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p-Methoxybenzoyl *p*-Nitrobenzoyl Peroxide Revisited: Catalysis by Silica

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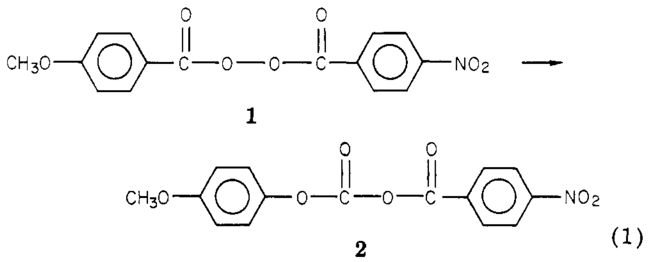
The decomposition of *p*-methoxybenzoyl *p*-nitrobenzoyl peroxide (1) in benzene/silica slurries at room temperature is faster than in benzene solution by 5 orders of magnitude. The first product of the reaction is entirely or mainly the carboxy inversion compound, *p*-methoxyphenyl *p*-nitrobenzoyl carbonate (2), which also decomposes on the silica. The products from experiments in which 2 is the initial reagent are the same as those from the peroxide. The most important are *p*-methoxyphenyl *p*-nitrobenzoate, *p*-methoxyphenol, and *p*-nitrobenzoic acid. The absence within the limits of GC/MS of anisic acid, *p*-methoxybiphenyl, *p*-nitrobiphenyl, *p*-nitrophenyl anisate, *p*-methoxy-*p*′-nitrobiphenyl, phenyl *p*-nitrobenzoate, phenyl anisate, and phenyl *p*-nitrobenzoate indicates that the decomposition of 1 under these conditions produces no free radicals.

The previous investigation of *p*-methoxybenzoyl *p*-nitrobenzoyl peroxide[1] (1) showed that in more polar media the decomposition became faster and the products more suggestive of ion-pair rather than radical-pair intermediates. Since then such behavior has been found in a large class of "polar" diacyl peroxides. One of the more frequently observed polar products is the carboxy inversion compound 2. (eq 1) Although an increase in rate accompanied by an increase in the proportion of polar products can often be explained in terms of competing heterolytic and homolytic dissociation reactions, this model sometimes seems to require implausible medium or substituent effects on the two competing reactions. As an alternative, the Walling hypothesis[2,3] postulates the rate-determing formation of a common hybrid radical pair/ion pair intermediate.



(1)

In order to determine whether peroxide 1 also requires the Walling or similar mechanism, we wished to obtain better data for a suitable polar reaction medium. Silica is a polar medium because of its hydroxyl groups but lacks the complicating sensitivity to attack by radicals characteristic of most polar organic solvents.[4]

In an earlier investigation of peroxides on silica we showed that β-phenylpropionyl (3), β-phenylisovaleryl (4), and β-phenylisovaleryl *p*-nitrobenzoyl (5) peroxides decomposed faster on silica than in solution by factors up to 160[6]. All three peroxides gave polar products, exclusively in the case of 5, mixed with products derived from radicals in the case of the others. However, no carboxy inversion products were detected among the polar products.

Catalysis by Silca

Fractional monolayers of reagents on silica surfaces are usually prepared from slurries of the silica with the reagent dissolved in some solvent that is then removed by filtration or by evaporation.[5,6] Removal of remaining traces of solvent is achieved by degassing at low pressure.

Our attempt to carry out this procedure with 1 led to the discovery that this peroxide undergoes a fast decomposition even at room temperature before the solvent is removed from the slurry. The half-lives at 21–22 °C ranged from less than 1 min to several minutes, depending on the choice of solvent and proportions of peroxide, solvent, and silica. The half-life of the small amount of peroxide found on the silica after hasty removal of the solvent and inadequate degassing is about 1 h. These half-lives contrast sharply with the 1.4-year half-life estimated for 1 in benzene solution.[7]

Reaction Products

The initial product from the decomposition of 1 in a slurry with silica is the carboxy inversion compound *p*-methoxyphenyl *p*-nitrobenzoyl carbonate (2). Compound 2 is also unstable on silica, although less so than the peroxide. If either reagent is left in contact with the silica overnight or longer, the products are the same. The major ones are *p*-methoxyphenol, *p*-methoxyphenyl *p*-nitrobenzoate, and *p*-nitrobenzoic acid. Minor products are bis(*p*-methoxyphenyl) carbonate and bis(*p*-nitrobenzoic) anhydride.

