

## Molecule-induced homolysis of *N*-hydroxyphthalimide (NHPI) by peracids and dioxirane. A new, simple, selective aerobic radical epoxidation of alkenes

Francesco Minisci,<sup>a,\*</sup> Cristian Gambarotti,<sup>a</sup> Monica Pierini,<sup>a</sup> Ombretta Porta,<sup>a</sup> Carlo Punta,<sup>a,\*</sup> Francesco Recupero,<sup>a</sup> Marco Lucarini<sup>b</sup> and Veronica Mugnaini<sup>b</sup>

<sup>a</sup>Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica 'G. Natta', Via Mancinelli 7, I-20131 Milano (MI), Italy

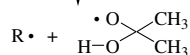
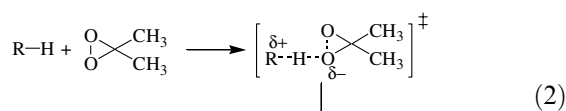
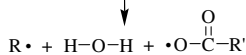
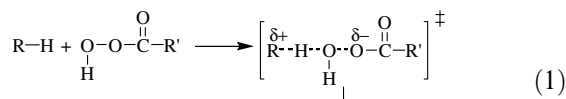
<sup>b</sup>Università di Bologna, Dipartimento di Chimica Organica 'A. Mangini', Via S. Giacomo, I-40126 Bologna (BO), Italy

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**Abstract**—Evidences are reported concerning the molecule-induced homolysis of NHPI by peracids and dioxirane; their combination can be utilized for the aerobic free-radical epoxidation of alkenes with selectivity quite different from the well-known epoxidation by peracids.

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Some years ago we reported evidences that the oxidation of a variety of organic compounds (hydrocarbons, alcohols, ethers, aldehydes, etc.) by dioxiranes<sup>1</sup> and peracids<sup>2</sup> can be explained by radical mechanism in clear contrast with the widely accepted<sup>3,4</sup> mechanism of 'concerted oxenoid oxygen insertion'. Our interpretation<sup>1,2</sup> involves a 'molecule-induced homolysis' in which the transition states are related to the hydrogen abstractions leading to radical pairs (Eqs. 1 and 2).



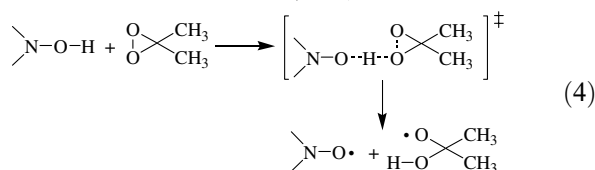
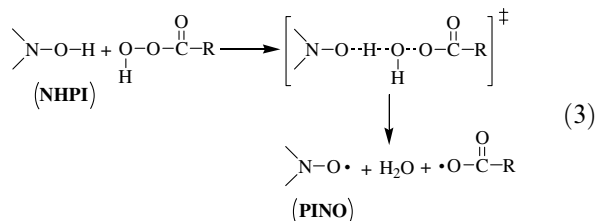
The controversial mechanisms, particularly with dioxiranes, are intriguing since the fast coupling of the radical pair in the solvent cage leads to the same reaction products of the oxygen insertion mechanism and only few radicals can escape from the cage giving typical free-radical reactions. Very recently this controversy has been resumed in the case of dioxiranes: one report<sup>5</sup> categorically states that 'a radical-type process has been experimentally and theoretically rigorously discounted', whereas another research group reports<sup>6</sup> that 'theoretical calculations support both alternative reaction mechanisms as feasible reaction pathways for the oxygenation of C–H bonds by dioxirane' and also the experimental results suggest that 'the process splits into two reaction pathways with different transition states leading to the O–O homolysis and the O-atom insertion, respectively, the incidence of each process depending on the structure of the dioxirane'.<sup>6</sup> What is not clear in this last interpretation is the reason why the coupling of the radical pair (Eq. 2), leading to the same products of the oxygen insertion mechanism, does not occur in the solvent cage.

We have ascribed the driving force for Eqs. 1 and 2 to the high bond dissociation enthalpies (BDE) of the O–H bonds formed in hydrogen abstraction, which are particularly effective with the weaker C–H bonds (tertiary alkyl, benzyl, RCO–H, etc.). Recently we have evaluated<sup>7</sup>

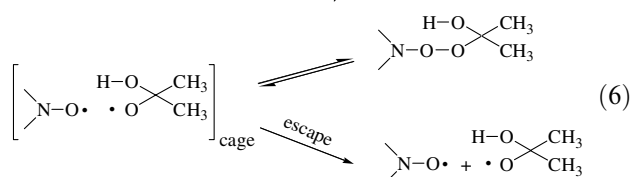
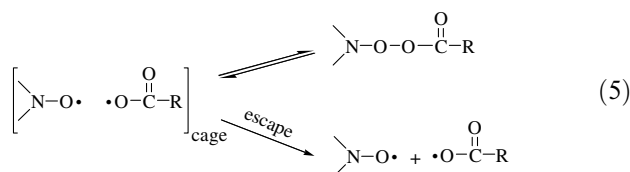
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\* Corresponding authors. Tel.: +39 02 23993030; fax: +39 02 23993080 (F.M.); tel.: +39 02 23993026; fax: +39 02 23993080 (C.P.); e-mail addresses: [francesco.minisci@polimi.it](mailto:francesco.minisci@polimi.it); [carlo.punta@polimi.it](mailto:carlo.punta@polimi.it)

the BDE value of the O–H bond in NHPI (88.1 kcal/mol); this value suggests to us that peracids and dioxiranes could give induced homolysis of NHPI (Eqs. 3 and 4) under mild conditions generating the phthalimido-*N*-oxyl (PINO) radical which plays a key role in the aerobic oxidations catalyzed by NHPI.<sup>7,8</sup>



