Decomposition of Bis(p-methoxybenzoyl) Peroxide and the Carboxy Inversion Product on Silica

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Substituted benzoyl peroxides in which one of the moieties is p-methoxybenzoyl (anisoyl) and the other has one or more nitro substituents are known to decompose heterolytically as well as homolytically.[1] In polar media the decomposition reactions are faster than those in nonpolar media and the free radical derived products begin to be accompanied by ion pair derived products such as the carboxy inversion compound. The surface of silica favors the polar reaction much more than do ordinary polar solvents.[2] For example, the half-life of anisoyl p-nitrobenzoyl peroxide in benzene–silica slurries is only a few minutes at room temperature,[2a] while its half–life in benzene *without* silica is estimated to be more than a year. A change to a more polar liquid medium, from solution in benzene to solution in nitrobenzene, increases the rate of that peroxide only by a factor of 8.[1a]

The literature contains evidence hinting that bis(p-methoxybenzoyl) peroxide (AP) may also react in part by a polar mechanism, even in relatively nonpolar solvents. Thus its rate of decomposition in acetophenone at 80 °C is about 2.4 times that of the next fastest symmetrically substituted benzoyl peroxide.[3] The reactions in dioxane in the presence of an inhibitor[4] and in styrene[5] are faster than predicted by the Hammett plots. The rate for the peroxide with a single p-methoxy substituent in dioxane also exceeds that predicted by the Hammett plot, but to a lesser extent. The behavior of AP and its carboxy inversion product, anisoyl anisyl carbonate (CIN), on silica are the subject of the present paper.

Results and Discussion

Peroxide Decomposition Rates. The half-life at room temperature of the symmetrical peroxide AP in silica slurries made from nonpolar solvents is comparable to that of anisoyl p-nitrobenzoyl peroxide. For example, in a stirred slurry containing 4.4 g of S157 silica, 50 mL of benzene, and 37.9 mg of AP, the half-life of the peroxide, determined by iodometric titration, was about 2 min. A similar experiment using CCl₄ gave a half-life of 1.5 min.

The half-life in a slurry depends on the loading of the silica surface. Lowering the amount of silica in a benzene slurry experiment like the one just described by a factor of about 4 increased the half-life of the peroxide by a factor of 3, even though it is probable that most of the peroxide was adsorbed in both cases. The half-life in the later part of a run is also somewhat greater than that for the early part. Both of these results are consistent with the existence of more than one kind of site on the silica.[6] A strongly

adsorbed product could prevent other molecules of the peroxide from reusing the relatively scarce faster reaction sites even in the presence of solvent. In support of this interpretation we note that the reaction in a benzene slurry made up with an amount of anisyl anisate about equal to that of the peroxide is slower by an order of magnitude. The reaction is also slower in slurries made with more polar solvents which might themselves be adsorbed on the fast sites. The half-lives in slurries with DMF, ethyl acetate, Me₂SO, or anisole are 30 min or more.

Products. The major initial product of the decomposition in a benzene slurry of S157 silica is the carboxy inversion compound p-methoxybenzoyl p-methoxyphenyl carbonate (CIN). Immediate filtration of a benzene slurry and extraction with ether gave a concentrate still showing the characteristic 1780 cm⁻¹ (m) and 1760 cm⁻¹ (s) infrared doublet of the peroxide. Allowing the reaction to proceed for 2 min gave an extract in which the peroxide carbonyl peaks were greatly reduced and obscured by those of the carboxy inversion compound. The spectrum of the extract after a 5-min reaction time on the silica had peaks at 1800 and 1740 cm⁻¹, like those of CIN (1810 and 1740 cm⁻¹ in CH₂Cl₂) but somewhat broadened. The carboxy inversion compound was readily isolated in yields of about 45% from runs after reaction times of 8 to 15 min.

