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Decomposition of 3-Chlorobenzoyl Cyclohexanecarbonyl Peroxide in a KBr Matrix

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Introduction

Alkali halide matrices have been used as media for the monitoring of various thermal and photochemical reactions.[1−4] This is because they allow reaction progress to be followed spectroscopically with a relatively small amount of reactant. Also gaseous products can be trapped in the matrix and investigated directly. In a unique work described by Michl,[5,6] guest molecules were "salted" individually in a KBr matrix. The chemistry of these guest molecules reflects a homogeneous "solution" and it is very different from the case in which the guest molecules are trapped as aggregates or clusters. Significantly, unlike molecules in a cluster, the chemistry of salted molecules is essentially free from the interference of intermolecular reactions among the guest molecules. For most cases, however, a sample is prepared by simply mixing a compound (usually solid) with KBr powder and pressed into a pellet. As a result, the guest molecules are trapped as clusters in an inorganic matrix. When interpreting spectroscopic results involving these clusters one must then consider the heterogenous nature of the sample. We recently reported the use of a KBr matrix for the study of the photochemical decomposition of dibenzoyl peroxide.[7] It was found that the IR absorption intensity depends not only on the amount of the materials trapped in the matrix but also strongly upon the sizes of the clusters. Since samples containing guest molecules as clusters or aggregates are much more often seen and are much easier to prepare, it is important to investigate the chemical environment that such clusters are trapped in. The focus of this work is to investigate the polarity distribution of across the clusters trapped in a KBr matrix.

The decomposition of asymmetrical peroxides via carboxyl inversion has been observed in various media. The first clear evidence of this process was presented by Denney *et al.*[8−10] and involved using an ^{18}O-tracer to investigate the thermal decomposition of *p*-methoxybenzoyl *p*-nitrobenzoyl peroxide. Kinetic studies indicate that the process has a lower activation enthalpy and entropy than the corresponding radical decomposition process.[11−13] Similar to Denney *et al.*'s work, Fujimori and Flowers studied carboxyl inversion involving 3-chlorobenzoyl cyclohexanecarbonyl peroxide in a range of environments.[14,15] The inversion was found to be sensitive to the physical nature of the environment, especially the polarity of the media. Deriving from this work, we have selected the decomposition of 3-chlorobenzoyl cyclohexanecarbonyl peroxide to illustrate the influence of a KBr matrix on the organic clusters and more particularly to examine the behavior of molecules at different locations of the clusters, i.e. at the interface or in the bulk.

In this paper, the thermal decomposition process of 3-chlorobenzoyl cyclohexanecarbonyl peroxide clusters trapped in a KBr matrix is first described. A reaction mechanism that explains the formation of all detected products and reactive intermediates is proposed. This is followed by a discussion of the corresponding photochemical decomposition process. The influence of sample preparations is then examined. Kinetic data for the thermal decompositions of the peroxide under different sample preparation conditions is correlated with a bilayer model and the rate constants for each layer are estimated.

Results and Discussion

Thermal Decomposition. A mixture of 3-chlorobenzoyl cyclohexanecarbonyl peroxide and KBr powder was ground in a mortar and made into an almost transparent pellet using a press device. The sample was then stored in a desiccator in the dark to prevent interference from moisture and light. The peroxide is best represented in its IR spectrum by the doublet, at 1801 cm^{-1} for the aryl carbonyl and at 1768 cm^{-1} for the carbonyl adjacent to the cyclohexyl group (Figure 1). The decomposition of the peroxide was followed by monitoring the decrease in the peak at 1768 cm^{-1} since it was expected that the cyclohexylcarbonyl group would migrate during the inversion process. IR spectral analysis indicated that 3-chlorobenzoyl cyclohexanecarbonyl peroxide (**1**) decomposed significantly after 3 days (Figure 1). As the 1768 cm^{-1} peak decreased, new bands emerged at 1795 and 1722 cm^{-1}. The 1722 cm^{-1} absorption was assigned to cyclohexyl 3-chlorobenzoate ester (**2**). This was verified by a comparison with the synthesized authentic ester which gave an IR peak also at 1722 cm^{-1}. After a significant amount of time, over three months, the 1795 cm^{-1} peak disappeared and a new peak at 1703 cm^{-1} developed (Figure 1). The product absorbing at 1703 cm^{-1} was identified as 3-chlorobenzoic acid (**3**) on the basis of the fact that the authentic acid gave a carbonyl band at 1703 cm^{-1} as well. Carbon dioxide was produced at the expense of peroxide **1** and the species with the 1795 cm^{-1} peak. CO_2 was trapped within the matrix as evidenced by an absorption at 2374 cm^{-1}. Precautions were taken to distinguish the carbon dioxide trapped in the matrix during sample preparation and decomposition of the peroxide. A controlled experiment indicates that the background CO_2 peak from sample preparation is generally much smaller than those from the decomposition of the peroxide. In addition, when the sample was stored in a sealed vial, cyclohexanol (**4**) and cyclohexene

