

MOLECULE-INDUCED RADICAL FORMATION WITH PEROXIDES

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O–O Bond homolysis in (hydro)peroxides is commonly believed to represent an important initiation pathway in autoxidation reactions, where the O-centered radicals formed in the homolysis step are subsequently involved in hydrogen abstraction reactions from substrate hydrocarbons. Using quantum chemically calculated and experimentally available thermochemical data we show that a combined "Molecule-Induced Radical Formation (MIRF)" process integrating both reactions into a single elementary step is highly competitive.^[1] Moreover, we also show for selected classes of hydrocarbons that reaction barriers for MIRF processes are lower than those for classical O–O bond dissociation reactions.^[2,3]

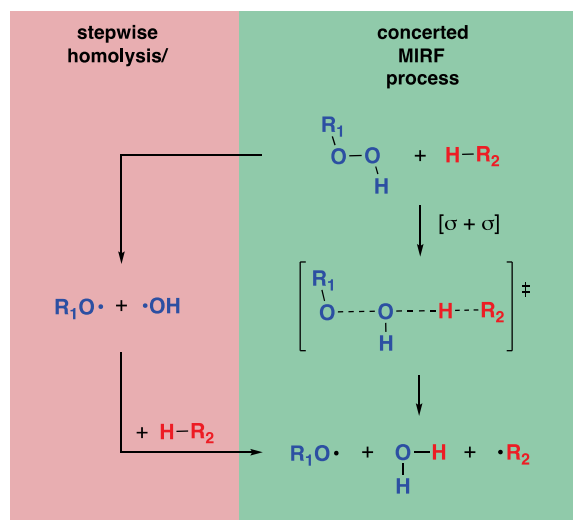


Figure 1: Competition between stepwise O-O bond homolysis and concerted MIRF pathways in the decomposition of peroxides.

REFERENCES

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