In runs allowed to proceed overnight the spectrum of the extracted material no longer showed any signs of CIN. The remaining absorption in the carbonyl region consisted of unresolved bands from about 1670 to 1770 cm⁻¹. Analysis by GLC of the products from runs in benzene or CCl₄ slurries after reaction times long enough to destroy all of the intermediate CIN gave (yields in moiety %) p-methoxyphenol (32% to 39%), anisic acid (37% to 49%), and anisyl anisate (4.1% to 7.7%). The mean material balance was 86% of the anisyl moieties. Minor products included 0.2 to 0.5 moiety % dianisyl and 2 moiety % dianisyl carbonate.[7]

¹³C-Enriched AP and Magic Angle ¹³C NMR. A sample of 0.140 g of the peroxide, 90% enriched at both carbonyl groups with ¹³C, was dissolved in a small amount of CHCl₃ and then diluted with cyclohexane and slurried with 1.05 g of S157 silica. The solvent was rapidly removed by suction filtration and the silica left on the filter until it was free-flowing. The silica was then loaded into an NMR tube. ¹³C NMR spectra were obtained by using magic angle spinning and simple polarization of the proton spins.

Accumulation of ¹³C NMR data from the dry silica was begun 9 min, 40 s after the mixing of the slurry. At this point there are strong ¹³C NMR signals from the carboxy inversion intermediate CIN, moderately strong signals from anisic acid and CO₂, and a very weak signal from the remaining peroxide. Figure 1 shows accumulations of the spectra in the δ 167 to 163 region summed at 1-min intervals. The peroxide peaks (P) at 165.0 ppm decayed with a half-life of about 100 s, while peaks (E) due to anisyl anisate grew in. The latter signal is also very weak at this stage, indicating that all or almost all of the ester is formed via the carboxy inversion product rather than directly.

Since the decomposition of the intermediate carboxy inversion product CIN on silica is an order of magnitude slower than that of the peroxide, its rate constant was determined in a continuation of the same run. The signals from the anisoyl and carbonate carbonyls of CIN occur at

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(2) (a) Leffler, J. E.; Barbas, J. T.; Flowers, G. C. *J. Org. Chem.* **1982**, *47*, 2286. (b) Leffler, J. E.; Barbas, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 7768.

(3) Blomquist, A. T.; Buselli, A. J. *J. Am. Chem. Soc.* **1951**, *73*, 3883.

(4) Swain, C. G.; Stockmayer, W. T.; Clarke, J. T. *J. Am. Chem. Soc.* **1950**, *72*, 5426.

(5) Cooper, W. *J. Chem. Soc.* **1951**, 3106.

(6) Albery, W. J.; Bartlett, P. N.; Wilde, C. P.; Darwent, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1854.

(7) In solution two modes of decomposition are known for carboxy inversion compounds, one leading to ester and CO₂, the other to carbonate, anhydride, and CO₂. Longosz, E. J.; Tarbell, D. S. *J. Org. Chem.* **1961**, *26*, 2161.
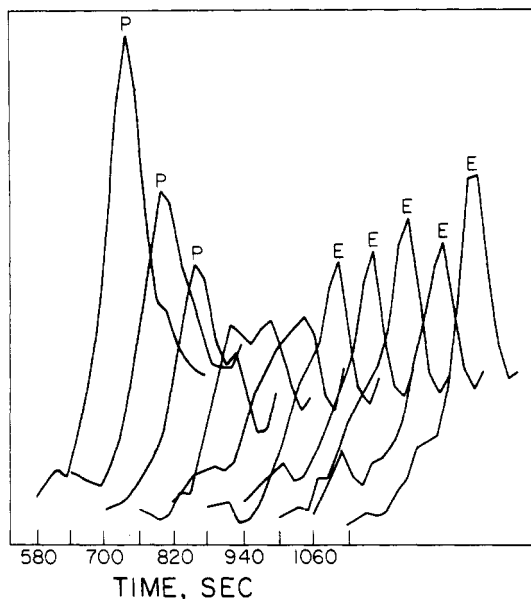
Figure 1. Scan sets of the 167–163-ppm ^{13}C NMR region summed at 1-min intervals. The times are the beginnings of the scan sets. The decaying peak is the 165.0-ppm peroxide carbonyl signal and the growing peak is the δ 164.15 signal of anisyl anisate.
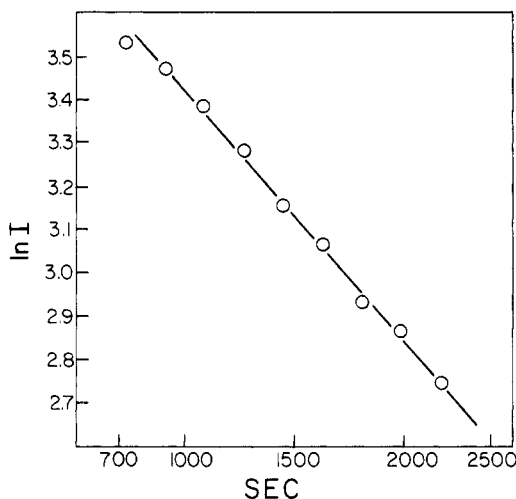

