Photochemical Decomposition of Dibenzoyl Peroxide and Phenyl Benzoate in Solid KBr Matrix

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Received February 17, 1993[●]

Physical and photochemical properties of dibenzoyl peroxide (DBPO) and phenyl benzoate (PB) in a solid KBr matrix were investigated. The photoinduced decompositions of DBPO and PB were monitored with infrared spectroscopy and HPLC. The organic molecules at different locations in the matrix contribute to the overall IR absorption differently. Therefore, they are affected differently during a photochemical decomposition. The bromide ions in the matrix intercept some of the radical intermediates in the decomposition of DBPO but have no influence on the radical pair in the rearrangement of phenyl benzoate.

A solid KBr matrix has been traditionally used as a medium to host organic compounds for IR measurement.[1–3] The system can be considered a suspension of organic crystals in the matrix. The physical and chemical changes of the compounds inside the matrix can be monitored spectroscopically. Studies on the feasibility of using such a medium to investigate thermal and photochemical induced organic[4–7] and inorganic[8–9] reactions have been seen since the pioneering work by Bent and Crawford.[10] We report here the use of the solid KBr matrix for monitoring the photochemical decomposition of dibenzoyl peroxide (DBPO) and phenyl benzoate (PB).

Results

Crystal Sizes and IR Absorption Intensities. A typical sample contains 0.4 mg of organic crystals and 50 mg of KBr powders. The sample was ground in a mortar and then made into an almost transparent pellet using a press device. In its IR spectrum, dibenzoyl peroxide is represented by the doublet of the two carbonyl groups at 1759 and 1784 cm^{-1}. The carbonyl group of phenyl benzoate is indicated by a singlet at 1735 cm^{-1}. When the pellets were prepared under the same conditions such as consistent grinding and pressure, the IR absorption intensity was directly proportional to the amount of the organic substance in the matrix. When the pellet was reformed by crushing it into powders and subsequently making it into a pellet again, a 30–50% increase in the carbonyl absorption for DBPO was observed. Continuous reformation eventually saturated this effect (Figure 1). The amount of this increase depends on the initial organic crystal sizes. Scanning electron microscopic (SEM) analysis of DBPO indicates that the crystals are in the range of 5–15 μm before the reformation and 1–8 μm after one time reformation. Phenyl benzoate crystals change from 8–30 μm to 1–8 μm after the reformation. For PB/KBr samples, the increase in carbonyl absorption is as high as 600% (Figure 2). The absorption increases are also a function of the extinction coefficient. There are less

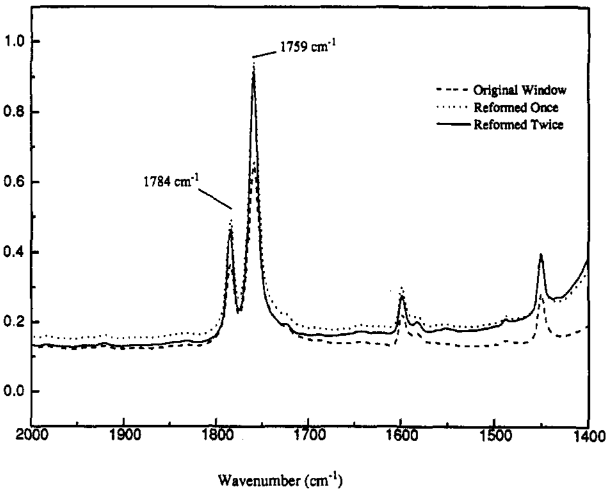

Figure 1. Infrared absorption spectra of DBPO upon reformation of the KBr pellets.

