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Decomposition of peracids and their salts with activated carbon

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Activated carbon-mediated reductive decomposition of several commonly used peracids, peracid salts, and alkyl hydroperoxides was investigated, and oxygen release was measured. Environmentally unfriendly reagents such as dimethyl sulfide, trimethyl phosphite, and triphenyl phosphine were ineffective in reducing the peracid salts. However, the environmentally friendly and waste-minimizing activated carbon proved an effective, simple, and safe method for the decomposition of peracids, peracid salts, and alkyl hydroperoxides.

Keywords: activated carbon; peracids and peracid salts; alkyl hydroperoxides

1. Introduction

Recent synthetic endeavors required the epoxidation of a diene with AcOOH/ Na_2CO_3 in CH_2Cl_2 [1,2], but the sensitivity of the resulting unsaturated epoxide to moisture precluded an aqueous work-up. Surprisingly, while non-aqueous reducing reagents, such as dimethyl sulfide, trimethyl phosphite, and triphenyl phosphine, successfully effected a negative peroxide test for the solution [#1,#2], they left behind an energetic solid [#3,#4] which tested positive for peroxides. Disposal of this energetic solid became a distinct problem on scale-up as the filter cake could not be safely allowed to go dry [#4]. Additionally, sufficient dilution of this energetic solid to allow aqueous reduction and disposal resulted in large volumes of aqueous waste streams. Safety, waste-minimization, and environmental concerns moved us to find

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[#1] The reagents dimethyl sulfide, trimethyl phosphite, and triphenyl phosphine quickly ($\leqslant 15$ min) removed peroxides from solution, but were ineffective in removing peroxides from the solids even after 4 h.

[#2] We employed 10% aqueous potassium iodide to test aliquots of filtered solution and portions of solids.

[#3] This solid presumably contained sodium peracetate [3].

[#4] Explosions have been documented in ref. [4].

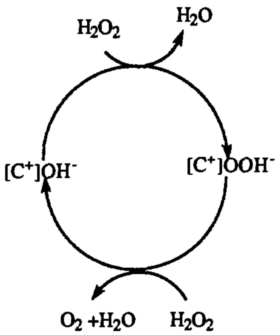
alternative decomposition methods. A search of the literature brought to our attention the use of activated carbon in the decomposition of hydrogen peroxide [5,6], where the mechanism was established [5] as given in scheme I, catalytic cycle I.

Although none of the literature gave examples of the decomposition of peracids or hydroperoxides, a recent communication [7] described a hydroxylation mediated by activated carbon; since this conversion proceeded via a putative

Scheme I

$[C^+]OH^- + H_2O_2 \longrightarrow [C^+]OOH^- + H_2O$

$[C^+]OOH^- + H_2O_2 \longrightarrow [C^+]OH^- + H_2O + O_2$



Catalytic Cycle I

Here [C+] indicates the carbon lattice; situation of the OOH- ion on a positive site of the lattice modulates its oxidation potential, allowing reduction of H2O2 to proceed7.

