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Kinetics and mechanism of alkane hydroperoxidation with *tert*-butyl hydroperoxide catalysed by a vanadate anion

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tert-Butyl hydroperoxide oxidizes alkanes in acetonitrile at 60 °C if the soluble vanadium(V) salt, n-Bu_4NVO_3, is used as a catalyst. Alkyl hydroperoxides are formed as main products which decompose during the course of the reaction to produce the more stable corresponding alcohols and ketones. Turnover numbers (*i.e.* numbers of moles of products per one mole of a catalyst) attained 250. The kinetics and selectivity of the reaction have been studied. The mechanism proposed involves the formation of a complex between the V^V species and t-BuOOH (K_5 was estimated to be 5 $dm^3\ mol^{-1}$) followed by decomposition of this complex ($k_6 = 0.2\ s^{-1}$). The generated V^{IV} species reacts with another t-BuOOH molecule to produce an active t-BuO$^•$ radical which attacks the hydrocarbon.

Introduction

Catalytic oxidative functionalization of various compounds and especially of hydrocarbons by organic hydroperoxides is an important field of contemporary organic chemistry.[1,2] Vanadium which is known to play an important role in biological and biochemical systems[3] also catalyses the oxidation of hydrocarbons,[4] (for example, epoxidation of olefins[5a–e]) and splitting C–C bonds in ketones.[5f–i]

Recently we have discovered a very efficient reagent for hydroperoxidation of saturated hydrocarbons.[6] This reagent uses atmospheric oxygen as an oxidant and hydrogen peroxide as a promoter of the oxidation, as well as a combination of *n*-tetrabutylammonium vanadate and pyrazine-2-carboxylic acid (PCA) as catalyst; acetonitrile has been used as the solvent. At ambient temperature the reaction with alkanes gives rise predominantly to the formation of alkyl hydroperoxides whereas lower amounts of the corresponding alcohols and ketones (aldehydes) are formed concurrently. It has been shown that atmospheric oxygen participates in this reaction, and when it is absent, no oxygenation occurs.

The present paper is devoted to the study of the analogous alkane oxidation but uses *tert*-butyl hydroperoxide instead of hydrogen peroxide. We have found that PCA is not required in this case.

Experimental

All reactions were carried out in MeCN at 60 °C in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 5 mL. In a typical experiment, initially, a portion of 70% aqueous *tert*-butyl hydroperoxide (Aldrich) was added to a solution of catalyst and cyclohexane in acetonitrile (distilled over P_2O_5 before the reaction). Synthesis of n-Bu_4NVO_3 is described in the literature.[6n,7]

In order to determine the concentrations of all the cyclohexane oxidation products samples of reaction solutions were typically analysed twice (before and after their treatment with PPh_3) by GC (LKhM-80-6 instrument, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon) measuring concentrations of cyclohexanol and cyclohexanone. This simple and convenient method (an excess of solid triphenylphosphine is added to the samples 10–15 min before the GC analysis) which was invented by us earlier[4c,6,8,9] allows one to detect alkyl hydroperoxides and to measure also the real concentrations of all three products (alkyl hydroperoxide, alcohol and aldehyde or ketone) present in the reaction solution, because usually alkyl hydroperoxides are decomposed in the gas chromatograph to produce mainly the corresponding alcohols and ketones.

Results and discussion

We have found that heating a solution of an alkane, RH, and t-BuOOH in acetonitrile in the presence of catalytic amounts of a soluble vanadate salt, n-Bu_4NVO_3, leads to the formation of the corresponding alkyl hydroperoxide, ROOH, which in the course of the reaction decomposes gradually to produce more stable ketones and alcohols. We mainly used cyclohexane as a substrate for kinetic measurements, as well as linear alkanes (*n*-hexane and *n*-heptane) in selectivity determinations. The vanadium derivative apparently catalyses the cyclohexyl hydroperoxide decomposition. Indeed, comparison of kinetic curves shown in graphs *A* and *B* of Fig. 1 demonstrate that at a higher vanadium complex concentration (5×10^{-4} instead of 2×10^{-4} mol dm^{-3}) the maximum of the ROOH concentration is reached more rapidly (at approximately 0.5 h *versus* 2 h) after which time the current concentration of the cyclohexyl hydroperoxide drops. The maxima of the ROOH concentration curves coincide in time with the inflection points on the accumulation curves for the cyclohexanone and cyclohexanol. At $[VO_3^-] = 5 \times 10^{-4}$ mol dm^{-3} cyclohexyl hydroperoxide has almost completely decomposed after 8 h. Turnover numbers (*i.e.* number of moles of products per one mole of catalyst) attained 250.

