* anisotropy than PB pairs, are stable indefinitely at 10 K in the dark, and are destroyed by visible light. Large fine structure splittings show that the radicals in these pairs are closer to one another than those in the PB pairs. These must be two benzoyloxy-benzoyloxy pairs. One of them, BB10K, may be formed by photolysis at

FIGURE 6 BB25K and PB signals in a BPO crystal irradiated at 23 K and kept at that temperature for 40 min while BB10K decayed. Although there is overlap among the PB signals, the four BB25K doublets are clearly resolved. The singlet in the center of the spectrum is from DPPH standard.

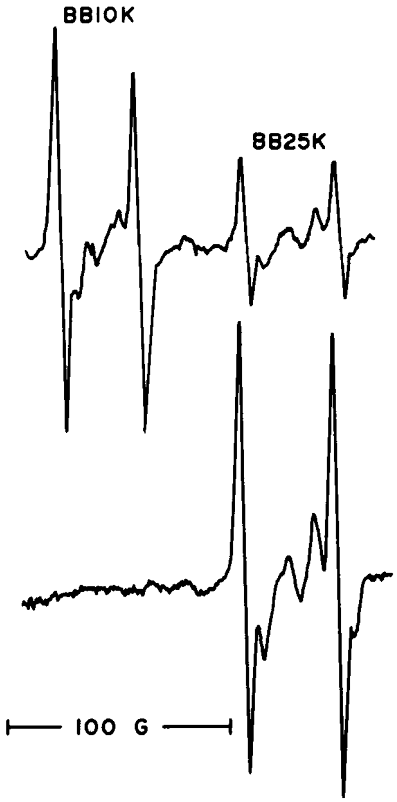


FIGURE 7 Scans of the low-field members of two BB10K doublets and two BB25K doublets showing the conversion of BB10K to BB25K. The upper trace was recorded after photolysis at 10 K; the lower, after warming briefly to 27 K and recooling to 10 K. The shoulders are probably due to slightly different crystal orientations resulting from fractures.

10 K, but it converts rapidly and quantitatively to the other, BB25K, when the crystal is warmed to 27 K (Figure 7). BB25K persists to about 35 K. *D* and *g* tensor analysis suggests that BB25K differs from BB10K by less than 0.08 Å in translation and 15° in rotation.[20]

It is remarkable that BB pairs are stable in the absence of a molecule to separate their radical centers. It is even more remarkable that molecules in this primitive state of decomposition are trapped after photolysis at 10 K, when they are not trapped after photolysis at 5 K, at which temperature PB5K *is* observed. Both of these facts support the hypothesis that thermally activated motion of the benzoyloxy radicals and their environment is necessary to achieve a geometry which hinders recombination to BPO.

Only at elevated temperature can the motion compete effectively with recombination.

The conversion of BB10K to BB25K is slow at 23 K, but photolysis at that temperature generates them in a ratio of only 3 to 1, while photolysis at 13 K generates a ratio of greater than 10 to 1. We have not yet tested whether the conversion during photolysis at 23 K is due to a general warming of the crystal during photolysis, or to excess energy in the site where BB10K formation has just occurred.

CONCLUSIONS

The epr spectra of BPO are more complex than had previously been suspected. At least two geometries of benzoyloxy-benzoyloxy pairs can be observed, and at least four geometries of phenyl-benzoyloxy pairs. It will be more difficult to tell how many phenyl-phenyl pairs exist, because of the increased hyperfine complexity and the reduced fine structure splitting. In some cases the geometric difference between chemically identical pairs is large, but in other cases it is so subtle that cooperative changes in the shape of the reaction cavity must be invoked to explain how two such similar geometries can both represent local energy minima. The barriers between some of these geometries are low, but during photolysis the products are not formed with sufficient excess energy to surmount them. The thermal barrier to appearance of trapped benzoyloxy-benzoyloxy pairs suggests that O-O homolysis is readily reversible in the crystal.

Although the absence of site symmetry means that loss of different CO_2 groups would give distinguishable sets of phenyl-benzoyloxy radical pairs, the three pairs we have studied carefully seem to have come from loss of the same CO_2. If PBT, the pair which is unstable at 5 K, has lost the other CO_2, it may be that immobilization rather than decomposition is selective. Complexing between a benzoyloxy radical and the adjacent phenyl group could explain both types of selectivity.

The coexistence of different PB radical pairs at 62 K complicates interpretation of the spectra of Barchuk, *et al.* Since the stable pairs have all lost the same CO_2, one must interpret spectral effects from polarized photolysis not through excitation localized in one end of a BPO molecule, but through the absence of exciton migration among molecules related by certain screw axes. The detail available in that publication is insufficient to support a thorough reinterpretation.

The relationship between the radical pairs observed in this work and the products of solid-state BPO decomposition remains to be established.

Acknowledgements

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9. When the crystal contains *n* classes of pairs not related by symmetry, there are 12*n* observations to determine 5*n* tensor elements and 3 eulerian angles.
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11. In BPO[7] the C-O-O-C torsional angle is 90.6°; in acetyl benzoyl peroxide,[4] 86.6°; in *p,p'*-dichlorodibenzoyl peroxide,[12] 81°; in di-β-naphthoyl peroxide,[13] 90.9°. The *o,o'*-dihalodibenzoyl peroxides have an angle of 112° in an otherwise centric conformation,[14] but bis-2,2,2-triphenylpropionyl peroxide[15] is fully centric with a torsional angle of 180°.
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16. Vaguely analogous carbonylperoxy-aromatic contacts occur in acetyl benzoyl peroxide,[4] *p,p'*-dichlorodibenzoyl peroxide,[12] and di-β-naphthoyl peroxide,[13] but these may be fortuitous.
17. The formation of PB pairs at 77 K seems to be a one-photon process.
18. Previously, on the basis of experiments with perdeuterated samples which gave broad lines, we suggested that the approximate site symmetry would conceal the difference between classes of PB pairs formed by loss of different CO_2 groups.[6] This cannot be so for the present spectra of unlabelled BPO.
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