ELSEVIER

Journal of Molecular Catalysis A: Chemical 136 (1998) 253–262

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Pyridines as bifunctional co-catalysts in the CrO_3-catalyzed oxygenation of olefins by *t*-butyl hydroperoxide

Gadi Rothenberg, Harold Wiener, Yoel Sasson *

Casali Institute of Applied Chemistry, Hebrew University of Jerusalem, Jerusalem, 91904, Israel

Received 1 September 1997; accepted 2 February 1998

Abstract

t-Butyl hydroperoxide (TBHP) oxidizes olefins to epoxides and allylic oxidation products in the presence of a Cr(VI) catalyst. A concurrent decomposition of the oxidant occurs. Pyridine-derived additives alter the behavior of this catalytic system: monodentate pyridines and *trans*-chelated bidentate bipyridines retard the decomposition of TBHP, and arrest the epoxidation reaction, shifting the product selectivity towards allylic oxidation. Adversely, *cis*-chelated bipyridines accelerate the decomposition of TBHP. Depending on ligand nature and concentration, the initial decomposition rate can be slowed down to 1/8th, or accelerated up to two orders of magnitude, (relative to CrO_3 catalysis). The allylic oxidation and the TBHP decomposition are free-radical reactions, but the epoxidation is evidently not. A reaction mechanism is proposed, where the diverse role of the pyridine ligands is attributed to specific complex formations.

Keywords: Allylic oxidation; Olefin epoxidation; Pyridine; *t*-Butyl hydroperoxide; Chromium trioxide; Semi-empirical calculations; Chelated complexes

1. Introduction

Alkyl hydroperoxides are useful reagents both as oxidants for catalytic processes, and as radical-chain initiators in catalytic autooxidations and polymerization processes. The advantages of TBHP over H_2O_2 and peroxyacetic acid as an oxygen transfer agent have received considerable attention in the last two decades [1]. Furthermore, Muzart et al. envisaged TBHP–CrO_3 complexes as the key intermediates in the oxidation of allylic, benzylic alcohols and activated methylenes, and the decomposition of TBHP in the presence of transition metal oxides was noted [2].

The prevalent practice, especially for Cr-catalyzed oxidations, is the use of an excess of 4:1 and higher equivalent ratios of TBHP:Substrate [3,4]. Pyridine, and substituted pyridine additives have been applied in Cr oxidations, usually in stoichiometric amounts, but their role is still unclear [5–7]. The use of large, rigid enveloping structures such as Salen ligands was thoroughly investigated by Srinivasan, Perrier, and Kochi, who deduced mechanistic differences between the epoxidation and the allylic oxidation reactions [8].

The catalytic decomposition of alkyl hydroperoxides has been investigated in numerous

* Corresponding author. E-mail ysasson@vms.huji.ac.il

1381-1169/98/$ - see front matter
PII: S1381-1169(98)00070-3

Table 1
Pyridine effects on hydroperoxide decomposition

Entry	Hydro-peroxide	Catalyst	Pyridine effect
1	ethylbenzene-	Ru(III)[a]	acceleration
2	cumyl-	Co(II)[b]	retardation
3	cyclohexyl-	Mn(III)[c]	acceleration
4	cumyl-	Fe(II)[d]	retardation
5	cumyl-	Ir(I)[e]	inhibition
6	*t*-butyl-	Rh(I)[e]	inhibition
7	benzyl-	Cu(II), Cu(I)[f]	acceleration
8	*t*-butyl-	Cr(VI)[g]	retardation

[a]Ref. [10]. [b]Ref. [11]. [c]Ref. [12]. [d]Ref. [13]. [e]Ref. [14]. [f]Ref. [15]. [g]This work.

environments, being one of the well established routes considered for the formation of alcohols and carbonyl groups by the autooxidation of alkanes and alkenes [9]. It has been observed that basic ligands, and particularly pyridine derivatives, affect catalytic oxidations with hydroperoxides. However, pyridine co-catalysts exhibit disparate effects on hydroperoxide decomposition, depending on the catalytic system (Table 1). This diversity makes extrapolations to other catalytic systems doubtful.

Herein we examine and quantify the retardation and acceleration effects of pyridine co-catalysts on TBHP decomposition, and we show that pyridines affect a change of selectivity in Cr-catalyzed oxidations of olefins by TBHP.