The product composition of a reaction of 1 in a benzene/silica slurry interrupted after 30 min is shown in Table I.

In solution two modes of decomposition are known for carboxy inversion compounds, one leading to ester and CO_2, the other to carbonate, anhydride, and CO_2.[8] For 2 in a silica slurry, reaction 2 is of major importance, and reaction 3 is only of minor importance. Bis(*p*-methoxyphenyl) carbonate, not analyzed for in the experiment reported in Table I, was found as a minor product by GC/MS. The other major products are hydrolysis products (eq 4).

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[2] Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonnou, C. G. *J. Am. Chem. Soc.* **1970**, *92*, 4927.

[3] Leffler, J. E.; More, A. A. *J. Am. Chem. Soc.* **1972**, *94*, 2483.

[4] Nozaki, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1946**, *68*, 1686.

[5] Leffler, J. E.; Zupancic, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 259.

[6] Leffler, J. E.; Barbas, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 7768.

[7] Estimated from $k = 2.08 \times 10^{-5}\ s^{-1}$ in benzene at 70 °C[1] and $k = 0.144 \times 10^{-5}\ s^{-1}$ in benzene at 50 °C (this paper).

[8] (a) Tarbell, D. S.; Leister, N. A. *J. Org. Chem.* **1958**, *23*, 1149. (b) Tarbell, D. S.; Longosz, E. J. *Ibid.* **1959**, *24*, 774. (c) Longosz, E. J.; Tarbell, D. S. *Ibid.* **1961**, *26*, 2161.

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Table I. Composition of the Reaction Mixture at 30 min[a]

compd	yield, mol %	compd	yield, mol %
peroxide 1	0.0	*p*-nitrobenzoic acid	32.0[c]
carboxy inversion compd 2	40.6[b]	*p*-methoxyphenol	32.0[c]
p-methoxyphenyl *p*-nitrobenzoate	17.5[b]	*p*-nitrobenzoic anhydride	2.0[c]

[a] 102 mg of 1 and 3.14 g of S 679 silica[5] in 13.6 mL of benzene. [b] From the IR spectrum of the benzene washings. [c] Isolated from the ether extract.

$$2 \rightarrow CH_3OC_6H_4OC(O)C_6H_4NO_2 + CO_2 \qquad (2)$$

$$2 \rightarrow (CH_3OC_6H_4)_2CO_3 + [O_2NC_6H_4C(O)]_2O + CO_2 \qquad (3)$$

$$2 + H_2O \rightarrow CH_3OC_6H_4OH + CO_2 + O_2NC_6H_4COOH \qquad (4)$$

If chloroform containing a few percent of ethanol is used rather than benzene in preparing the slurry, alcoholysis of 2 occurs and diverts some of the product to ethyl *p*-methoxyphenyl carbonate and ethyl *p*-nitrobenzoate. The yield of ester is decreased by about 50%.

Yields of the three major products of the complete reaction of 1 or 2 were determined under a variety of conditions. The major variations in the conditions, besides the use of 1 vs. 2, were the use of a less pure grade of silica (S 157[5]) and conducting the first part of the reaction in the slurry and the last part after removal of the solvent. Since none of these variations seemed to have an important effect, we report only the mean mole percent yields: *p*-nitrobenzoic acid, 73%; *p*-methoxyphenyl *p*-nitrobenzoate, 23%; *p*-methoxyphenol, 49%. Bis(*p*-methoxyphenyl) carbonate, though present, was not determined quantitatively.

Since the carboxy inversion reaction in solution is known to be catalyzed by acids[1,3], it is appropriate to inquire whether the acidity of the surface is a factor in the rapid carboxy inversion reaction. Two silicas were used, S 157 and S 679.[5] The indicator *p*-(dimethylamino)azobenzene changes color in water from yellow to red in the pH range 4.0–2.9. On S 157 silica this indicator is red and on S 679 it is yellow, but within the limits of our very rough estimates of the rates of decomposition of 1 there did not appear to be any difference in rates on the two silicas.

Similar lack of sensitivity of rate to acidity of the surface has been observed in other experiments. Peroxide 4 decomposes faster on S 157 than on S 679, but only by 20%.[6] In an experiment in which isobutyryl peroxide was allowed to react with alumina,[9] only the reaction leading to the usual surface oxidant was observed, even though the alumina was acidic and the peroxide one that decomposes to carboxy inversion compound quite rapidly in solution.