In the experiments shown in Fig. 1 we used a very simple method invented by us earlier[4c,6,8,9] based on comparison of the chromatograms of the reaction solution made before and after the treatment of the sample with triphenylphosphine. If an excess of solid triphenylphosphine is added to a solution of alkane oxidation products before the GC analysis, the resulting chromatogram usually differs drastically from that of a sample not subjected to the reduction with PPh_3. In the case of cyclohexane oxidation, the cyclohexanol peak rises markedly after the reduction while the intensity of the cyclohexanone peak decreases. Usually the sum of alcohol and ketone concentrations in the reduced sample is approximately equal to the total concentration of products in the solution untreated with triphenylphosphine. These results can be explained by the fact that the mixture of products of the reaction under investigation contains cyclohexyl hydroperoxide as the main component. In many cases cyclohexyl hydroperoxide totally decomposes in the

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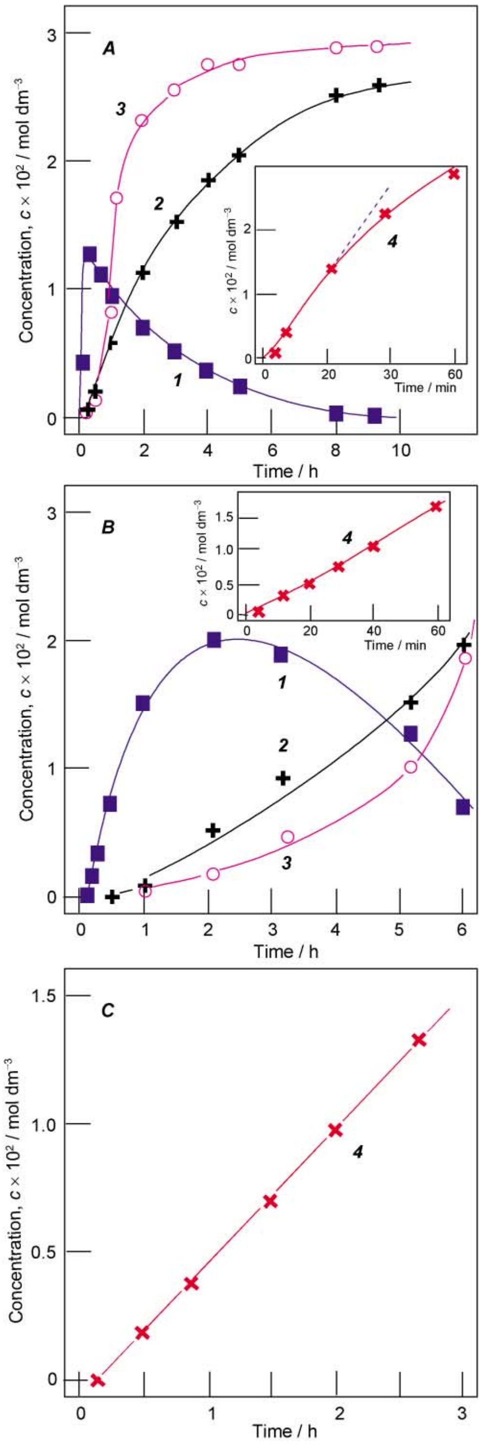

Fig. 1 Accumulation of oxygenates (cyclohexyl hydroperoxide, curve *1*; cyclohexanone, curve *2*; cyclohexanol, curve *3*; and the sum of all products, curve *4*, the reaction rate was determined from the slope of the dashed straight line) in the reaction of cyclohexane (0.92 mol dm^{-3}) with *t*-BuOOH (0.78 mol dm^{-3}) in MeCN at 60 °C catalysed by *n*-Bu_4NVO_3 (5×10^{-4} mol dm^{-3}, graph *A*; 2×10^{-4} mol dm^{-3}, graph *B*; 0.5×10^{-4} mol dm^{-3}, graph *C*).