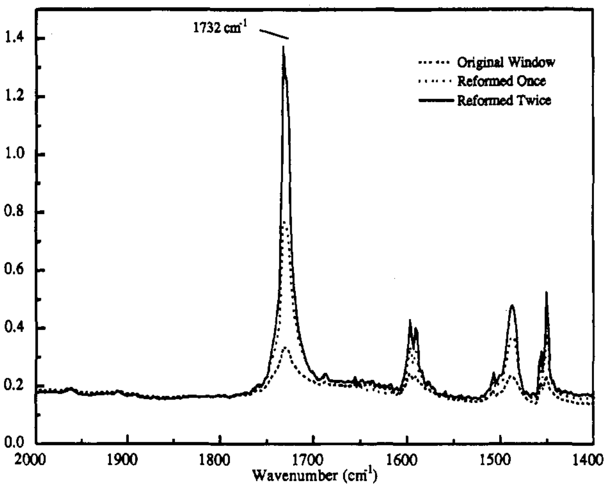

Figure 2. Infrared absorption spectra of phenyl benzoate upon reformation of the KBr pellets.

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[●] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) *Infrared Spectroscopy*; Conley, R. T., Ed.; Allyn and Bacon, Inc.: Boston, 1966.

(2) Schiedt , V.U.; Reinwein, H. *Naturforsch* **1952**, *76*, 270.

(3) *Organic Solid State Chemistry, Studies in Organic Chemistry 32*, Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987.

(4) Baro, J.; Dudek, D.; Luther, K.; Troe, J. *Z. Phys. Chem. Neue Folge* **1984**, *140*, 167.

(5) Pitts, J.N., Jr., Wan, J. K. S.; Schuck, E. A. *J. Am. Chem. Soc.* **1964**, *86*, 3606.

(6) Bansel, A.K.; Ameta, S. C.; Bokadia, M. M. *Proc. Nat. Acad. Sci., India* **1982**, *52*, 257.

(7) Bansel, A.K.; Dubey, R. D. *Acta Cienc. Indica, Chem.* **1983**, *9c*, 215.

(8) Tanaka, K. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2999.

(9) Porter, G.B.; Rest, A. J. *J. Chem. Soc. Chem. Commun.* **1980**, 869.

(10) Bent, H. A.; Crawford, B. Jr. *J. Am. Chem. Soc.* **1957**, *79*, 1793.

0022-3263/93/1958-6203$04.00/0

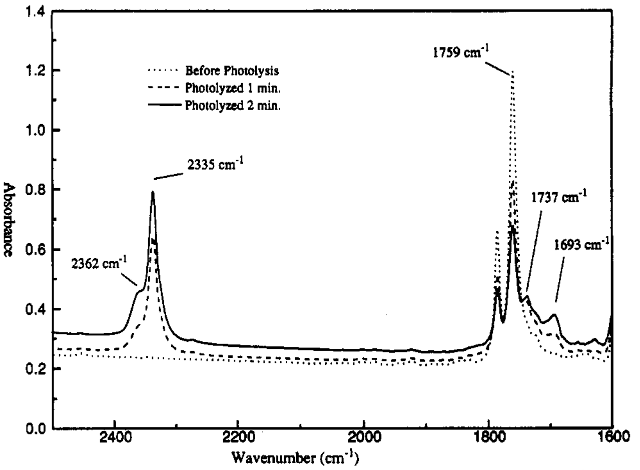


Figure 3. Photolysis of dibenzoyl peroxide in KBr.

Table I. Dibenzoyl Peroxide Analysis after Photolysis

sample and photolysis time	DBPO, %[a]	DBPO, %[b]	DBPO, %[c]
4 mg/0.5 g, not reformed, t = 0 min	98	100	100
4 mg/0.5 g, not reformed, t = 1 min	94	55	76
4 mg/0.5 g, not reformed, t = 2 min	84	31	56
4 mg/0.5 g, reformed, t = 2 min	40	39	38
2 mg/0.5 g, not reformed, t = 1 min	59	47	61
4 mg/0.5 g, not reformed, t = 10 h[d]	67	65	68

[a] Determined by HPLC, average percent error = 6.7%. [b] Determined by IR absorption intensity at 1759 cm^{-1}, average percent error = 7.5%. [c] Determined by IR absorption intensity at 847 cm^{-1}, average percent error = 7.5%. [d] Photolysis was carried out with a 350-nm light source.

increases in absorption intensities for those peaks with smaller extinction coefficients. There is virtually no increase for the absorptions in the fingerprint region. The IR spectrum of a reformed pellet is closer to that of a solution sample in terms of the relative intensities of the absorptions with different extinction coefficients.

