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Isotopic and Optical Studies of the Decomposition of Crystalline Dibenzoyl Peroxide

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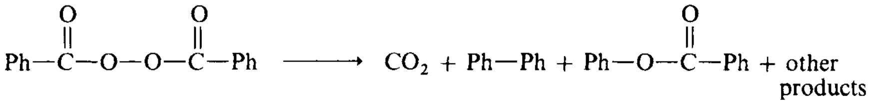
Mass spectral analysis of volatile products from thermolysis or photolysis of a solid solution of dibenzoyl peroxide (BPO) and 4,4′-dideutero BPO shows that most phenyl benzoate is formed intramolecularly, while most biphenyl is formed intermolecularly, presumably by radical-molecule reactions. The strong visible dichroism in uv-irradiated BPO crystals appears to be due to selective scattering of light polarized along [010], not to the selective absorption which would have indicated an oriented product with a strong visible chromophore. Thermal development of the dichroism may be due to radical chain reactions. Studies on selective decarboxylation of BPO molecules using plane polarized light are discussed in terms of the birefringence of crystalline BPO.

INTRODUCTION

For understanding free radical processes in organic solids it is important to know whether radical-radical reactions or radical-molecule reactions predominate in product formation. Low-temperature photolysis of crystalline diacyl peroxides often generates clean epr spectra of radical pairs. The spectra allow identification of the pairs and detailed analysis of their geometry and dynamics.[1,2] The signals of pairs typically decay without appearance of those for isolated free radicals. Although most of the product may be formed by radical-radical reactions within pairs,[3] this is not required by the epr observations, since an undetectable concentration of free radicals could give large amounts of product through a chain of radical-molecule reactions. This paper describes our preliminary investigations on the role of radical-molecule reactions in the decomposition of solid dibenzoyl peroxide (BPO).



$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}Ph} \longrightarrow \mathrm{CO_2 + Ph{-}Ph + Ph{-}O{-}\overset{\overset{O}{\|}}{C}{-}Ph} + \text{other products}$$

In 1864, eight years after he had first prepared BPO, C. B. Brodie reported that thermolysis of the crystalline material diluted with sand commenced at 85°C.[4] Since BPO melts with decomposition between 103 and 110°C, it is virtually certain that his sample melted at some point. Although Brodie observed a weight loss consistent with phenyl benzoate formation, he found a mixture of products among which he mentioned only benzoic acid and "a soft glutinous residue." More than fifty years ago Dietrich[5] and Fichter and Fritsch[6] reported biphenyl yields of 53% and 39%, respectively, from thermolysis of pure BPO at 180–200°C. In 1930 Fichter and Schnider reported biphenyl yields as high as 86% from photolysis of cooled, solid BPO.[7] By contrast Morsi, Thomas, and Williams reported recently that thermolysis of BPO without melting gives phenyl benzoate in "almost quantitative" yield.[8] They suggested that this product is formed by a radical-molecule chain reaction at crystal dislocations.

Crystal defects can also be important in solid-state photochemistry. When exciton migration is rapid, reaction may occur only at defects, where excitation can be trapped and where atomic motion can be unusually easy. Recently Barchuk, Dubinsky, Grinberg, and Lebedev suggested that excitation in crystalline BPO remains localized in one end of a molecule until that end loses its CO_2.[9] If this be so, the initial photochemistry in BPO probably takes place in typical lattice sites rather than at defects. On the other hand, Sagdeev *et al.* have interpreted an anomalous carbon isotope effect on CO_2 evolution from BPO at 4.2 K in terms of irreversible excitation transfer from ^{13}C to ^{12}C carbonyl groups.[10]

We have used deuterium labels to test whether the phenyl benzoate and biphenyl formed from pure BPO under various conditions arise from chain reactions. We have also studied crystals before, during, and after partial decomposition to see if their optical properties, particularly the reaction-induced dichroism, provide evidence for the occurrence of chain reactions. These optical observations bear on the difficulty we have had in trying to repeat the important work which led Barchuk *et al.* to propose that excitation is localized in one end of a BPO molecule.