Radical Products

Because of our interest in the mechanisms leading to mixtures of ionic and radical products in most solvents, we looked for evidence for radical products in the silica experiments. None were detected within the limits of our capillary GC (flame ionization) and GC/MS techniques. Anisic acid, which might have been difficult to detect as such, was absent since no methyl anisate was found after methylating the acid fraction with diazomethane. Also absent were *p*-methoxybiphenyl, *p*-nitrobiphenyl, *p*-nitrophenyl anisate, *p*-methoxy-*p*′-nitrobiphenyl, phenyl anisate, and phenyl *p*-nitrobenzoate. The decomposition of 1 in benzene solution at 80 °C gave anisic acid (27%), *p*-nitrobenzoic acid (47%), anisyl *p*-nitrobenzoate (4%), *p*-methoxyphenol (5%), *p*-methoxybiphenyl (15%), and *p*-nitrobiphenyl (36%). Photolysis of 1 in acetonitrile gave anisic acid (27%), *p*-nitrobenzoic acid (51%), anisyl *p*-nitrobenzoate (2.4%), and *p*-nitrophenyl anisate (1.6%).

Experimental Section

Preparation of Slurries. Slurries were prepared by adding 4–20 mL of the solvent per gram of S 679 or S 157 silica.[5] A solution of the peroxide or of the carboxy inversion compound was then added with stirring. The amount of the organic reagent was typically about 2% of the weight of the silica, or less than a monolayer.

Preparation of Solvent-Free Samples. The slurry was filtered, the filtrate kept for assay of nonadsorbed material, and the silica degassed to remove traces of the solvent. A second procedure, which causes the solvent to remain in contact for a longer time, was to remove the solvent by rotary evaporation before degassing. Using the faster procedure left about 10% of the adsorbed peroxide still undecomposed.

Rates. Decomposition rates were measured either by iodometric titration of the peroxide or spectrophotometrically by using the carbonyl IR region. The carboxy inversion compound produces a band due to CO_2 in NaCl cells but not in CaF_2 cells.

***p*-Methoxyphenol** was identified by spiking with an authentic sample on a quartz capillary column fitted with a flame-ionization detector and by its low-resolution mass spectrum: *m/e* 124 (parent), 109 (base).

Ethyl *p*-methoxyphenyl carbonate was identified by low-resolution GC/MS and by high-resolution mass spectroscopy of the product mixture: *m/e* 196 (parent ion), 124 (base); (calcd for $C_{10}H_{12}O_4$ 196.0742, found 196.0739.

Ethyl-*p*-nitrobenzoate was identified by GC/MS and high-resolution mass spectroscopy of the mixture: *m/e* 195 (parent), 150 (base); calcd for $C_9H_9O_4N$ 195.053, found 195.048.

Dianisyl carbonate was identified by low-resolution GC/MS: *m/e* 274 (parent), 123 (base); calcd for $C_{15}H_{14}O_5$ 274.0892, found in the mixture 274.0867.

Anisyl *p*-nitrobenzoate was identified by spiking with an authentic sample on the capillary column and by its GC/MS: *m/e* 273 (parent), 150 (base); *m/e* calcd for $C_{14}H_{11}NO_5$ 273.0710, found in the mixture 273.0674.

Capillary GC. The column was a 25-m quartz capillary methylsilicone column with a flame-ionization detector. Quantitative analyses used diphenyl ether and *p*-chlorobenzophenone as internal standards.

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Registry No. 1, 1829-89-6; 2, 81372-24-9; *p*-methoxyphenyl *p*-nitrobenzoate, 13245-59-5; *p*-nitrobenzoic acid, 62-23-7; *p*-nitrobenzoic anhydride, 902-47-6; *p*-methoxyphenol, 150-76-5; anisic acid, 100-09-4; *p*-methoxybiphenyl, 613-37-6; *p*-nitrobiphenyl, 92-93-3; *p*-nitrophenyl anisate, 7464-46-2; ethyl *p*-methoxyphenyl carbonate, 22719-84-2; ethyl *p*-nitrobenzoate, 99-77-4; dianisyl carbonate, 5676-71-1.

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(9) Leffler, J. E.; Miller, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 480.