chromatograph to produce more stable cyclohexanol and cyclohexanone. On the other hand, alkyl hydroperoxides can be readily and quantitatively reduced by triphenylphosphine to yield corresponding alcohols. In the case of cyclohexyl hydroperoxide the reduction gives cyclohexanol. After treatment of the reaction solution with PPh_3, the GC analysis will give the amount of cyclohexanone which corresponds to the real concentration of this product in the reaction solution. The amount of cyclohexanol will give the sum of the real concentrations of cyclohexyl hydroperoxide and cyclohexanol. Thus, by comparing the data of chromatographic analysis of the reaction solution before and after reduction with triphenylphosphine, the amounts of cyclohexyl hydroperoxide, really present in the solution at a given moment can be estimated quantitatively. One of the merits of this method is the possibility of estimating the concentration of the alkyl hydroperoxide formed from the alkane in the presence of an excess of an oxidant (hydrogen peroxide, alkyl hydroperoxide, peroxy acid or metal peroxide).

In all our kinetic studies described below, we measured the concentrations of cyclohexanone and cyclohexanol after reduction of the reaction mixture with PPh_3. This gives precisely the concentrations of all the oxygenates which can then be used for obtaining the reaction rates.

It should be noted that in the course of cyclohexane oxidation the reaction solution becomes yellow, and the intensity of the yellow colour is higher at higher initial concentrations of the catalyst. It is probable that in the initial period of the reaction vanadium ions exist in the form of orthovanadate, *i.e.* $Bu_4N[H_2VO_4]$ or $(Bu_4N)_2[HVO_4]$, and also as di- and tetravanadadate depending on the medium acidity. The appearance of the yellow colour is apparently due to oligomerisation of starting catalyst to produce mainly decavanadates. Such condensation can be caused by the formation of protons and an increase in the medium acidity during the oxidation period. Indeed, simply adding any acid to the solution of *n*-Bu_4NVO_3 in acetonitrile leads to the yellow colour. Since decavanadates probably exhibit less catalytic activity we can explain why the rate of alkane oxidation becomes very low when not all *tert*-butyl hydroperoxide is consumed. Certain other side-reactions are also responsible for the low oxygenate yield during the developed reaction period. Due to all these circumstances we only investigated initial rates of cyclohexane oxidation by the system under consideration.

The rate dependency of the cyclohexane oxygenation catalyzed by compound *n*-Bu_4NVO_3 is first order with respect to the initial vanadium salt (Fig. 2). The dependence of the initial cyclohexane oxidation rate on the initial cyclohexane concentration (a plateau at $[\text{cyclohexane}]_0 > 1$ mol dm^{-3}) is in accordance with the assumption concerning competition between cyclohexane and the solvent S (acetonitrile) with an active oxidising species X.

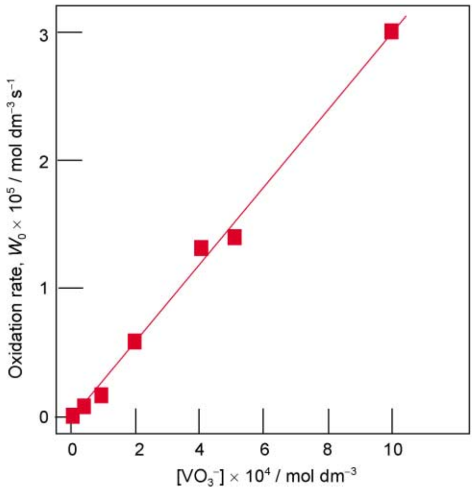

Fig. 2 Plot of the initial rate of cyclohexane (0.92 mol dm^{-3}) oxidation with *t*-BuOOH (0.78 mol dm^{-3}) in MeCN at 60 °C *versus* the initial concentration of *n*-Bu_4NVO_3.