EXPERIMENTAL

Reagents

Dibenzoyl peroxide (Fisher Reagent Grade) was recrystallized from reagent grade benzene by evaporation at room temperature.

4-Deuterotoluene was prepared by quenching the corresponding Grignard reagent (from 100 g 4-bromotoluene and 30 g magnesium in 600 mL anhydrous ether under nitrogen) with 12 g D_2O. Distillation after drying gave a fraction at 109–110°C containing 30 g (55 %) of the product. PMR (60 MHz, CCl_4, δ): 2.28 (3.00 H, s); 7.07 (4.02 H, s).

4-Deuterobenzoic acid was prepared in 59 % yield from 30 g 4-deuterotoluene by the procedure of Ullman and Uzbachian.[11] PMR (60 MHz, $CDCl_3$, δ): 7.45 d, 8.13 d (AA'BB', $J = 8$ Hz); 12.07 s.

4-Deuterobenzoyl chloride was prepared from 23.4 g 4-deuterobenzoic acid and 20 mL thionyl chloride heated to 95°C for 60 min and distilled. The fraction at 194–195°C contained 22.5 g (83 %) of the product. PMR (60 MHz, $CDCl_3$, δ): 7.45 d, 8.05 d (AA'BB', $J = 8$ Hz).

4,4'-Dideuterodibenzoyl peroxide (BPO-d_2) was prepared by adding dropwise a solution of 22 g 4-deuterobenzoyl chloride in 25 mL benzene to 150 mL water and 8 g sodium peroxide at 5°C with stirring. After stirring for 90 min at 10–15°C, the product was extracted into benzene, which was dried with $MgSO_4$, filtered, and evaporated at room temperature to give 15.2 g (80 %) of the product, mp 108 (dec). PMR (60 MHz, $CDCl_3$, δ): 7.45 d, 8.03 d (AA'BB', $J = 8$ Hz).

Isotopically mixed crystals were prepared by dissolving equal parts of BPO and BPO-d_2 in benzene at room temperature, stirring well, filtering twice, and letting the solution evaporate at room temperature. The crystals were washed with low boiling petroleum ether.

Decomposition and analysis

Weighed crystals of BPO (15–50 mg) were placed in the curved sidearm of an 8 mm Pyrex tube fitted with a Teflon high vacuum stopcock and a ground joint. After the tube was purged with nitrogen at atmospheric pressure and sealed off with the stopcock, the sidearm was heated in an oil bath or illuminated by a medium pressure Hanovia mercury arc. The tube was then attached to a vacuum system and nitrogen was removed with the sample at 77 K. With the sample warmed to -78°C, CO_2 was collected by Toepler pumping and measured by volume at low pressure. Next the tube was sealed off at about 10^{-4} Torr, and the sample region was warmed to 75°C for 1 hr to sublime phenyl benzoate and biphenyl into the main arm of the tube, which was cooled to 77 K. Under these conditions unreacted BPO does not decompose,[12] and it sublimes only to the unheated portion of the sidearm. The sublimate was either analyzed directly by mass spectrometry or dissolved in ether with a known amount of *o*-terphenyl for rough estimation of yield by gas chromatography. After thermolysis at 200°C the sidearm contained a large amount of non-volatile residue. GC of this residue with *o*-terphenyl standard showed that it contained about 2% biphenyl and 1% phenyl benzoate based on initial BPO. In one experiment BPO was ground to a fine powder and mixed with five times its weight of powdered quartz.[7] This mixture was placed in the narrow annulus created by a long cylindrical invagination in a quartz tube. After nitrogen purge and 40°C photolysis the sample was extracted repeatedly with ether. The extracts were placed in the sidearm tube, solvent was removed by a stream of nitrogen, and analysis proceeded as above.

The deuterium position in 4,4-dideuteriobiphenyl obtained by heating BPO-d_2 at 200°C was confirmed by 270 MHz pmr.[13] ($CDCl_3$, δ): 7.592 d, 7.435 d (AA′BB′, $J = 8.7$ Hz); less than 10% para hydrogen judging by spectral intensity at δ 7.35.