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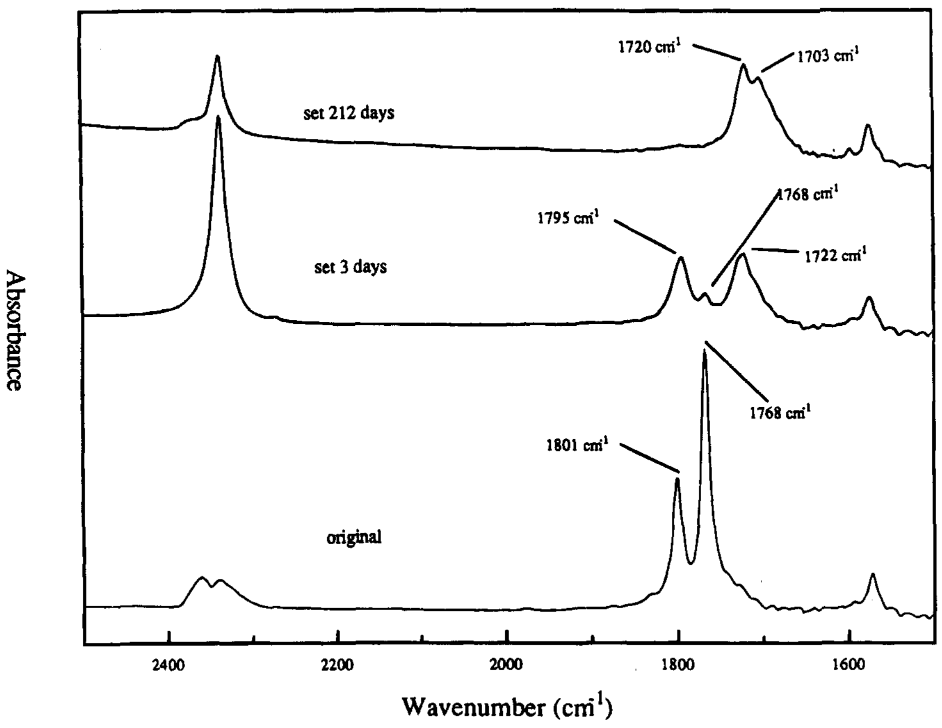

Figure 1. IR spectra for the thermal decomposition of 3-chlorobenzoyl cyclohexanecarbonyl peroxide.