One can imagine the following processes:

$$\text{oxidant} \longrightarrow X^{\bullet} \qquad \text{generation of } X^{\bullet} \text{ with rate } W_i \tag{1}$$

$$X^{\bullet} + C_6H_{12} \longrightarrow R^{\bullet} \qquad k_{RH} \tag{2}$$

$$X^{\bullet} + CH_3CN \longrightarrow \text{products} \qquad k_S \tag{3}$$

Table 1 Selectivity parameters in alkane oxidations by various systems

Substrate	System	Selectivity / C(1) : C(2) : C(3) : C(4)[a]
n-Hexane	t-BuOOH–VO_3^-	1 : 6 : 6
	H_2O_2–n-Bu_4NVO_3–PCA[b]	1 : 8 : 7
n-Heptane	t-BuOOH–VO_3^-	1 : 15 : 8 : 11
	H_2O_2–n-Bu_4NVO_3–PCA[b]	1 : 6 : 6 : 5
	H_2O_2–Mn_2^{IV}–MeCOOH[c]	1 : 46 : 35 : 34
	m-CPBA–$Co(ClO_4)_2$[d]	1 : 104 : 128 : 126

[a] Parameter C(1) : C(2) : C(3) : C(4) is normalized (*i.e.*, calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms in positions 1, 2, 3 and 4 of the hydrocarbon chain, respectively. The reactivities were measured as concentrations of the corresponding isomers of alcohols after the reduction of the reaction solution with PPh_3. [b] PCA is pyrazine-2-carboxylic acid; for this system, see Refs. 4*c*,*d*,6,8*g*. [c] Mn_2^{IV} is $[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$, where L is 1,4,7-trimethyl-1,4,7-triazacyclononane; for this system, see Refs. 4*c*,8*g*,9. [d] *m*-CPBA is *m*-chloroperoxybenzoic acid; for this system, see Ref. 10.

The equation for the cyclohexane oxidation rate, W_{RH}, can be written as follows:

$$W_{RH} = \frac{W_i}{1+\dfrac{k_3[CH_3CN]}{k_2[RH]}} \qquad (4)$$

Eqn. (4) describes adequately the experimental data shown in Fig. 3, if we accept $W_i = 2.7 \times 10^{-5}$ mol dm^{-3} s^{-1} and $(k_S[CH_3CN]/k_{RH}) = 1.3$. It can be calculated from these parameters that $k_S/k_{RH} \approx 0.07$. This value of the constant ratio is somewhat different to that reported for hydroxyl radicals, *i.e.* $k_S/k_{RH} = 0.012$. Thus, it can be concluded that the radical $HO^\bullet$ is not the main species that induces the cyclohexane oxidation. We assume that the species that attacks the hydrocarbon is the radical t-$BuO^\bullet$ formed in the catalytic *tert*-butyl hydroperoxide decomposition.

The mode of the oxidation rate dependence on initial *tert*-butyl hydroperoxide concentration (Fig. 4) is consistent with the generation of a complex, *comp*, formed between the catalyst and *t*-BuOOH and that this complex takes part in the production of oxidising species, *i.e.*, t-$BuO^\bullet$:

$$V^V + t\text{-BuOOH} \rightleftarrows comp \qquad k_5;\ k_{-5};\ K_5 = (k_5/k_{-5}) \qquad (5)$$

$$comp \longrightarrow V^{IV} + t\text{-BuOO}^\bullet + H^+ \qquad k_6 \qquad (6)$$

$$V^{IV} + t\text{-BuOOH} \longrightarrow V^V + t\text{-BuO}^\bullet + HO^- \qquad k_7 \qquad (7)$$

It should be noted that previously Talsi *et al.*[5b] and very recently Talsi, Bolm and their co-workers[5d] detected, by NMR, the formation of complexes between $VO(acac)_2$ or $VO(Oalkyl)_3$–hydroxamic acid and *tert*-butyl hydroperoxide.

We can not exclude the formation of some hydroxyl radicals *via* the following route:

$$V^{IV} + t\text{-BuOOH} \longrightarrow V^V + t\text{-BuO}^- + HO^\bullet \qquad k_{7'} \qquad (7')$$

The mechanism of the oxidising species generation is similar to that of hydroxyl radical formation in the hydrogen peroxide decomposition under the action of a complex of vanadium with pyrazine-2-carboxylic acid (PCA), which was proposed by us earlier.[6n,o]

Taking into account the data shown in Fig. 3, the process of cyclohexyl hydroperoxide formation can be presented as a sequence of non-rate-limiting transformations:

$$t\text{-BuO}^\bullet + CH_3CN \longrightarrow \text{products} \qquad k_8 \qquad (8)$$

$$t\text{-BuO}^\bullet + RH \longrightarrow t\text{-BuOH} + R^\bullet \qquad k_9 \qquad (9)$$

$$R^\bullet + O_2 \longrightarrow ROO^\bullet \qquad k_{10} \qquad (10)$$

$$ROO^\bullet + V^{IV} + H^+ \longrightarrow ROOH + V^V \qquad k_{11} \qquad (11)$$