Irradiation of DBPO in KBr. Irradiation of DBPO in KBr with a 254-nm light source causes decomposition of the peroxide, which is evidenced by the decrease of carbonyl absorption and the formation of carbon dioxide (Figure 3). Carbon dioxide generated from the photolysis is trapped in the matrix for at least 5 days. Carbon dioxide is retained longer in a pellet that has been reformed before photolysis. This is consistent with the fact that the reformed pellets are much less porous. The absorption of $C^{13}O_2$ at 2272 cm^{-1} indicates that the gas is in its dimer form.[11] The remaining peroxide and the products after the photolysis are extracted from the pellet and analyzed with HPLC. A 2-min photolysis causes ca. 40% decrease of the carbonyl absorptions at 1759 cm^{-1}. However, the HPLC analysis indicates that only a small portion (<5%) of the peroxide is consumed (Table I). This difference becomes much smaller for a pellet that is irradiated with wavelengths greater than 300 nm. The changes of the IR absorptions with smaller extinction coefficients are more consistent with the HPLC analysis. In addition to carbon dioxide, phenyl benzoate, biphenyl, bromobenzene, potassium benzoate, and benzene are also detected (eq 1). A small amount of bromine is found in the reaction mixture as well.

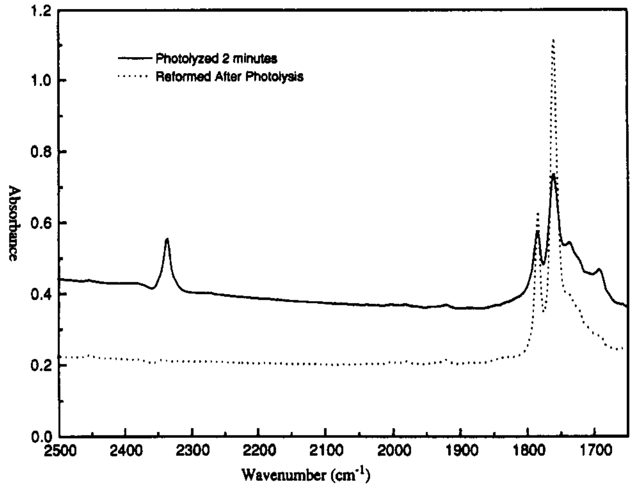
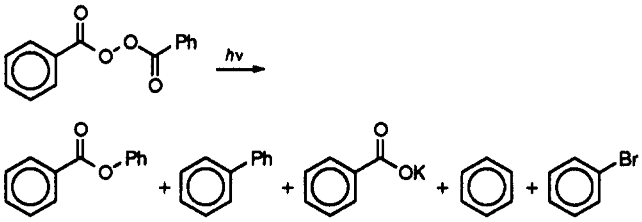


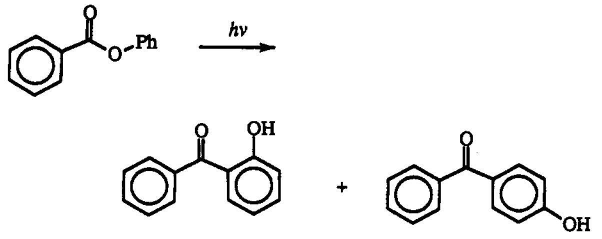
Figure 4. Reformation of the DBPO/KBr pellet after photolysis.



(1)

Reformation of a DBPO/KBr pellet after photolysis gives intriguing infrared changes. While the carbonyl absorption for the peroxide increases slightly, the absorptions for the products, mainly phenyl benzoate and potassium benzoate, decrease (Figure 4). The amount of the decrease is smaller for a pellet that has been reformed before photolysis, a pellet with less DBPO, or a pellet that has been extensively photolyzed.