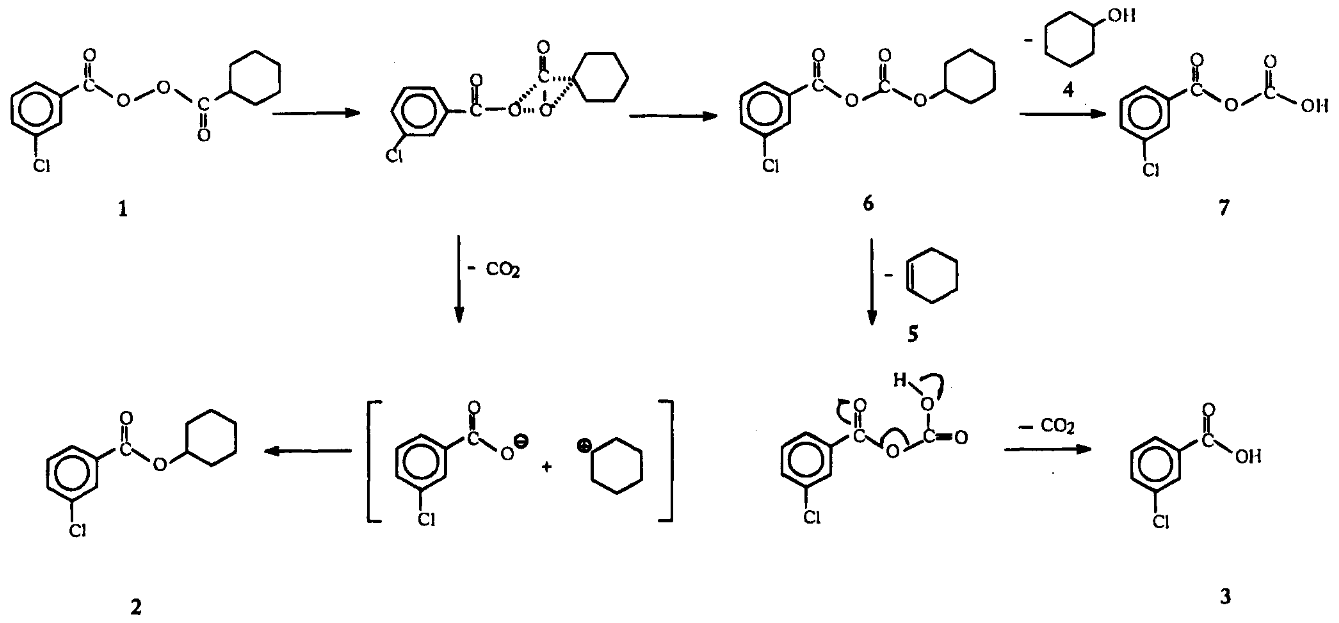

Figure 2. Proposed mechanism for the decomposition of 3-chlorobenzoyl cyclohexanecarbonyl peroxide in KBr pellets.

(**5**) were also detected in the head space during the decomposition.

The identity of the 1795 cm^{-1} product and a reaction mechanism to account for the formations of all products were proposed in Figure 2. The formation of ester **2** was caused by the decomposition of the peroxide and the elimination of one molecule of carbon dioxide via an ionic mechanism.[14] In addition, peroxide **1** decomposes via a molecular rearrangement to form cyclohexyl 3-chlorobenzoyl carbonate (**6**) with an IR absorption at 1745 cm^{-1}. The carbonate then decomposed as soon as it was generated and was never accumulated. This is supported by the fact that a sample of the synthesized carbonate **6** in the KBr matrix rapidly decomposed to 1795 cm^{-1} without giving off carbon dioxide. Since cyclohexene and cyclohexanol were indeed generated during this decomposition, it was concluded that the 1795 cm^{-1} product was 3-chlorobenzoyl bicarbonate (**7**), a product derived from the inversion product **6** eliminating the cyclohexyl ring. The structure of the bicarbonate was confirmed by a comparison with a synthesized authentic sample. To further verify the proposed mechanism, the synthesized bicarbonate **7** was placed in a KBr matrix, and its decomposition was monitored. The bicarbonate was converted into 3-chlorobenzoic acid (**3**) and carbon dioxide.

Photochemical Decomposition. The photochemical decomposition of 3-chlorobenzoyl cyclohexanecarbonyl peroxide was also investigated. A KBr pellet does not have significant absorption above 200 nm except some

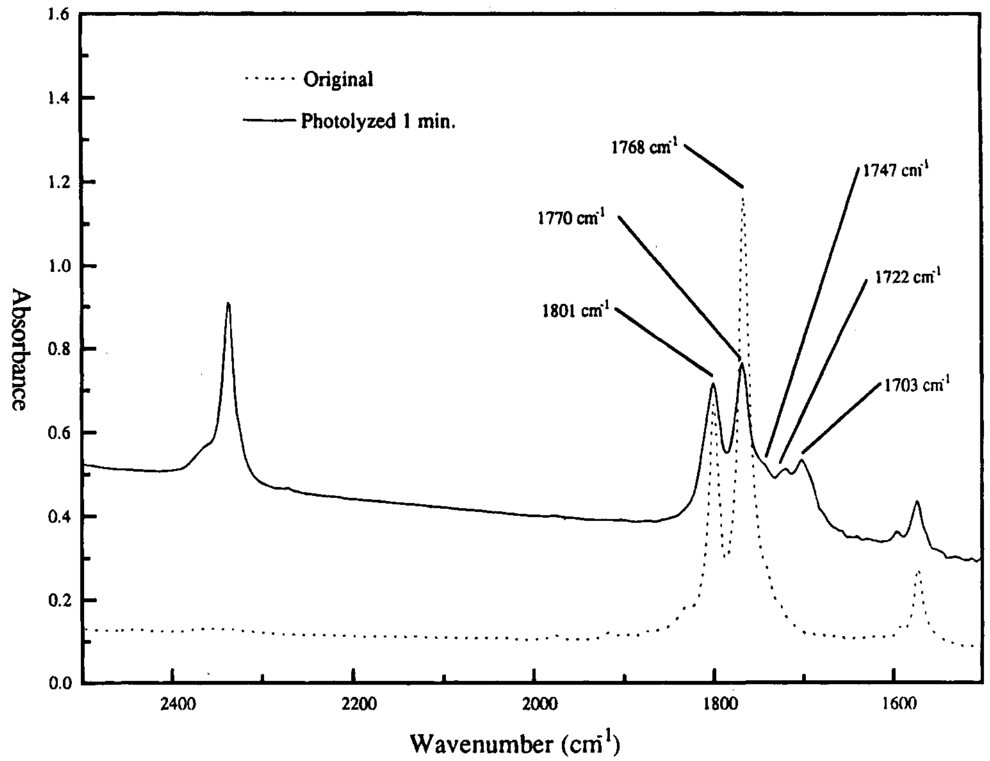

Figure 3. IR spectra for the photolysis of 3-chlorobenzoyl cyclohexanecarbonyl peroxide in KBr pellets.