If we assume that the concentration of *complex* is in quasi-equilibrium, the concentrations of all intermediate species (V^{IV}, t-$BuO^\bullet$, $R^\bullet$, $ROO^\bullet$) are quasi-stationary and that radicals t-$BuOO^\bullet$ do not take part in the oxidative transformations, an analysis of eqns (8)–(11) leads to the following expression for the hydrocarbon oxidation rate:

$$W_{RH} = \frac{k_6K_5\left[VO_3^-\right]_0\left[t-\text{BuOOH}\right]_0}{2\left(1+K_5\left[t-\text{BuOOH}\right]_0\right)} \times \frac{1}{1+\dfrac{k_8[CH_3CN]}{k_9[RH]}} \qquad (12)$$

It should be noted that the proposed eqns (8)–(11) do not fully explain the decrease in the oxidation rate at high *t*-BuOOH concentrations (see Fig. 4). This can be due to a noticeable increase in water content when large amounts of aqueous *t*-BuOOH are introduced to the reaction mixture. However, using the data given in Fig. 4 at $[t\text{-BuOOH}]_0 < 0.4$ mol dm^{-3} the analysis based on eqns (8)–(11) allows one to estimate values $K_5 = 5$ dm^3 mol^{-1} and $k_6 = 0.2$ s^{-1}.

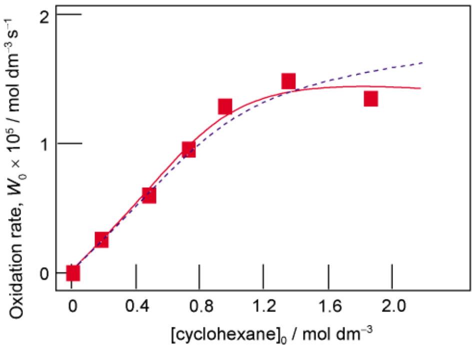

Fig. 3 Plot of initial rate of cyclohexane oxidation with *t*-BuOOH (0.78 mol dm^{-3}) in MeCN at 60 °C catalysed by n-Bu_4NVO_3 (4×10^{-4} mol dm^{-3}) *versus* the initial concentration of cyclohexane. The dashed curve is simulated using eqns (5)–(11) and eqn (12).

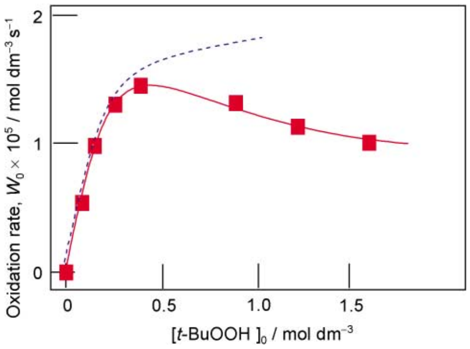

Fig. 4 Plot of initial rate of cyclohexane (1.36 mol dm^{-3}) oxidation with *t*-BuOOH in MeCN at 60 °C catalysed by n-Bu_4NVO_3 (4×10^{-4} mol dm^{-3}) *versus* initial concentration of *t*-BuOOH. The dashed curve is simulated using eqns (5)–(12).

We also found that regio-selectivities determined for the oxidations of *n*-hexane and *n*-heptane (Table 1) are in accordance with the proposed radical mechanism. Indeed, comparison with the same parameters obtained for certain other systems show that the *t*-BuOOH–VO_3^- system is similar to the H_2O_2–*n*-Bu_4NVO_3–PCA reagent which has been shown by us earlier to operate *via* hydroxyl radicals.[6]

Thus we can conclude that the system under discussion (like the "O_2–H_2O_2–V complex–PCA" reagent described by us previously[6]) efficiently transforms alkanes to corresponding alkyl hydroperoxides. In both catalytic systems molecular oxygen from the atmosphere plays the role of "true" oxidant whereas used in stoichiometric amounts peroxide (hydrogen peroxide or *t*-butyl hydroperoxide) is a promoter of the process.

Acknowledgments

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