Irradiation of PB in KBr. Photolysis of phenyl benzoate in KBr gives *o*- and *p*-hydroxybenzophenone as the only products (eq 2). Similar to DBPO, HPLC analysis of the PB reaction mixture indicates that the nonlinearity is also true for the IR carbonyl absorption. Less deviations are observed for the absorption peaks with smaller extinction coefficients. Reformation of an irradiated pellet gives similar results as for DBPO (Table II): the intensity of phenyl benzoate absorption increases slightly and those of the product absorptions decrease. However, when a PB/KBr pellet is extensively irradiated until a very small



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[11] Hollingsworth, M.D.; McBride, J. M. In *Advances in Photochemistry*; Volman, D.; Hammond, G.; Gollnick, K. Eds.; Academic Press: London, 1990; Vol. 15.

Table II. Product Yield Determination of Dibenzoyl Peroxide in KBr Matrix by HPLC Analysis[a]

compound	unreformed, % yield	reformed, % yield
dibenzoyl peroxide	60.9	40.7
phenyl benzoate	5.7	9.5
benzoic acid	5.4	9.0
bromobenzene	29.8	57.0
biphenyl	0.7	1.3
benzene	not detected	
o-hydroxybenzophenone	1.2	1.8
p-hydroxybenzophenone	not detected	

[a] 400 μg DBPO/50 mg KBr, photolyzed 2 min @ 254 nm.

amount of starting material is remained, mechanical reformation intensifies the product absorptions (Figure 5).

Discussion

Nonlinearity of IR Absorptions. In a DBPO/KBr or PB/KBr sample, the organic crystals are suspended in the KBr matrix. For a series of given samples prepared under the same conditions, the IR absorption intensities have a linear relationship with the amount of the organic substrate added.[12] This has been seen in a report by Jensen[13] and recently by Falk on the quantitative investigation of a nitrate hosted in solid KBr matrix.[14] However, this linear relationship cannot be viewed as a validation of the Lambert-Beer's law for this heterogeneous system. A suspension of fine organic crystals is not equivalent to a solution unless some criteria are met. For a DBPO/KBr sample, a simple calculation based on its density and extinction coefficient indicates that the IR absorption at 1759 cm^{-1} would have a linear relationship with the amount of the peroxide if the sum of the IR path lengths is shorter than 2.2 μm,[12] i.e., the sum of particle diameters that an IR beam passes through must be shorter than 2.2 μm for the linear relationship to be held. According to the SEM results, a considerable amount of the organic crystals are larger than 2.2 μm. The molecules at different locations contribute to the overall IR absorption differently. The molecules in small crystals should have greater contributions than those in large ones. The molecules on the surface of a large crystal ($d > 2.2$ μm) should absorb more IR than those inside of the crystal. The crystals closer to the edges of the KBr pellet should receive more photons than those inside of the matrix. For a large crystal, the molecules on a surface with transition moments perpendicular to the IR beam should absorb more photons than those on the surfaces parallel to the IR beam. Therefore, a nonlinearity between the IR absorption intensity and its amount in a pellet would be expected. However, for a series of given pellets with different amounts of substrate, as long as the crystal size distribution is kept relatively the same, the IR intensity should be still proportional to the amount of the substrate in the matrix. This consistency can be easily achieved by using the same grinding method and pressure to make the pellets. When a pellet is being reformed, large crystals of the substrate are broken down to smaller ones. A greater percentage of small crystals translates to a stronger IR absorption. For PB, a larger change in crystal size results in a more dramatic change in its carbonyl absorption after reformation of the pellet.

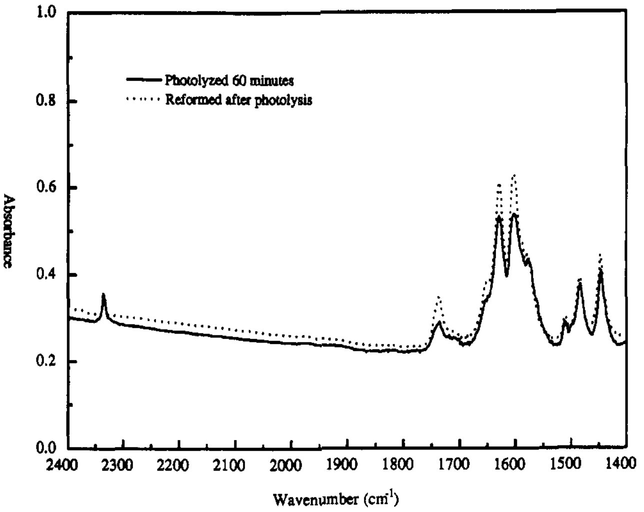

Figure 5. Reformation of the phenyl benzoate/KBr pellet after photolysis.