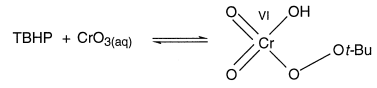
2. Results and discussion

2.1. CrO_3-catalyzed decomposition of TBHP

We have observed that TBHP, while thermally stable at room temperature in a metal-free diluted CH_2Cl_2 solution, decomposed rapidly in the presence of 1 mol% CrO_3 at 22°C (Eq. (1)). The formation of *t*-BuOH accounted for ca. 90% of the substrate, with di-*t*-butyl peroxide being the minor product [16,17].

$$2\,\text{TBHP} \xrightarrow[\text{CH}_2\text{Cl}_2,\,\text{Ar},\,22^\circ\text{C}\,4\,\text{h}]{\text{CrO}_3\,1\%} 2\,t\text{-BuOH} + \text{O}_2 + \underset{\text{minor product}}{(t\text{-BuOO}t-\text{Bu})} \quad (1)$$

The CrO_3-catalyzed decomposition of TBHP to *t*-BuOO$^{\cdot}$ and *t*-BuO$^{\cdot}$ free radicals can be rationalized (Eqs. (2)–(4)) according to the Haber–Weiss mechanism:



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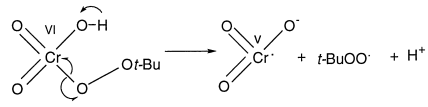

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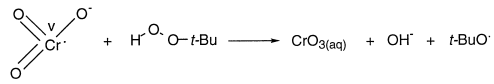


(4)

The reaction can then proceed via Eqs. (5) and (6):

$$t\text{-BuO}^{\cdot} + t\text{-BuOOH} \rightarrow t\text{-BuOOH} + t\text{-BuOO}^{\cdot} \quad (5)$$

$$2\,t\text{-BuOO}^{\cdot} \rightarrow 2\,t\text{-BuOH} + \text{O}_2 \quad (6)$$

This decomposition was retarded by the presence of catalytic amounts (1–10%) of pyridine additives, viz. pyridine **1a**, quinoline **2**, 3-picoline **1b**, 3,5-lutidine **1c**, 2,6-lutidine **1d**, and 1,2-bis(2-pyridyl)ethylene **3**. Surprisingly, this decomposition was strongly accelerated by the presence of catalytic amounts (1–2%) of 2,2′-bipyridine **4** or 1,10-phenanthroline **5**. Fig. 1 shows the reaction profiles of CrO_3-catalyzed TBHP decomposition with monodentate pyridine co-catalysts.

Deriving a rate expression for the decomposition reaction is problematic, due to the participation of *t*-BuOO$^{\cdot}$ and *t*-BuO$^{\cdot}$ radicals both in the catalytic cycles and in the classical free-

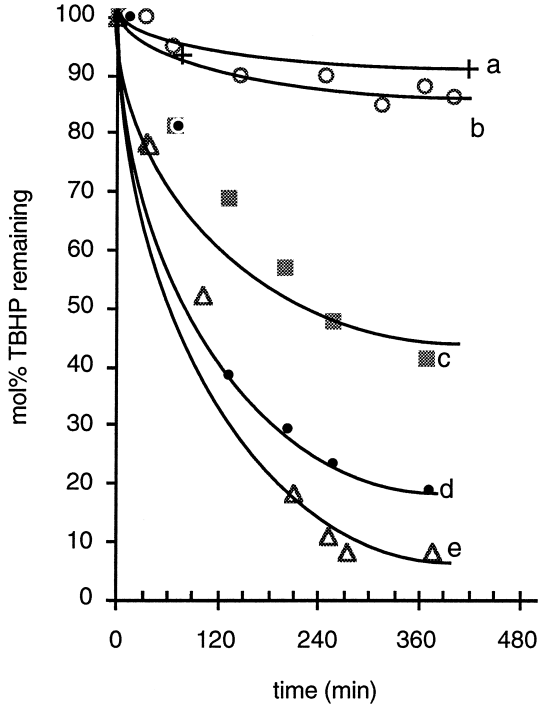
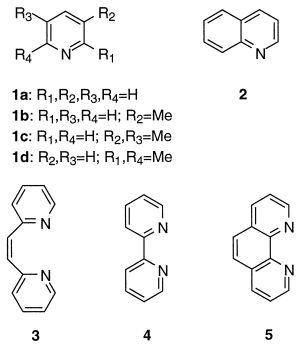


Fig. 1. Decomposition of TBHP at 22°C. Conditions: 20 mmol TBHP (70% aq), 10 ml CH_2Cl_2, (a) no catalyst. (b) 1 mol% CrO_3, 10 mol% **1d**. (c) 1% CrO_3, 10% **1a**. (d) 1% CrO_3, 10% **2**. (e) 1% CrO_3.

radical decomposition of TBHP. Therefore, we used the initial decomposition rate as a comparison parameter (see Table 2).



A significant difference was observed when pyridines substituted with positive inductive groups were employed: the retardation was found to correlate with the relative strength of the inductive effect, i.e., **1d** > **1b** ≈ **1c** > **1a** > **2**.