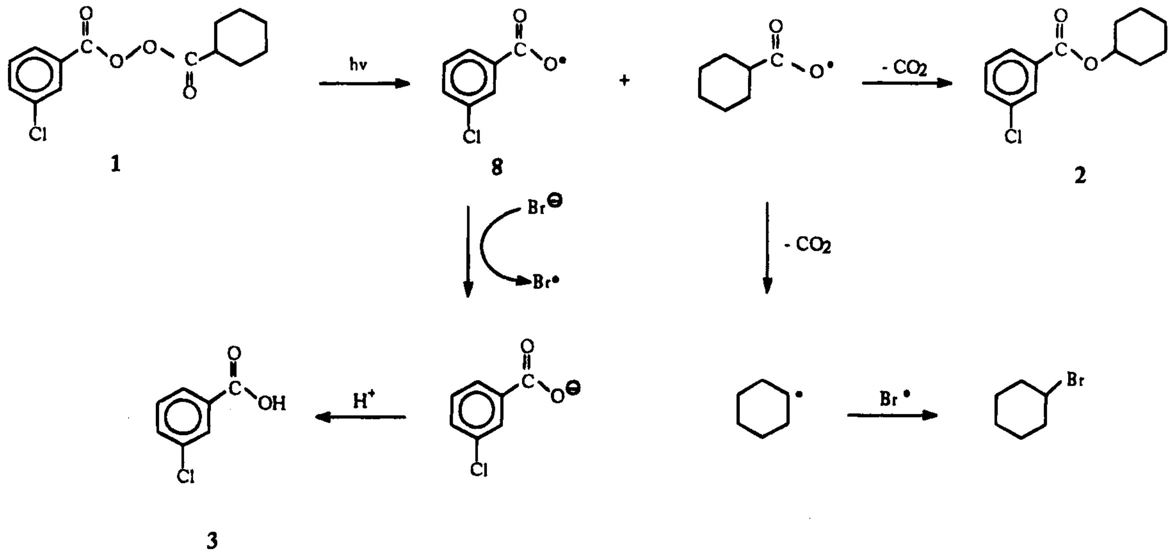

Figure 4. Proposed mechanism for the photochemical decomposition of 3-chlorobenzoyl cyclohexanecarbonyl peroxide in KBr pellets.

reflectance due to the opaque nature of the pellet. According to the UV–vis absorption spectra, the KBr matrix would not interfere with the strong absorption of the peroxide at 254 nm. After a KBr pellet containing the peroxide was irradiated with a 254 nm light source for 1 min, cyclohexyl 3-chlorobenzoate (**2**), 3-chlorobenzoic acid (**3**), and carbon dioxide were formed, as evidenced by the 1722, 1703, and 2374 cm^{-1} absorptions, respectively (Figure 3), in addition to the remaining peroxide **1** (1801 and 1770 cm^{-1}). The ionic inversion products, **6** and **7**, were absent according to the IR spectra. This result strongly suggests that the photochemical process follows the radical mechanism proposed in Figure 4. The irradiation causes a homolytic cleavage of the oxygen–oxygen bond. The loss of carbon dioxide, followed by a recombination of the radical pair, resulted in ester **2**. Due to a trace amount of water in the system, it is possible that acid **3** could be generated by the hydrolysis of the ester. This, however, is not the case since the ester absorption at 1722 cm^{-1} does not decrease as the acid absorption at 1703 cm^{-1} increases following the photolysis (Figure 5). Therefore, it was concluded that the acid was generated from the reduction of the 3-chlorobenzoyloxy radical **8** by the bromide anions in the matrix, followed by a protonation. The proton may come from the dissociation of carbonic acid (CO_2 + water). A similar reduction was seen in the photochemical decomposition of benzoyl peroxide.[7] It has been reported that the decomposition of a peroxide via a radical mechanism in solution often involves both inter- and intramolecular