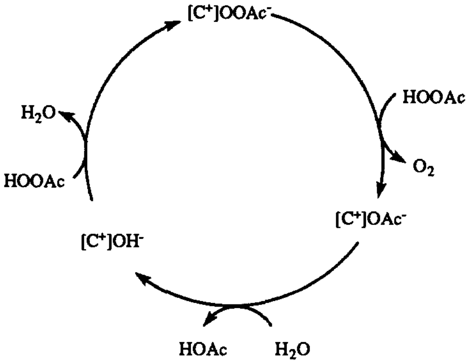
Scheme II

$[C^+]OH^- + HOOAc \longrightarrow [C^+]AcOO^- + H_2O$

$[C^+]AcOO^- + HOOAc \longrightarrow [C^+]AcO^- + O_2$

$[C^+]AcO^- + H_2O \longrightarrow [C^+]OH^- + HOAc$

Catalytic Cycle II



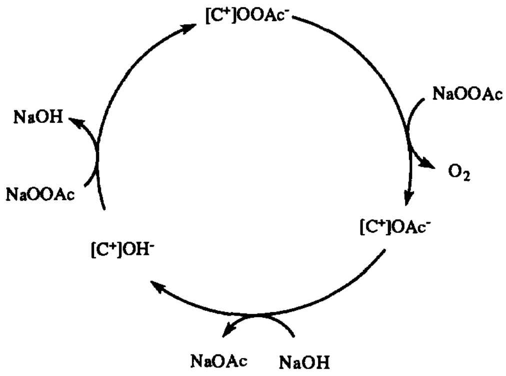
Scheme III

$[C^+]OH^- + NaOOAc \longrightarrow [C^+]AcOO^- + NaOH$

$[C^+]AcOO^- + NaOOAc \longrightarrow [C^+]AcO^- + O_2$

$[C^+]AcO^- + NaOH \longrightarrow [C^+]OH^- + NaOAc$

Catalytic Cycle III



hydroperoxide, and since no further reducing agent was required, the putative hydroperoxide must have undergone activated carbon-mediated reduction. Although mechanistically dissimilar, solid silica gel has been reported to decompose cumyl peracetate [8], but silica gel, as well as Celite®, had previously been shown to cause hydrolysis of our desired unsaturated epoxide.

We found that certain activated carbons [#5] quickly ($\leqslant 30$ min) and successfully catalyzed the decomposition of residual peracetic acid in solution, *with the concomitant decomposition of the peroxides in the solid.* In the absence of activated carbon, the solids tested positive for peroxides *even after 4 days.* Differential scanning calorimetry [#6] established that the resulting activated carbon-derived solid did not possess energetic properties, and this reaction has now been *safely scaled into 100 gallon fixed equipment, allowing waste-minimization.* By analogy to literature precedence [5], we hypothesize the mechanisms to be as in schemes II and III, and catalytic cycles II and III.

2. Discussion

To confirm our hypothesis, we measured over time the O_2 gas evolution from a typical activated carbon-mediated decomposition of peracetic acid, and this proved to be within 3% of theoretical (fig. 1). Moreover, after first decomposing $HOOAc/Na_2CO_3$ in solution with Me_2S, we found further O_2 gas evolution when we treated the filtered solids with activated carbon, thus confirming the decomposition mechanism for peracid salts.

Encouraged by these results, we further investigated the utility of activated carbon in the decomposition of some commonly used peracids, their salts, and alkyl hydroperoxides. We report here our results.

The carbon loads and decomposition times are given in table 1. Note that higher loading and longer reaction times were required for the hydroperoxides. To further explore and test these ramifications, activated carbon-mediated reductions of other oxidants (i.e., OsO_4, Cr-, B-, ClO_2- and Mn-) will be investigated.

3. Experimental

In one experiment, peracetic acid (10.59 mol of a 35% solution) was added slowly over 2 h to a stirring slurry composed of sodium carbonate (42.45 mol), the diene (10.59 mol) and dichloromethane (12 ℓ), keeping the temperature at -10 to