Figure 2. First-order plot of the decay of the integrated ^{13}C NMR signal from the carbonyl groups of the carboxy inversion compound.

δ 161.95 and 150.1 ppm and are of approximately equal intensity. The rate constant for the decay of these signals (Figure 2) is 5.7×10^{-4} s^{-1} at 26 °C. The ordinate in Figure 2 is the log of the sum of the integrated areas of the two signals accumulated during a 3-min period. The abscissa is the time of the mid-point of the data accumulation period. The decay of the CIN is accompanied by the growth of signals from CO_2 (125.4 ppm[8]), anisic acid (171.3 ppm), and anisyl anisate (164.15).

Discussion. Products from the polar decomposition of peroxides can arise indirectly from secondary reactions of the carboxy inversion compound[7] or more directly from primary intermediates such as free radicals, radical pairs, or ion pairs. In some cases reported in the literature polar substituents and/or polar solvents appear to have accel-

erated the formation not only of products ascribed to ion pair intermediates but also of those that require radical precursors. In order to account for the apparent acceleration of *both* the radical and ionic branches of the reaction, it has been suggested that the two branches stem from a common intermediate, either a hybrid or a rapidly equilibrating ion pair/radical pair.[11]

Since the ^{13}C NMR experiment showed that most of the anisic acid, CO_2, p-methoxyphenol, and anisyl anisate product appeared only after most of the AP was gone, it is clear that the greater part (but not necessarily all) of each of these products is formed by secondary reaction (eq 2–4) of the CIN. The small amount of anhydride predicted by eq 4 was not seen but may have hydrolyzed on the silica.
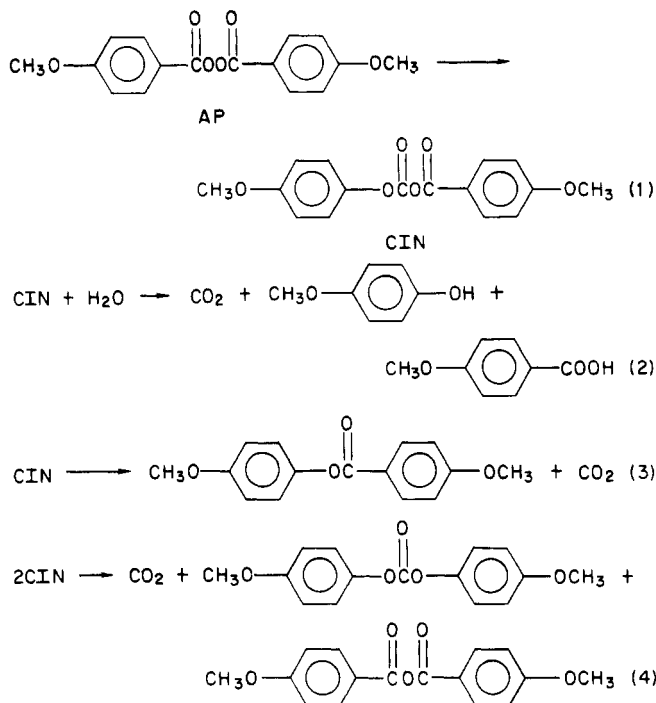
Since the GLC yields of anisic acid exceeded, on the average, the yields of p-methoxyphenol plus dianisyl carbonate by about 15%, part of this product was probably formed by processes that bypass the CIN. This conclusion is supported by the ^{13}C NMR signal of the acid at about the fifth half-life of the AP, at which time it is stronger than predicted by the sequential first-order mechanism (eq 1, eq 2) for the formation of the acid. The formation of dianisyl, although in very low yield,[9] requires a radical reaction. Whatever the radical process may be, its rate has to be considerably increased over that in an ordinary nonpolar solvent in order to compete with the very fast ionic reactions.