Mass spectral analysis of products from isotopically mixed crystals was performed on samples leaked from a heated reservoir into an Hitachi-Perkin Elmer RMU 6 spectrometer equipped with a strip chart recorder. The parent ion regions of phenyl benzoate (m/e 201–198) and biphenyl (157–154) were scanned at about 4 sec per peak, and the $d_0 : d_1 : d_2$ proportions were calculated from peak height ratios corrected by the ratios measured for unlabelled standards. Results are presented in Table I. The biphenyl signals from photolysis samples were too weak for accurate estimation, and the ester signals from thermolysis samples were weak enough that the isotope ratios are less reliable than for ester from photolysis or for biphenyl from thermolysis. In calculating the fraction of intermolecular product formation it was assumed that 10% of the para positions in labelled BPO contained hydrogen. This assumption was based on the isotopic distribution in ester from photolysis of BPO-d_2 at −78°C.

UV spectra of BPO were measured with a Shimadzu Spectronic 200 UV instrument. A single crystal 3 mm thick was masked on (110) with an opening 1.5 × 4.5 mm to give a path with fairly even faces and no internal damage. A sheet filter was approximately adjusted to give polarization either along [001] or in a plane containing [010]. A matching mask and filter were placed in the reference beam. The method was crude, but in the 325–425 nm range it showed only the tail from a shorter wavelength absorption. The former polarization (the ordinary or *o* beam) gave 50% transmission through the 3 mm path at about 330 nm. The latter polarization (the extraordinary or *e* beam) gave 50% transmission at about 360 nm.

Three BPO crystals (total weight 847 mg), which had become opaque after exposure to room light for more than 8 months, were chopped coarsely and placed in a side arm connected to a quartz cell containing 4 mL benzene. The apparatus was outgassed by repeated freeze-pump-thaw cycles and sealed off at $\sim 10^{-4}$ Torr. Within 10 min of dissolution at room temperature, the near uv spectrum was measured. It showed only the tail of BPO absorption: ε (λ nm); 0.5 (350), 0.04 (400), 0.015 (450).

Refractive indices were determined with a Fuess single circle optical goniometer by measuring the minimum angular deviation of a light beam passing through the (110) and ($\bar{1}$10) faces in the (001) plane or passing through the (011) and (01$\bar{1}$) faces in the (100) plane. The 64.2° angle of the former pair of faces permits observation in air both of the *o*-beam, polarized along [001] within the crystal, and of the *e*-beam, polarized along [010]. The 66.8° angle between the latter pair permits observation of the *o*-beam, polarized along [100], only.

This optical difference allows one to discriminate between the {011} and {110} faces of a well-formed crystal without equipment for accurate determination of interfacial angles. The crystal is placed on a thin piece of white paper which covers a pinhole in an opaque sheet illuminated from the opposite side. The white paper disperses light passing through the pinhole, so that it is incident from all angles at a spot on the crystal's bottom face. From angles greater than some minimum the spot is visible through the face related to the bottom face by rotation about [010] (this direction is easily identified, since the spots on the top face are doubled by birefringence in the direction of its projection on that face and because the crystal extinguishes between crossed polaroids when one of the polarization planes contains [010]). Through a polaroid filter set to pass light polarized perpendicular to [010] the spot becomes visible about 75° above the plane of the bottom face, whether it be {110} or {011}. With the filter turned to pass light polarized in a plane containing [010], however, the spot is visible only through the {110} faces, with red light becoming visible at 105°.