The hypothetical coupling of the radical pairs generated in Eqs. 3 and 4 is very likely reversible, so that the PINO radical and the acyloxyl (Eq. 5) or the alkoxy (Eq. 6) radicals can escape from the solvent cage giving the typical free-radical reactions.



Spectroscopic and chemical evidences, actually, support this assumption. The EPR spectrum of the PINO radical<sup>7,9</sup> was readily observed simply by adding at rt NHPI to a solution of *m*-chloroperbenzoic acid in acetonitrile ( $a(2\text{H}) = 0.46$  G;  $a(\text{N}) = 4.77$  G) or dimethyldioxirane in acetone ( $a(2\text{H}) = 0.44$  G;  $a(\text{N}) = 4.70$  G), as it is shown in Figure 1.

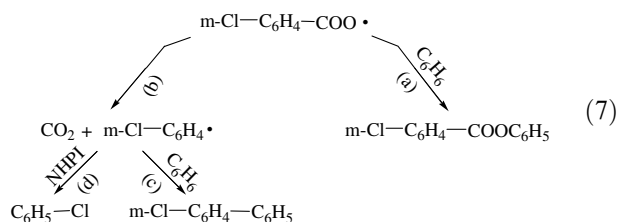
HPLC and GC analysis of the products arising from *m*-chloroperbenzoic acid and NHPI in acetonitrile at rt reveal the presence of *m*-chlorobenzoic acid as main reaction product (~90%) and chlorobenzene (~10%) as by-product. Moreover the same reaction in benzene



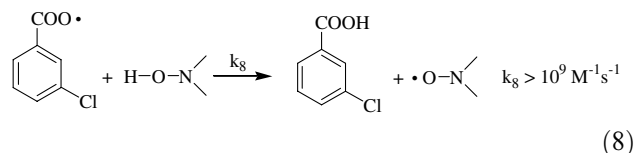
**Figure 1.** EPR spectrum of PINO obtained by mixing NHPI (0.01 M) with *m*-CPBA (0.01 M) in  $\text{CH}_3\text{CN}$  at room temperature.

solution at rt always leads to *m*-chlorobenzoic acid as the main reaction product, whereas phenyl *m*-chlorobenzoate and *m*-chlorobiphenyl are the by-products.

The only possible explanation for these last by-products and for chlorobenzene is the formation of the acyloxyl radical (Eq. 3), which reacts according to Eq. 7a–d.

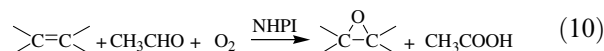
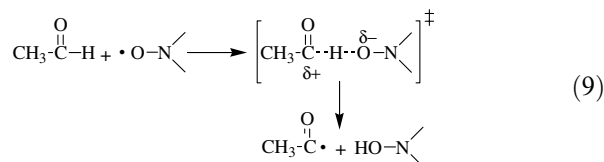


*m*-Chlorobenzoic acid is the main reaction product because it is formed by hydrogen abstraction from NHPI by the acyloxyl radical (Eq. 8).



We expect Eq. 8 to be a very fast reaction on the basis of the known rate constants for the hydrogen abstraction by the peroxy radical ( $7.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>7</sup> and alkoxy radical ( $10^9 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>10</sup>; Eq. 8 is more exothermic respectively of 22 and 6 kcal/mol than the corresponding hydrogen abstractions by the peroxy and alkoxy radicals.

Our recent results<sup>7,8</sup> have shown that the hydrogen abstractions from C–H bonds by the PINO radical are considerably faster than the corresponding hydrogen abstractions by peroxy radicals, in spite of the same enthalpy variation; a more marked polar effect in the reaction by the PINO radical is, in our opinion,<sup>11</sup> a factor which contributes to this behavior. These results, combined with the induced homolysis of NHPI by peracids (Eq. 3) have suggested to us the possibility to utilize the aerobic oxidation of aldehydes, catalyzed by NHPI, for the epoxidations of alkenes by peracids generated ‘in situ’ under mild conditions (Eq. 10).



Actually the aerobic oxidation of acetaldehyde in acetonitrile solution at rt and atmospheric pressure of oxygen in the presence of alkenes and catalytic amount of NHPI leads to the corresponding epoxides. No oxidation occurs under the same conditions in the absence of NHPI, clearly indicating that Eq. 9 plays a key role in the aerobic epoxidation. However the selectivity observed with several alkenes is quite different from that well-known<sup>12</sup> with peracetic acid (Table 1).

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