If a typical DBPO/KBr pellet is treated as a solution sample, the Lambert–Beer expression gives the expected values of 2.8–4.2 for the IR absorption at 1759 cm^{-1}. However, experimental results show observed values of 0.7–0.8. It is apparent that the observed IR response with a large extinction coefficient does not reflect the entire collection of the particles within the pellet. A comparison between IR spectra obtained from a solution sample of DBPO and a DBPO/KBr pellet indicates that absorptions with smaller extinction coefficients already closely represent the actual amount of material in a pellet. Therefore, reformation of a pellet would not increase the absorption intensities significantly for those peaks.

DBPO has a much higher extinction coefficient in the UV region than those of IR absorptions,[15] thus, the photons can only reach the molecules in selective areas such as the surface of an organic crystal. It is those molecules that are the major contributors for the IR absorptions with large extinction coefficients. Decomposition of these molecules, although a small amount, should cause large decreases in those IR absorptions (Table I). This accounts for the discrepancy between the IR and HPLC results. When the photolysis is carried out with wavelengths greater than 300 nm, because of the small extinction coefficient of DBPO in the visible region, random photolysis throughout the sample is expected. Therefore, the yield obtained from IR is much closer to that from HPLC. This is also consistent with the observations by McBride and his co-workers.[16–18]

When a pellet is reformed after the photolysis, the carbonyl absorptions of the remaining starting materials are enhanced due to the formation of smaller particles. The reformation of a pellet also randomizes the orientations of the crystals, making the products less detectable by the IR beams. This translates to a smaller product absorption. For PB, it starts with larger crystals. There-

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(12) When 99% of the light is absorbed by the substrate (o.d. = 2). The expression o.d. = $l\epsilon C$ is used to solve pathlength l. Solid DBPO has an equivalent concentration of 5.51 M.

(13) Jensen, J.B. *Acta Chem. Scand.* **1954**, *8*, 393.

(14) Falk, M. *Can. J. Appl. Spectrosc.* **1991**, *36* (1), 22.

(15) Extinction coefficient for DBPO are 1.6×10^4 dm^2/mol at 1759 cm^{-1} and 2.1×10^5 dm^2/mol at 254 nm in benzene solution.

(16) Vary, M.W.; McBride, J. M. *Mol. Cryst. Liq. Cryst.* **1979**, *52*, 133.

(17) McBride, J.M.; Gisler, M. R. *Mol. Cryst. Liq. Cryst.* **1979**, *52*, 121.

(18) Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729.

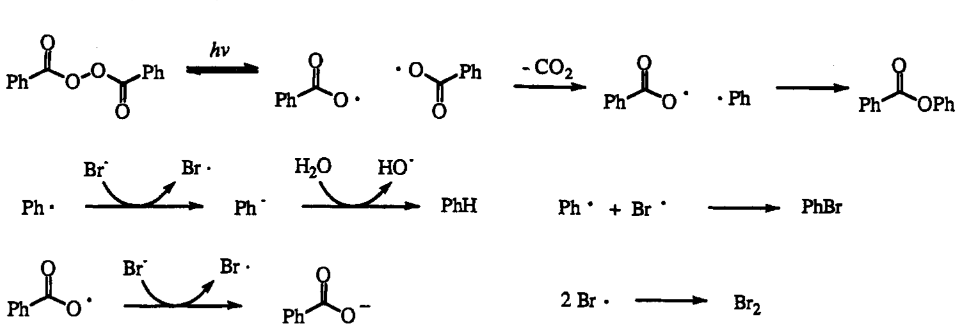

Figure 6. Photochemical decomposition of dibenzoyl peroxide.