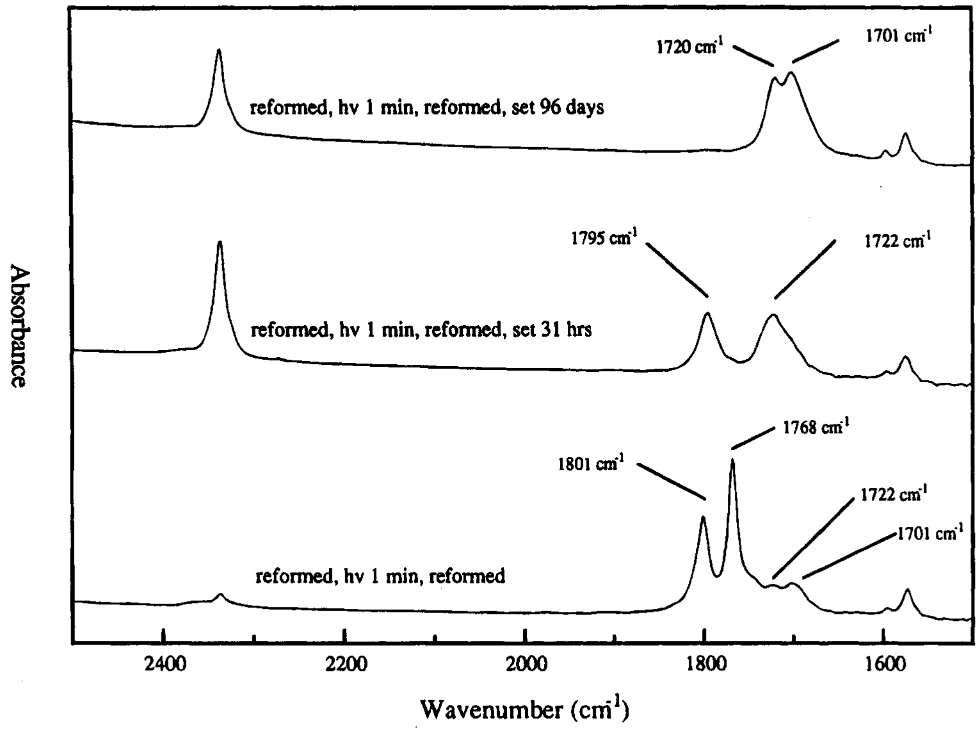

Figure 5. IR spectra for the thermal decomposition of 3-chlorobenzoyl cyclohexanecarbonyl peroxide in KBr pellets after photolysis.

reactions. Due to the dense nature of the organic clusters, it is very likely that the decomposition of the peroxide involves intermolecular reactions. Specifically, the acid may also be a result of hydrogen abstraction of another peroxide molecule by the 3-chlorobenzoyloxy radical **8**. Further studies in this area are clearly needed.

The production of color centers (F and H) in nominally pure alkali halide crystals as a function of photon energy in the ultraviolet region has been investigated.[16] CsI crystals give substantial numbers of color centers upon irradiation at 254 nm. The centers catalyze reactions via an electron-transfer and back-electron-transfer mechanism, similar to the photoinduced catalytic reactions on semiconductor particles.[17] The 254 nm light, however, is not absorbed efficiently by KBr and color centers are formed with a much lower quantum yield.[5,16] Therefore, the involvement of a color center in the photoinduced decomposition of peroxide in KBr matrix may not be important at all.

The Influence of Sample Preparations. Eight samples, A–H, were prepared and monitored in the dark at room temperature to examine the influence of the matrix on the decomposition process. All samples except sample H were wrapped with aluminum foil and stored in a desiccator to prevent the influence from moisture and light. For sample A, peroxide **1** was simply mixed with a KBr powder and set aside. For sample B, the peroxide **1** was mixed with KBr powder and then made into a pellet. Sample C was prepared in the same manner as sample B except the pellet was broken into powder and then set aside. Sample D was the same as sample B except that the pellets were broken and then re-formed. The re-formation process is accomplished by crushing a pellet into a powder and then pressing it into a new pellet. Sample E was a control sample that contained the peroxide crystals only. Samples F and G were the same as sample D except they were re-formed two and three times, respectively. Sample H was the same as the sample B except it was not stored in a desiccator. The decomposition of peroxide **1** was followed by monitoring the decrease of the 1768 cm^{-1} peak. The decomposition rate was found to be in the order of G > F > D > B > E > A > C. The apparent half-lifes of the peroxide under these conditions are listed in Table 1. The kinetic data for some of the samples are illustrated in Figure 6. The re-formation process (in sample D) clearly enhances the decomposition rate because the organic clusters are smaller and more peroxide molecules have direct contact with ionic KBr matrix than in sample B.[7] It is consistent with the fact that the peroxide decomposes faster in a polar medium.[14,15] Samples F and G gave even shorter half-lifes for the peroxide due to the additional re-formation that produces smaller peroxide clusters. The two KBr powder samples have slower decomposition rates than the control sample E. It may be attributed to the fact that KBr powders dissipated the heat generated from the thermal decomposition and prevented the

Table 1. Apparent Half-lifes of 3-Chlorobenzoyl Cyclohexyl Peroxide and Fluorescence Emission Maxima of 1-Pyrenecarboxaldehyde in Various Media

medium (sample[a])	half-life (h)[b]	emission maxima (nm)[c]
MeOH	32	450
MeOH/H_2O = 1:9 (v/v)	18	471
KBr powder (C)	124	
KBr powder (A)	102	
peroxide powder (E)	82	
KBr pellet (B)	44	530
KBr pellet re-formed (D)	20	530
KBr pellet re-formed 2× (F)	13	530
KBr pellet re-formed 3× (G)	8	530

[a] See text for detailed preparation procedures of samples A–G. [b] Apparent half-lifes were estimated from the 1768 cm^{-1} peak at room temperature ca. 25 °C. [c] Excitation wavelength was 366 nm.