Experimental Section

Bis(p-methoxybenzoyl) Peroxide. Hydrogen peroxide (5.5 g, assay 28%, 0.0453 mol) was added dropwise during 30 min to a cold (ice bath) solution of 13.5 g (0.0791 mol) of p-anisoyl chloride in 7 mL of ether. This was followed by the dropwise addition of an aqueous solution of 4.0 g of NaOH (0.100 mol, volume 10 mL) during 60 min. The resulting white precipitate of the crude peroxide, after washing with 15 mL each of ether and water, was crystallized from cold acetone/water. The peroxide assay by titration was 99.7%: mp 126.5–127 °C (lit.[3] mp 127 °C); IR (CH_2Cl_2) 1780 (m), 1755 (s).

(8) Ettinger, R.; Blume, P.; Patterson, A.; Lauterbur, P. C. *J. Chem. Phys.* **1960**, *33*, 1597.

(9) The possibility that the dianisyl might have been present as an impurity in the peroxide was eliminated by GLC of a sample after reduction with HI.

(10) Greene, F. D.; Kazan, J. *J. Org. Chem.* **1963**, *28*, 2168.

(11) (a) Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonnou, C. G. *J. Am. Chem. Soc.* **1970**, *92*, 4927. (b) Leffler, J. E.; More, A. A. *J. Am. Chem. Soc.* **1972**, *94*, 2483.

Anisoyl peroxide with 90% ^{13}C in the carbonyl groups was made from the labeled acid and ethereal H_2O_2 by the dicyclohexyl-carbodiimide method:[10] mp 123.5–124 °C (lit.[10] mp 124.5–125 °C).

Anisoyl Anisyl Carbonate (CIN). To 3.20 g (0.0176 mol) of diphosgene was added dropwise with stirring 8.8 mL of 0.2 M aqueous sodium p-methoxyphenolate during 30 min. At this point 10 mL of ether was added and the stirring continued for 10 min. After adding a further 15 mL of ether and 10 mL of H_2O and shaking, the water layer was removed and discarded. Then 1.8 g of triethylamine in 10 mL of CH_2Cl_2 was added dropwise with stirring during 10 min to a mixture consisting of the ether solution, 2.70 g of anisic acid, and 25 mL of CH_2Cl_2. After more water and ether were added, the mixture was shaken and the organic layer was washed with water and twice with aqueous Na_2CO_3 and dried over Na_2SO_4. The ether was then removed by rotary evaporation and the residue crystallized from benzene: yield, 1.8 g (34%); mp 92–94 °C dec (gas evolution); IR 1810 cm^{-1} (s), 1740 cm^{-1} (m).

Dianisyl Carbonate. A 12-mL sample of 0.2 M sodium p-methoxyphenolate was stirred with 1.62 g of diphosgene for 30 min. Water and CH_2Cl_2 were added and the precipitate that had formed dissolved in the CH_2Cl_2. This solution was washed twice with water and dried over Na_2SO_4, and the solvent was removed by rotary evaporation. The residue was crystallized from benzene/pentane: yield 0.5 g; mp 85–89 °C, main GLC peak 99 area %; IR (CH_2Cl_2) 1800 cm^{-1} (shldr), 1770 cm^{-1} (s).

Product Analysis. Slurries for product runs were allowed to stand in the dark for at least 24 h. The products were recovered from the supernatant liquid and from the silica by extraction with ether. Identification was by GLC retention times, spiking of the GLC mixtures with authentic samples, GC/mass spectrometry, ^{13}C NMR, IR, or isolation. Yields were obtained by GLC runs using internal standards.

