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LETTER

Origin of High Reactivity of Alkylhydroperoxides in Several Vanadium(V) Compounds

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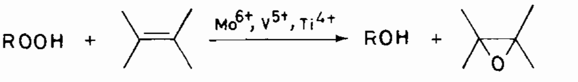
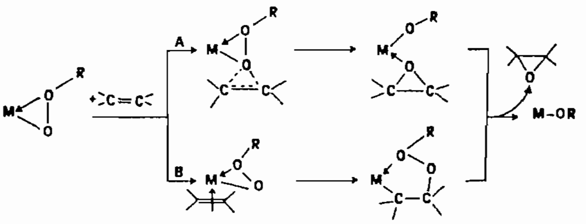
Epoxidation of alkenes, and especially asymmetric epoxidation, is a fundamental and important organic reaction type [1]. Selective epoxidation of olefins by alkylhydroperoxides catalyzed by d^0 metal complexes (Mo^{6+}, V^{5+} and Ti^{4+}) has become the most important process for the manufacture of propylene oxide, due to the recent utilization of t-butylalcohol as an octane booster in gasoline (Halcon process, see below; olefin = propylene, R = t-butyl, M = Mo) [2].



Despite intensive studies, the mechanism of this reaction still remains a matter of controversy, since the nature of the actual epoxidizing species has not been clearly established. However, in view of its high selectivity and stereospecificity, it is generally accepted that it proceeds via a heterolytic rather than a homolytic mechanism. Two alternative mechanisms, (A) and (B), which involve d^0 alkylhydroperoxidic intermediates emerge from the numerous interpretation proposed (see below): (A) nucleophilic attack of olefin on the electrophilic oxygen atom covalently bonded to the metal; (B) coordination of olefin to a metal followed by its insertion between the metal–oxygen bond, forming a five-membered dioxametallocyclopentane, which decomposes to the epoxide and the metal alkoxide [3]. However, the most important question, why does the coordinated alkylhydroperoxide react with olefins, remains unsolved at present.



In previous papers [4], we have pointed out that the peroxide ion trapped in several metal compounds exhibits a very different reactivity from that of free H_2O_2, and the high reactivity of these peroxides toward DPBF (1,3-diphenylisobenzofuran, one of the efficient singlet oxygen ($^1\Delta_g$) scavengers [5]) implies that the peroxide in the metal compounds is activated to contain to some degree singlet oxygen ($^1\Delta_g$) character, due to the coordination to the metal ion [6]. On the basis of these facts, we have proposed [7] the mechanism for the formation of 'crypto-OH$^{\bullet}$' [8], frequently referred to in biological papers. In order to elucidate the reaction mechanism of epoxidation of olefins, catalyzed by metal alkylhydroperoxides, it seems necessary to clarify the origin of reactivity of alkylhydroperoxides toward olefins, and thus in this study we have investigated the reaction between DPBF and several vanadium(V) compounds with alkylhydroperoxides.

The vanadium(V) compounds, $[(dipic)VO_2(H_2O)]^+$ and [VO(OO-t-Bu)(OPhsal)] were prepared according to the methods of Mimoun *et al.* [9, 10], where dipic represents the dianion of dipicolinic acid. The t-butyl(70%)- and cumyl-hydroperoxide were obtained from Nakarai Chemicals Ltd. DPBF was obtained commercially (Tokyo Kasei Co. Ltd.), and its purity was checked by the absorbance at 414 nm (24700 M^{-1} cm^{-1}) [11, 5]. The solvents, *N,N*-dimethylformamide (dmf) and dimethyl sulfoxide (dmso) were purchased from Nakarai Chemicals (Guaranteed Reagent), and were used without further purification. The degradation of DFBF was monitored by measuring the absorbance at 414 nm of the reaction mixture of alkylhydroperoxide, DPBF and the vanadium(V) compound at 290 K.

We have observed that no decomposition of DPBF occurs in the reaction mixture of DPBF and vanadium(V), and DPBF and alkylhydroperoxide, respectively. On the other hand, notable degradation of DPBF was observed when DPBF was mixed with vanadium(V) and alkylhydroperoxide together, as shown in Fig. 1. This indicates that the vanadium(V) complexes with alkylhydroperoxide [9, 10] play a role in the degradation of DPBF. The degradation of DPBF was also observed in dmso, one of the effi-

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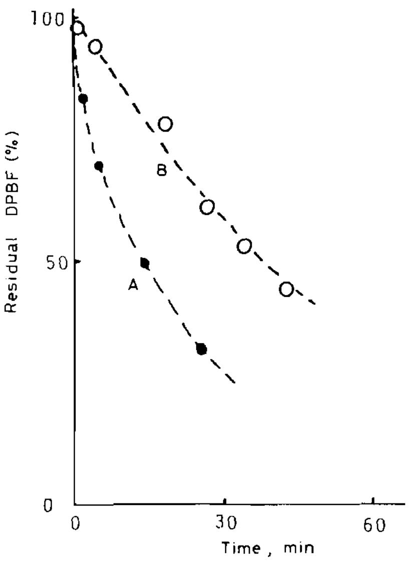
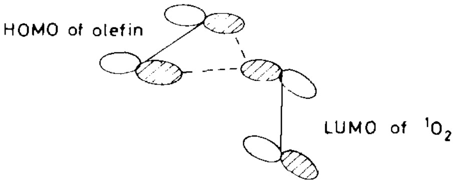


Fig. 1. Time course of DPBF degradation in the reaction mixture of DPBF (1×10^{-4} mol dm^{-3}), alkylhydroperoxide (1×10^{-2} mol dm^{-3}) and [(dipic)$VO_2(H_2O)$]H (1×10^{-8} mol dm^{-3}) at 290 K. A: t-butylhydroperoxide in dmf; B: cumylhydroperoxide in dmso.

cient scavengers of the OH$^•$ radical [12]. The above results demonstrate that the alkylhydroperoxides in the vanadium(V) compounds are activated, similar to the case of the peroxide ion [4], to contain to some degree singlet oxygen ($^1\Delta_g$) character, and that the decomposition of DPBF is not caused by the singlet oxygen evolved in the course of reaction, and also not by OH$^•$ radical.

The reaction mechanism between the olefin and the singlet oxygen ($^1\Delta_g$) has been studied in terms of the orbital interaction model. According to Fukui *et al.* [13], the main reaction intermediate is assumed to be



where the electron flows from the olefin to the oxygen molecule. Thus, the present results, e.g. the alkylhydroperoxides in the vanadium(V) compounds are activated to contain to some degree singlet oxygen character, suggest that the reaction mechanism (A) described before is the likely one in these reactions.

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