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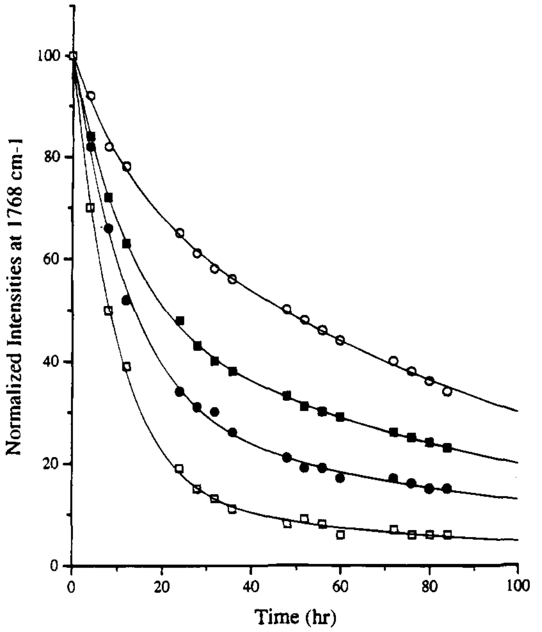

Figure 6. Thermal decomposition of 3-chlorobenzoyl cyclohexanecarbonyl peroxide in KBr pellets (not re-formed, ○; re-formed once, ■; re-formed twice, ●; re-formed three times, □). The initial intensities at 1768 cm^{-1} were normalized to 100% for all peroxide samples.

peroxide from rapid decomposition. Since the peroxide in sample C was better suspended in KBr powders than in sample A, the decomposition of the peroxide in sample C is slower. For sample H, the adsorption of water was apparent as indicated by the increase in the water peak at 3300 cm^{-1}. The influence of the adsorbed water on the decomposition process is, however, minimal. This is because adsorption mainly occurred at the surface of the KBr pellet and the chemical reactions monitored are mainly inside of the pellets.

The influence of a KBr matrix was also observed in the decomposition of bicarbonate **7**. For example, the bicarbonate was completely converted to acid **3** within 46 days in sample D while it took 96 days for sample B. The decomposition was even faster for the bicarbonate in samples F and G.

The sample preparation also affects the photochemical decomposition. As we reported previously, the quantum efficiency of a photoinduced decomposition process was less for a sample that had not been re-formed.[7] Unlike the polarity effect in thermal decomposition, however, the increase in quantum efficiency for a re-formed sample is primarily due to the fact that the organic clusters are smaller and have less of an internal filtering effect.

Organic fluorescent compounds have been widely used as molecular probes for heterogeneous systems. It is well known that a polar medium stabilizes the excited singlet states of an organic compound more than its ground state. Therefore, a red shift of the fluorescent emission maximum is expected for these probes in a polar medium.[18,19] It has been demonstrated that the degree of the shift for 1-pyrenecarboxaldehyde emission in a series of water and methanol mixtures is linearly proportional to the percentage of water content.[19] As shown in Table 1, the emission maximum of the aldehyde in KBr matrix is significantly red shifted, indicating that the organic crystals are influenced by a very polar medium. Although it has been clearly demonstrated that the peroxide decomposition rates are very sensitive to the total surface area of the clusters, the amount of the emission maximum shift is almost independent of how the sample is prepared. This is because sample preparation alters only the percentage of the molecules that are in contact with the inorganic matrix. This percentage determines the rate of decomposition, but not the physical properties of the matrix. The fluorescence signals mainly originate from the peroxide molecules that are in contact with the matrix. A percentage increase of this type of molecules may increase the signal intensity of the fluorescence but it has no influence on the emission maximum.