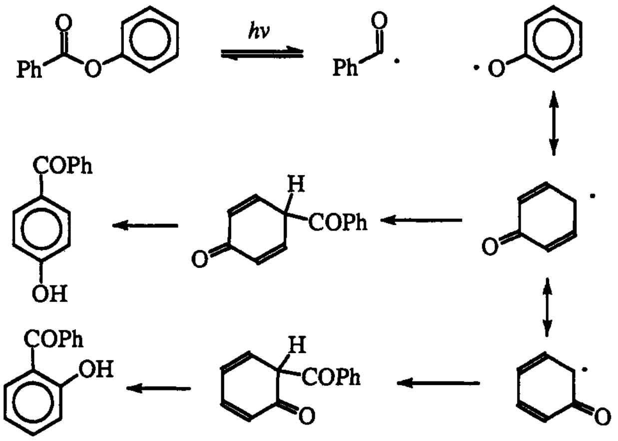

Figure 7. Photochemical decomposition of phenyl benzoate.

fore, an extensively photolyzed sample converts most of the large crystals into products. The reformation process breaks these large particles into smaller ones, hence, the signals of the products increase.

Bromide and Radical Intermediates.. The mechanism for the photochemical decomposition of dibenzoyl peroxide in solutions has been well investigated.[19-22] The pathways for the formation of phenyl benzoate and biphenyl in KBr matrix are expected to be similar to those in solutions as illustrated in Figure 6. The formation of potassium benzoate and bromobenzene is unique for the KBr system.[23] According to some simple semiempirical calculations,[24] the electron transfer from bromide (E_{HOMO} = −2.04 eV) to benzoyloxyl radical (E_{SOMO} = −8.38 eV) to give a benzoate anion and a bromine atom is an exothermic process (ΔH_{rx} = −45.25 kcal/mol). Similarly, a phenyl radical (E_{SOMO} = −4.97 eV) is quite capable of accepting an electron from bromide, undergo protonation, and form benzene. It is also possible that bromide is oxidized by an excited state of DBPO (E_{SOMO} = −3.48 eV) directly. The formation of bromobenzene may be the result of a combination between a phenyl radical and a bromine atom. The involvement of bromide from the matrix is also supported by the fact that the photolysis of DBPO in a KCl matrix gives chlorobenzene instead of bromobenzene as a product.

Table III. Product Ratios for Phenyl Benzoate Based on GC-MS Analysis

medium	photolysis time (min)	ratio of *o*-/*p*-hydroxybenzophenone
KBr matrix, not reformed	4	3.06
KBr matrix, reformed once	4	7.76
KBr matrix, reformed twice	4	9.10
5 × 10^{-3} M methanol solution	15	1.73
5 × 10^{-3} M methanol solution	30	1.65
5 × 10^{-3} M methanol solution	45	1.51
5 × 10^{-3} M methanol solution	60	1.62

Upon irradiation, PB forms a benzoyl and a phenoxyl radical. The phenoxyl radical can combine with the benzoyl radical at different sites to produce the *o*- and *p*-hydroxybenzophenone products (Figure 7).[25] Due to the rigidity of the matrix and the crystals, the movement of the phenoxyl radical is limited. This results in a higher ratio of *ortho* to *para* products in KBr compared to that in solution (Table III). The pellet that is reformed before the photolysis gives even higher *ortho*/*para* product ratio, indicating the increase in the rigidity of the matrix upon reformation. Although both radicals generated in the rearrangement may be reduced by the bromide ions according to their reduction potentials (E_{SOMO} = −3.86 eV for benzoyl and E_{SOMO} = −5.51 eV for phenoxyl radical),[24] due to their strong association with each other in the matrix, the electron transfer from the bromide ions does not take place.