Dispersion of the indices was determined using the following Corning color filters: 5-74(440 nm), 5-75(460), 4-105(520), 4-102(550), 2-73(585), 2-64(670). For this series of six wavelengths the indices for light polarized along [100] are 1.562, 1.559, 1.547, 1.546, 1.542, and 1.537. For light polarized along [001] they are 1.561, 1.558, 1.548, 1.547, 1.542, and 1.538. For light polarized along [010] they are: unobserved, 1.869, 1.842, 1.839, 1.829, and 1.817. Except for the values at 520 nm, these indices give good linear plots of $1/(n^2 - 1)$ vs. λ^{-2}, with deviations corresponding to index variations of 0.001. Extrapolating these lines to 330 nm predicts indices of 1.97 for [010] polarization and 1.60 for the orthogonal polarizations. The strong similarity between two of the axes makes the crystal effectively uniaxial and justifies referring to the beams as ordinary and extraordinary.

Single crystal photolysis at room temperature was observed with a Bausch and Lomb Stereozoom 7 microscope. In one experiment a 4 × 5 × 3 mm crystal bounded by {110}, {011}, and (001) was glued on $(1\bar{1}0)$ to a small dowel and mounted to be viewed through (001). A beam of light normal to (110) from an Osram HBO-200W/2 lamp ($\lambda > 440$ nm, $CuSO_4$ and Corning 3-72 filters) was focussed on that face through a 1.6 × 0.6 mm slit (the narrow dimension along [001], the direction of microscopic observation). The crystal, which had been stored for four months in subdued room light, contained damaged regions, which scattered light. Some regions showed diffuse, cloudy damage, others showed streaks of damage in (100) extending about 0.2 mm along [010] and 0.5 mm along [001]. The streaks were separated by about 0.2 mm. When the long slit was replaced by one of the same depth (0.6 mm) but only 0.15 mm wide, well-resolved *o* and *e* beams could be seen leaving the crystal, but only the *e* beam was scattered within the crystal. After removing the 3-72 filter for 6 min to expose the crystal to 300–400 nm light, the narrow slit was replaced by the wide one. New diffuse damage was observed along the first 2 mm of the track of the uv *e* beam, but no new damage was visible along the track of the uv *o* beam. Only after 48 min of uv irradiation did the *o* track show up as clearly as the *e* did after 6 min. After 111 min uv, most of the *e* track was dark because of intense scattering along its first 0.4 mm.

In other experiments fresh crystals were irradiated with uv through (110) or (011) and examined microscopically with a polaroid filter after heating or the passage of time.

EPR spectra were measured with a Varian E-9 spectrometer. A single BPO crystal 2–3 mm on an edge was mounted on the end of an nmr tube with silicone grease and irradiated for 2000 sec at the focus of the Osram HBO-200W/2 lamp with copper sulfate filter (briefer irradiation gave very little signal). The crystal showed a weak absorption near $g = 2$ with no resolvable hfs. Over a period of 10 hr at room temperature the signal amplitude decayed as follows: 10 min (83 units high), 65 (61), 190 (48), 400 (36), 535 (38).

RESULTS AND DISCUSSION

Ester and biphenyl

The isotopic crossover results of Table I show that the source of phenyl benzoate from photolysis or thermolysis of pure BPO under our conditions was predominantly, perhaps exclusively, *intra*molecular. We thus favor a mechanism involving collapse of phenyl-benzoyloxy radical pairs over the chain reaction suggested by Morsi, Thomas, and Williams.[8] We chose con-

TABLE I

Volatile products from decomposition of solid BPO

Decomposition mode[a]	Temp. (°C)	Time (hr)	CO_2 yield (%)[b]	biphenyl[c]	%Intramolecular[d]	
				ester	ester	biphenyl
$h\nu$	−78	106	1		111	
$h\nu$	40	18	3		102	
$h\nu$	40	20	3		102	
$h\nu$	40	24	4	0.07		
$h\nu$[e]	40	12	5	0.09		
Δ	90	4.5	12		70[f]	0
Δ[g]	90	20	31		75[f]	5
Δ[g]	90	21	35	3		
Δ[g]	90	23	37	3		
Δ[h]	200	[h]	78		80[f]	5
Δ[h]	200	[h]	78	22		

[a] Photochemical ($h\nu$) or thermal (Δ); although photochemical samples discolored, the crystals did not appear to soften except as noted.