Silica. The silica S157 is the same as that called P_oH_1 in an earlier paper.[12]

Slurry Preparation and Titration. In preparing a slurry it is important to avoid the effect of adsorption exotherms by adding solvent to the silica before adding the solution of the reagent. The following is a typical procedure: 2.2 g of silica gel is slurried with 20 mL of solvent. Then 10.0 mL of a solution containing 20 mg of the peroxide is pipetted into the slurry while stirring. For titrimetric rate measurements, after an elapsed time measured from the mid-point of the addition of the peroxide, 2 mL of saturated aqueous KI and 30 mL of carbonated glacial acetic acid are added together. The flask is stoppered again and stirring continued for another 3 min. Then 80 mL of carbonated water is added and the iodine titrated with thiosulfate.

Registry No. AP, 849-83-2; CIN, 98634-05-0; p-anisoyl chloride, 100-07-2; diphosgene, 503-38-8; sodium p-methoxyphenolate, 1122-95-8; p-anisic acid, 100-09-4; silica, 7631-86-9; p-methoxyphenol, 150-76-5; anisyl anisate, 60127-34-6; dianisyl carbonate, 5676-71-1; anisoyl peroxide-$^{13}C_2$-carbonyl, 98612-59-0; anisic acid-^{13}C-carboxy, 69838-89-7.

(12) Leffler, J. E.; Zupancic, J. J. J. Am. Chem. Soc. 1980, 102, 259.

^{33}S NMR Spectra of Sulfonic Acids and Sulfonate Salts

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The field of ^{33}S NMR has expanded rapidly since Faure's[1a] report, but the emphasis has been on sulfones,[1] sulfides,[2] and other derivatives.[2,3] The problems associ-

Figure 1. Concentration dependence of ^{33}S line width.

ated with natural abundance work on the quadrupolar ^{33}S nucleus have been discussed[1-3] and will not be repeated here. An approximate magnetic shielding scale has also been proposed.[4] Sulfonic acids are very strong acids[5] which are used in many reagents and ion exchange resins and are produced in degradative oxidation reactions during structural studies on coal.[6] Faure reported spectra of several acids, but nothing further has appeared. Table I is a summary of our initial results[7] on a series of sulfonic acids and sulfonic acid salts run in water at 6.104 MHz on a Varian FT-80 spectrometer (see Experimental Section).

Aromatic sulfonic acids are clearly more shielded than aliphatic sulfonic acids; a similar result was observed for sulfones,[1a] and a similar result was observed for the C-13 chemical shifts of the carbonyl carbon of carboxylic acids and carboxylic acid derivatives.[8] Clearly the greater polarizability of the aromatic π system shields the adjacent carbon or sulfur better than an aliphatic system can shield an adjacent carbon or sulfur. Another interesting result is the increased shielding and increased line width of 1,2-benzenedisulfonate in comparison to either the 1,3-disulfonate or benzenesulfonic acid. Apparently the ubiquitous γ effect[9] is also present in ^{33}S NMR. Preliminary results showed that higher temperatures narrowed the line width of benzenesulfonic acid from 52 Hz at 32 °C to 27 Hz at 41 °C, so most of the spectra were run at approximately 40 °C.

It mattered little whether one started with the acid or with a salt of the acid, because the chemical shift and line

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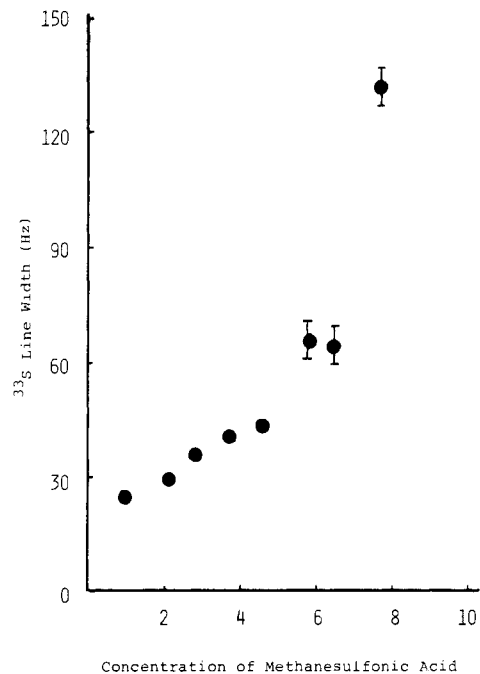
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