Conclusion

A matrix prepared with potassium bromide offers a unique medium for study of photochemical reactions of organic compounds in their solid states at room temperature. Compared to a crystal sample, a KBr matrix is easier to prepare and handle. Although the compounds in the matrix are spectroscopically accessible, certain precautions must be taken when interpreting the IR absorption changes. The organic molecules at different locations in the matrix contribute to the overall IR absorption differently. The reduction ability of bromide in the matrix should also be considered.

Experimental Section

Materials. Potassium bromide (99+%, FT-IR grade), phenyl benzoate (99%), and benzoic acid (99+%) were used as receivedfrom Aldrich. Dibenzoyl peroxide (Polysciences Inc., Reagent Grade), Biphenyl (reagent grade, Eastman Organic Chemicals), bromobenzene (reagent grade, T. J. Baker), methylene chloride (reagent grade, J. T. Baker), and methanol

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(19) Nakata, T.; Tokumaru, K.; Simamura, O. *Tetrahedron Lett.* **1967**, *34*, 3303.

(20) Smith, W.F., Jr., Rossiter, B. W. *Tetrahedron* **1969**, *25*, 2059.

(21) McBride, J.M.; Segmuller, B. E.; Hollingsworth, M. D.; Mills, D. E.; Weber, B. A. *Science* **1986**, *234*, 830.

(22) McBride, J.M. *Acc. Chem. Res.* **1983**, *16*, 304.

(23) Hollingsworth, M. D.; Harris, K. D. M.; Jones, W.; Thomas, J. M. *J. Inclusion Phenom.* **1987**, *5*, 273.

(24) All semiempirical calculations are performed on *Hyperchem* 3.0, autodeck, with AM1 option. RHF energies were used for the comparison. For a radical, the geometry was first optimized with UHF option and SOMO energy was obtained by a single point RHF calculation.

(25) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; CRC Press: Boca Raton, FL, 1991; pp 407.

(reagent grade, Fisher) were used without purification. KBr and KCl were oven dried before use.

Instrumentation. All routine analyses were performed on a Mattson 2020 Galaxy Series FT-IR spectrophotometer and a Hewlett-Packard 1050 Series HPLC equipped with a 5 μm 125 × 4 mm HP Spherisorb ODS2 column. GC-MS analyses were conducted with a Hewlett-Packard 5890 II GC with an HP1 capillary column interfaced with a Model 5971A mass spectrometer. A Hewlett-Packard 5890 GC equipped with FID and a 20-m carbowax column was employed. SEM micrographs were obtained on a JEOL JSM 6300 scanning electron microscope. Digital image processing was performed on collected data with a NORAN Voyage EDS workstation.

General Procedures for KBr Pellet Preparation. A mull of organic crystals and KBr was prepared in a mortar with a pestle. An average of 40–60 mg of the mull was added into a dye assembly that was then placed in a Carver hydraulic press. It was subjected to 9000 pounds of pressure for 2 min, after which the dye was removed and disassembled. The pellet was mounted on an Econo card (Aldrich) which had a portion of its adhesive paper removed in order to allow for an even photolysis on both sides of the pellet. When a sample was reformed, the KBr pellet was removed form the Econo card and carefully cut away from the paper ring. After removal from the ring, the pellet was crushed using a mortar and pestle, creating a fine powder. This powder was then placed back into the dye and pressed into a pellet again.

General Procedures for Photolysis and Extraction. Irradiation of the KBr pellets was carried out in a Rayonet photochemical reactor equipped with 16 Hg lamps (350 nm). After photolysis, the pellet was carefully removed from the Econo card, cut away from the paper ring, and weighed. For the HPLC or GC analysis, the separated pellet was placed in a 4-mL vial, to which was added 1 mL of methylene chloride and 1 mL of 0.2 M HCl. The vial was capped and shaken vigorously to dissolve the pellet. The organic layer was removed and analyzed. To verify the formation of benzene, a photolyzed DBPO/KBr pellet was placed in a vial that is then immediately sealed. The pellet was broken by vigorous shaking of the vial and released any benzene into the head space. Three milliliters of the gas from the head space was injected into GC (FID and MS) and the production of benzene and bromine was verified.