The nature of a heterogeneous system and its influence on the guest molecules are often complex. Ware *et al.* reported that the fluorescence signals from organic guest molecules in a heterogeneous environment are better described with a distribution of lifetimes.[20] Champagnon determined the fractal dimension of the silica gel pores to be less than 3 on the basis of the fluorescence decay from guest molecules.[21] Despite complexity, a simple model sometimes is adequate enough to describe a key feature of a heterogeneous system. For example, a bilayer (surface and bulk) model is often used to treat the nuclear relaxation time data obtained by NMR technique for water molecules trapped in silica pores.[22] The treatment does not require a monosurface layer. The so-called "surface layer" often includes molecules that are not in direct contact with the silica surface. The influence of the silica surface on these molecules is transmitted through a intermolecular dipole–dipole interaction or a rapid molecular exchange. This bilayer model, in our opinion, is also suitable for the clusters/KBr system. Upon examination of the decay data illustrated in Figure 6, it is found that they are indeed much better fitted with a biexponential than a single exponential model. The biexponential fitting gives one component having a half-life of 8 h that is clearly correlated to the peroxide molecules at the interface. The second component has a half-life of 77 h which is similar to that for the bulk peroxide (Tables 1 and 2). The influence of the matrix can be transmitted through intermolecular reactions from the interface to the molecules that are not in direct contact with the matrix. Since the data analysis does not require the surface layer to be a monolayer, those molecules affected by the intermolecular reactions would simply be included into the so-called surface layer.

The percentages of molecules at different locations (interface or bulk) can be estimated from the kinetic data shown in Figure 6. The analysis indicates that a pellet which has been re-formed three times contains ca. 80% of the peroxide molecules at the interface, while the pellet that has been re-formed less than three times consisted of a smaller percentage (Table 2). The initial intensities at 1768 cm^{-1} for all re-formed samples are essentially the same; the pellet not re-formed by contrast is signifi-

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Table 2. Half-lifes of 3-Chlorobenzoyl Cyclohexyl Peroxide Obtained from a Biexponential Analysis of the Data Shown in Figure 6

	half-life (h)[a], wt%[b]	
sample	peroxide 1 at surface	peroxide 1 in bulk
MeOH	32.0, 100	
MeOH/H_2O = 1:9 (v/v)	18.0, 100	
KBr pellet (B)	72.9, 77.7	7.9, 22.3
KBr pellet re-formed (D)	78.0, 48.6	8.6, 51.4
KBr pellet re-formed 2× (F)	89.0, 28.0	8.9, 72.0
KBr pellet re-formed 3× (G)	69.0, 13.0	7.0, 87.0

[a] Two components obtained from a biexponential fitting of the decay data shown in Figure 6. [b] Two exponential coefficients obtained from a biexponential fitting of the decay data shown in Figure 6.

cantly lower than the others (ca. 40%). This is a result of the nonlinear absorption effect caused by large organic particles, i.e., not all molecules in the pellet are contributing to the IR absorption equally.[7] Therefore, the initial intensities for the organic peroxide at 1768 cm^{-1} were normalized to 100% in Figure 6. Thus, the percentage of the peroxide at interface shown in Table 2 is only the upper limit for the pellet not re-formed.

Conclusion

A KBr matrix offers its guest molecules a unique reaction medium. In most cases, these guest molecules are trapped in the matrix as clusters. The average size and total surface area of the clusters heavily depend upon the sample preparation. The overall kinetics for thermal reactions are significantly affected by these factors. The relative ratio of the guest molecules at different locations can be estimated by the measurement of physical or chemical properties of some molecular probes such as 3-chlorobenzoyl cyclohexyl peroxide in this report.

Experimental Section

General. Unless stated otherwise all reagents were obtained from Aldrich and used without purification. GC-MS spectra were obtained on a Hewlett-Packard model 5890 series II gas chromatograph with a model 5917A mass spectrometer. All products were identified by GC-MS or confirmed by a comparison with the authentic sample on a Hewlett-Packard 1050 series HPLC equipped with a spherisorb ODS-2 column (5 μm, 125 × 4 mm). Infrared spectra were obtained on a Mattson Glaxy 2020 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC250 NMR spectrometer. Irradiations were conducted in a Rayonet photochemical reactor equipped with 16 light bulbs (General Electric G8T5, 254 nm). Thermal decompositions were conducted at ambient temperatures by wrapping the samples with aluminum foil and storing them in a desiccator. In the case of monitoring the formation of volatile organic compounds such as cyclohexene and bromocyclohexane, each pellet was stored in a capped 4 mL Shell vial wrapped with aluminum foil. Prior to the instrumental analysis, the pellet was broken down with sonication and a gas sample was drawn from the vial with a syringe. The gas sample was then analyzed with GC. All measurements were repeated at least three times either parallel or sequentially.

Sample Preparation. All KBr pellets were prepared in the following manner unless otherwise stated. A mull was prepared by weighing the required amount of organic material and oven-dried FT-IR grade KBr in a mortar and the two were ground together. To form a pellet, a paper ring was placed on the base of the dye assembly, then enough of the mull was placed on the stub to cover the surface. The top block portion was lowered onto the stub and the plunger piece was placed in the hole. The entire assembly was placed in a Carver hydraulic press and subjected to 9000 pounds of pressure for 2 min. The dye assembly was then removed and dissembled. The pellet was mounted on an Econo card which had a portion of its adhesive removed to allow for even photolysis on either side of the sample. When a sample was re-formed, the pellet was removed from the Econo card and carefully punched out from the paper ring. It was crushed with a mortar and pestle, creating a fine powder which was then placed on the stub with a new paper ring and pressed into a pellet in the same manner as above.