[b] Based on 2 moles/mole of BPO.

[c] Product ratio estimated by gc.

[d] Estimated accuracy ±15%, except as noted.

[e] Crystals powdered and mixed with powdered quartz.

[f] Estimated accuracy ±25%.

[g] Sample melted after about 5 hr.

[h] Sample exploded in about 15 sec and was not heated longer.

ditions somewhat different from theirs, since in our hands BPO sublimed unchanged when heated to 75°C in a tube sealed at about 10^{-4} Torr. Thus our thermolyses were conducted under one atmosphere of nitrogen, while their kinetic studies were at 90°C and 10^{-4} Torr.[14] The small amount of phenyl benzoate from 200° explosion was still mostly intramolecular. Perhaps it was formed before the sample reached explosion temperature.

Biphenyl predominated over phenyl benzoate in the product mixture from each of our thermolyses, all but one of which involved melting or even explosion. The yield of biphenyl from solid-state photolysis was negligible. The crossover experiments show that the source of biphenyl was predominantly, perhaps exclusively, *inter*molecular. The PMR spectrum of biphenyl from 200° thermolysis of BPO-d_2 shows that deuterium persisted in the para position of the phenyl rings. While this is consistent with formation of biphenyl by combination of phenyl radicals, we think a more likely source is a chain reaction involving attack of phenyl radical at the 1-position (or conceivably the 4-position[15]) of BPO.

In several cases where we estimated yields of phenyl benzoate and biphenyl their sum did not exceed 30% of the theoretical expectation based on CO_2 evolved. This was true both in thermolysis and in low conversion solid-state photolysis. In some gc traces a small peak appeared after terphenyl standard. This was perhaps due to a higher polyphenyl. While a complex product mixture is not surprising from analogy with solution decomposition of BPO,[16] these results contrast with earlier reports of high yields of biphenyl[5–7] and of ester.[8] The only obvious difference between our photolysis of powdered BPO, which gave almost no biphenyl, and that of Fichter and Schnider, which gave 86% of this product, is that theirs was conducted in a stream of air.[7] Conceivably oxygen could influence the reacting system to favor biphenyl formation. We have not yet attempted to characterize other products from decomposition of solid BPO, but we suppose that most, if not all, of them arise from radical-molecule reactions.

Photoinduced Dichoism

In 1864 Brodie noted that he had obtained BPO as "splendid crystals ... as much as three-fourths of an inch in diameter."[4] In 1862 W. H. Miller indexed the crystals and measured their birefringence ($n_y = 1.837$; n_x and $n_z = 1.545$).[17] Figure 1 shows the orientation of a BPO molecule with respect to the {110} and {011} faces, which are usually well developed in crystals grown from benzene.[1,18] The *b* axis, which exhibits high refractive index,