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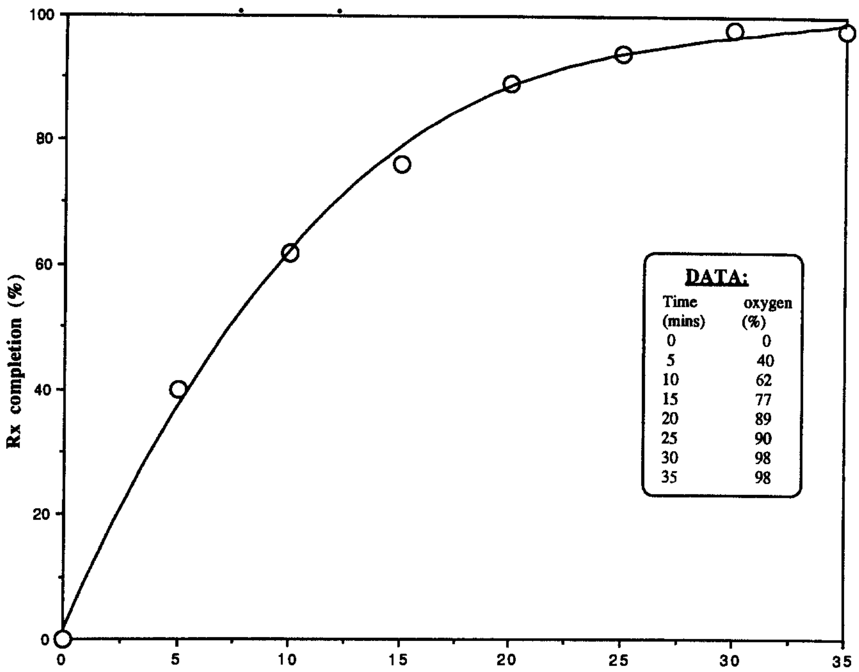
[#5] We employed Darco G-60, 100 mesh powder (from Aldrich). While other activated carbons, notably Norit® A, were essentially equally effective, simple decolorizing carbon was not effective; by no means did we explore all the available activated carabons. These results are in accordance with the information provided in ref. [7].

[#6] Lower temperatures retarded the rate of decomposition.



Time (mins)	oxygen (%)
0	0
5	40
10	62
15	77
20	89
25	90
30	98
35	98

Fig. 1. Rx completion (oxygen evolution). Decomposition of peracetic acid.

0°C with external cooling. When the addition was complete, the mixture was stirred mechanically for 16 h at 15 ± 2°C under a nitrogen atmosphere. Analysis of a filtered aliquot of the mixture indicated that (i) the reaction was $\geqslant$96% complete

Table 1
Carbon loading and reaction times

Peracid/peroxide	Load[a] (g/mmol)	Time (min)
AcOOH[b]	0.2	30
AcOOH/Na_2CO_3	0.2	30
*m*CPBA[c]	0.4	60
*m*CPBA/Na_2CO_3	0.4	60
MPPM[d]	0.2[e]	30
*t*BuOOH[f]	0.6	60
*t*BuOOH/Na_2CO_3	0.6	60
CumOOH[g]	0.6	60
CumOOH/Na_2CO_3	0.6	60

[a] ±0.03 g.

[b] Peracetic acid, 35% solution.

[c] 3-chloroperoxybenzoic acid, 50–60% technical grade.

[d] Monoperoxyphthalic acid, magnesium salt hexahydrate, 80% technical grade; this decomposition was conducted in H_2O and 1 : 1 CH_2Cl_2 : H_2O

[e] Two eq. of peracid/mol of MPPM.

[f] *t*-butyl hydroperoxide, 3.0 M in 2,2,4-trimethylpentane.

[g] Cumene hydroperoxide, 80% technical grade.

(NMR), thus leaving behind a putative ⩽4% (0.42 mol) of peracetic acid, and (ii) peroxides were present in both solution and solids. To the stirring slurry was added activated carbon. (70 g, 0.17 g/mmol of putative peracetic acid). After 30 min at 17 ± 2°C[#6], analysis of a filtered aliquot indicated that the peroxides were absent in both solution and solids. The mixture was then filtered under an atmosphere of nitrogen, and the solids were washed with dichloromethane (2 × 3 ℓ). Concentration of the combined filtrates in vacuo (⩽25°C) gave the crude unsaturated epoxide, which was used without further purification.

In a typical decomposition experiment, a solution of the peracid or alkyl hydroperoxide (1 M) in dichloromethane, or a slurry of the peracid or alkyl hydroperoxide (1 M) and sodium carbonate (4 M) in dichloromethane, was stirred mechanically and was treated with activated carbon (when using monoperoxyphthalic acid, water and water : dichloromethane, 1 : 1, were used).

Evolution of oxygen gas was measured by displacement of water from an inverted and filled graduate cylinder.

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