Synthesis of 3-Chlorobenzoyl Cyclohexanecarbonyl Peroxide (1). 3-Chlorobenzoyl cyclohexanecarbonyl peroxide was prepared following the procedure described by Govindan and Kaelin.[23] A yield of 33% unpurified product was obtained. Further purification by recrystallization was performed according to the method provided by Fujimori and Oae[14] with a 74.8% yield. Product purity was verified by NMR and IR analysis. The IR spectrum indicated the presence of the characteristic carbonyl doublet at 1801 and 1768 cm^{-1}. ^1H NMR: δ 1.32−2.10 (m, 10H), δ 2.55 (m, 1H), δ 7.42 (t, 1H), δ 7.57 (d, 1H), δ 7.88 (d, 1H), δ 7.98 (s, 1H).

Synthesis of Cyclohexyl 3-Chlorobenzoyl Carbonate Inversion Product 6. The cyclohexyl 3-chlorobenzoyl carbonate inversion product was synthesized according to the method provided by Fujimori and Oae.[14] 3-Chlorobenzoyl cyclohexanecarbonyl peroxide (30 mg) was added to 5 mL of carbon tetrachloride and stirred at 47 °C for 2.5 h. A portion of this reaction mixture (1 mL) was mixed with 0.75 g of KBr. The solvent was then removed by vacuum and pellets were made. IR (KBr): found 1803 and 1747 cm^{-1} IR: lit.[12] 1805 and 1750 cm^{-1}. ^1H NMR (CCl_3D): found δ 1.36−1.98 (m, 10H), δ 4.77 (m, 1H), δ 7.44 (t, 1H), δ 7.51 (d, 1H), δ 7.96 (d, 1H), δ 8.04 (s, 1H). ^1H NMR (CCl_3D): lit.[12] δ 1.36−1.98 (m, 10H), δ 4.77 (m, 1H), δ 7.44 (t, 1H), δ 7.51 (d, 1H), δ 7.96 (d, 1H), δ 8.04 (s, 1H).

Synthesis of Cyclohexyl 3-Chlorobenzoate Ester (2). Purified 3-chlorobenzoic acid chloride (1.5 g, 8.6 mmol) was added to an oven-dried 25 mL single neck round bottom flask (SNRBF) along with 0.78 g (7.8 mmol) of cyclohexanol, 10 mL of benzene, and 5 mL of pyridine. The solution was heated under reflux for 2 h and then washed with water (3 × 10 mL). The solvents, benzene and pyridine, were removed from the organic layer under reduced pressure. A 10 mL portion of ethyl ether was added to the remains left after vacuum drying. This ether solution was then washed with 10 mL of 0.01 M KOH solution to remove any remaining 3-chlorobenzoic acid or 3-chlorobenzoic acid chloride. After drying the ether layer with anhydrous magnesium sulfate, the ether was removed under vacuum. A colorless oil was obtained. IR (NaCl): found 2924, 2852, 1722 cm^{-1}. IR: lit.[14] 1720 cm^{-1}. GC/MS: 238, 139, 111, 82 *m/e*.

Synthesis of 3-Chlorobenzoyl Bicarbonate (7). 3-Chlorobenzoic acid chloride (0.75 g, 4.3 mmol) was added to an oven-dried 25 mL SNRBF. To this were added 5 mL of ethyl ether and 0.5 mL of pyridine. The solution was cooled in an ice bath and stirred vigorously. Through a condenser, 0.63 g (6.4 mmol) of oven dried and ground potassium bicarbonate was added. The production of 3-chlorobenzoyl bicarbonate was monitored by periodic IR analysis. After 2 h, the ether solution was washed with water to extract the salt and then with 0.2 M HCl to extract the pyridine. After the solvent was removed with a rotoevaporator, white crystals were obtained. IR (KBr): 1786 and 1724 cm^{-1}. ^1H NMR: δ 4.86 (s, 1H), δ 7.50 (t, 1H), δ 7.82 (d, 1H), δ 7.98 (d, 1H), δ 8.11 (s, 1H). ^{13}C NMR: δ 128.69 (s, 1C), δ 130.28 (s, 1C), δ 130.47 (s, 1C), δ 134.77 (s, 1C), δ 135.16 (s, 1C), δ 148.68 (s, 1C), δ 160.84 (s, 1C). Melting point: 81−83 °C. Anal. Calcd for $C_8H_5O_4Cl$: C, 48.12; H, 2.00; Cl, 17.80. Found: C, 48.26; H, 1.90; Cl, 17.98.

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