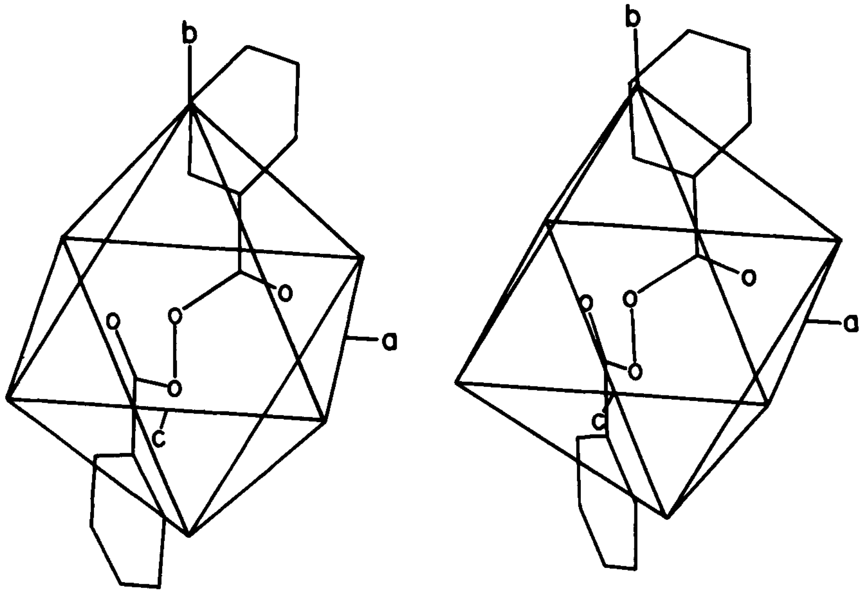


FIGURE 1 Stereo pair view of the orientation of a BPO molecule relative to the {110} and {011} faces shown by most benzene-grown crystals. Atoms in the lower half of the molecule bear lower numbers in discussions of the crystal structure. The other three molecules in the $P2_12_12_1$ unit cell have orientations related to the one shown by rotation about *a*, *b*, and *c*.

lies in the planes of both halves of the molecule and is parallel to the O-O bond within 1°. The equivalence of the two lower indices is not surprising, since both planes of the molecule make angles very near 45° with both [100] and [001]. To the extent that the halves of a molecule behave independently in the electronic transitions responsible for the index, the two axes should be equivalent.

Because BPO crystals are strongly birefringent and approximately uniaxial, light incident normal to {110} or {011} faces splits into an ordinary (*o*) beam polarized perpendicular to [010], which passes straight through the crystal, and an extraordinary (*e*) beam polarized in a plane containing [010], which is diverted toward parallelism with [010] by more than 9°. (The divergence between *e* and *o* beams in calcite is 6.7°) This means that *o* and *e* beams 0.15 mm in diameter become completely resolved in a distance less than 1 mm.

Fresh crystals were transparent to both *o* and *e* beams through the visible spectrum, but an absorption tail began in the 300–400 nm region. The *e* beam was much more strongly absorbed than the *o*, so the optical transition moment is nearly parallel to the O-O bond. It is presumably this transition which is responsible for the visible birefringence.

Crystals which had been exposed to light <400 nm became dichroic in the visible. Irradiated regions of the crystals transmitted the *o* beam cleanly, but they strongly attenuated the *e* beam. Regions which had not been irradiated continued to transmit both beams. When crystals which had been irradiated only enough to give barely perceptible dichroism were heated to 60°C for several hours, strong dichroism developed in the irradiated region only. Dichroism did not spread more than 0.05 mm from the irradiated region, nor did it intensify in the irradiated region over a period of months in the dark at room temperature. Since epr spectra showed that free radicals persisted for many hours after uv irradiation, one could attribute thermal development of dichroism to chain reactions which can proceed only as long as isolated radicals survive and only over a short distance in the crystal.

If the dichroism were due to selective absorption of *e* light, one could infer that reaction had given an oriented product which absorbed most of the visible spectrum. This would suggest product formation by a radical-molecule process, since no plausible intramolecular product would have this property. However, we find no evidence for the existence of a strongly absorbing product. A spectrum measured immediately after dissolution of heavily damaged crystals in benzene under vacuum showed no absorption in the visible. The solution extinction coefficient showed that more than one centimeter of the heavily damaged solid would be required to absorb half of 450 nm light, unless the chromophore was destroyed on dissolution. Furthermore, attenuation of *e* (but not of *o*) light is expected from the selective scattering we observed in damaged regions of the crystal.

We have not yet analyzed the selectivity of the scattering process to see what information it may contain about the nature of thermal and photochemical damage. Thus far optical observations have provided no convincing evidence that chain reactions are involved in the decomposition of solid BPO. They show only that *e* light is more strongly absorbed than *o* in the uv, that it is some 5–10 times as effective as *o* in damaging the crystal, and that the damage selectively attenuates the *e* beam, primarily, if not entirely, by scattering.

Selective Decarboxylation

The conclusion of Barchuk *et al.* that excitation does not migrate from one benzoyloxy group to another in the time required for decomposition is important for understanding the photochemistry of crystalline BPO.[9] It was based on experiments in which plane polarized light selectively excited particular benzoyloxy groups and epr spectroscopy distinguished among the eight phenyl-benzoyloxy radical pairs which could be formed by loss of each of the eight CO_2 groups in the unit cell.[19] Where this technique is applicable, it can tell not only whether exciton migration occurs, but also among what class of molecules it occurs (those related by a particular screw axis, for example). Since their paper supplied little experimental detail, and the work of Sagdeev *et al.* could suggest migration,[10] it seemed possible that excitons were confined to a class of molecules among which Barchuk *et al.* were not distinguishing.

Because we want to know whether decomposition occurs in typical lattice sites, we have made preliminary attempts ourselves to observe selective decarboxylation by plane polarized light in crystals of BPO. Thus far we have not been successful, and we have discovered three reasons why this experiment is especially difficult, whether or not there is exciton migration. First, as shown above, the transition moment responsible for decomposition lies near [010].[20] If it lay exactly along this axis, all molecules would be photochemically equivalent by space group symmetry, and the ends of a single molecule would be as equivalent as possible because of the approximate molecular symmetry.[1] Selective decarboxylation would clearly be impossible. Second, photolysis at 62 K, the temperature used by Barchuk *et al.*, generates two sets of four symmetry-related phenyl-benzoyloxy radical pairs, where they believed there was only one set.[1] Because the sets are geometrically similar, small changes in crystal orientation can give large changes in first-derivative epr amplitude through interference among these species. Third, crystal birefringence is probably a little stronger between 300 and 375 nm than it is in the visible. This limits the types of polarization that may be studied. For example, if light incident on (001) were plane polarized in $(1\bar{1}0)$, the crystal would transform almost all of the light through elliptical polarization to (110) plane polarization and back to $(1\bar{1}0)$ again in a distance of about 1 μm.[21] A simple attempt to reproduce the spectra in Figure 4 of Reference 9 would thus fail, because there would be practically no difference in the photolysis light between experiments which are reported to give different spectra. Irradiating other faces would give more complex behavior because of the divergence of *e* and *o* rays.

CONCLUSIONS

Thermolysis or photolysis of pure BPO is a complex process. It is likely that radical-molecule reactions contribute to product formation in the solid state, as they most certainly do to biphenyl formation in the melt. They do not, however, contribute substantially to phenyl benzoate formation either in the melt or, as had been proposed by Morsi, Thomas, and Williams,[8] in the solid.

The dichroism in damaged BPO crystals is due primarily to selective scattering of visible light polarized along [010], the same polarization which for uv light is absorbed and causes the damage. Since visible absorption plays little or no role in the dichroism, we cannot infer radical-molecule reactions. The thermal development of dichroism, and the existence of localized as well as diffuse damage in crystals subjected to months of room light require further study.

This work has raised many questions. Why did sublimation complicate our thermolysis studies, but not those of Morsi, Thomas, and Williams, who used higher temperature and lower pressure? What conditions are necessary to observe the polarized photoselection results of Barchuk *et al.*? How did they avoid the problem of birefringence? Does the transition moment for creation of dichroism really differ from that for decarboxylation of BPO? Are the results of Sagdeev *et al.* correct, and if so, what type of exciton migration occurs in solid BPO? What products beside phenyl benzoate are formed in solid BPO decomposition? Are they formed by lattice-controlled chain reactions or other radical-molecule reactions? What is the molecular mechanism of selective scattering in damaged BPO? These and other aspects of the BPO problem are under continuing investigation in this laboratory.

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18. The benzene-grown crystal illustrated in Figure 1a of Reference 8 is indexed incorrectly. This raises additional questions about the subsequent interpretation in that paper.
19. Although Barchuk *et al.* did not claim this fine a distinction, it is almost surely attainable.[1]
20. Barchuk *et al.* proposed that the transition is polarized along the C—O(peroxy) bond, which makes an angle of 70° with [010]. If this be so, it must be completely different from the transition we have characterized above.
21. This description is approximate because the {110} planes make angles of 32.1° rather than 45° with [010].