Table 2
Initial TBHP decomposition rates

Entry	Co-catalyst (mol%)	Initial rate[a]	relative rate ± 0.05[b]
1	**3** (1%)	−0.04	0.12
2	**1d** (2%)	−0.13	0.38
3	**1c** (2%)	−0.17	0.50
4	**1b** (2%)	−0.20	0.58
5	**1a** (2%)	−0.22	0.65
6	none (control)	−0.34	1.00
7	**1a** (1%)	−0.36	1.05
8	**4** (1%)	−24.5	72.00
9	**5** (1%)	−25.0	73.50

Conditions: 20 mmol TBHP (70% aq), 10 ml CH_2Cl_2, 22°C. [a] $r^2 \geq 0.98$. [b] Relative rate = $\text{i.r.}_{exp}/\text{i.r.}_{control}$.

Another interesting phenomenon is the effect of the molar ratio of **1d**:CrO_3 on the decomposition of TBHP. Fig. 2 shows that little retardation was observed for ratios under 2:1.

^{1}H NMR and UV–Vis spectroscopic measurements were used to monitor the various chromium species present in this redox system. Although CrO_3 readily dissolves in water, form-

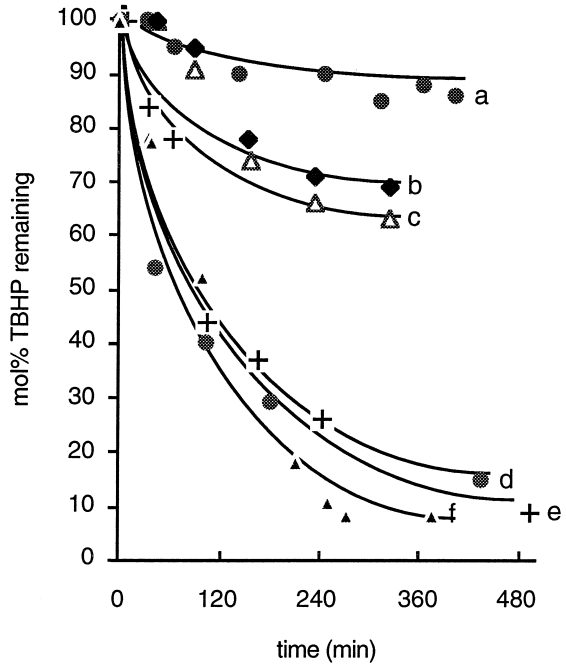


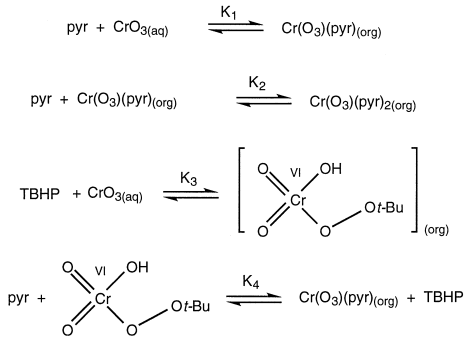
Fig. 2. Effect of **1d**:CrO_3 ratio. Conditions: 20 mmol TBHP (70% aq), 10 ml CH_2Cl_2, 22°C. (a) 10:1. (b) 5:1. (c) 2:1. (d) 1:1. (e) 0.5:1. (f) 0:1 (blank).

ing a yellow solution (maxima at 350 and 257 nm), it does not dissolve in CH_2Cl_2. However, when 1 mol% CrO_3 was added to a mixture of 70% TBHP in CH_2Cl_2, the organic phase turned dark red (maxima at 473 and 255 nm), and the aqueous phase became clear. This indicates an extraction of CrO_3 into CH_2Cl_2 by TBHP. CrO_3 can also be extracted into CH_2Cl_2 by various pyridines (Table 3). The addition of **1a** to a dry solution of TBHP/CrO_3 in CH_2Cl_2 shifted λ_{max} from 473 nm to 355 nm.

Comparison of the ^{1}H NMR spectra of neat TBHP in $CDCl_3$ and 1:1 TBHP:CrO_3 in $CDCl_3$, showed a 0.1 ppm downfield shift of the singlet (9H) corresponding to the *t*-Bu group when CrO_3 was present. This finding correlates with the findings of Mimoun et al. [18] for TBHP–M complexes. Furthermore, a 2.2 ppm upfield shift of the singlet (1H) signal was observed, suggesting the formation of a metallic hydroxide derivative. The pH of a mixture of 70% TBHP/30% water/1% CrO3 was between 1 and 2. This pertains to a large fraction of chromic acid, H_2CrO_4, with negligible amounts of $Cr_2O_7^{-2}$ and $HCrO_4^-$ [19].

The addition of 1–10% of 2,6-di-*t*-butyl-4-methylphenol (BHT) to the TBHP/1% CrO_3 mixture also inhibited the decomposition of TBHP, suggesting the presence of free-radical intermediates in the catalytic cycle.

When co-catalysts **1a**–**d** were used, the organic phase cleared after 12 h and the aqueous phase turned a blue–green color (maxima at 572 and 251 nm). Such a 'light-green solution' has been previously reported as the 'dead catalyst' in the CrO_3/TBHP benzylic oxidation systems [20]. We have isolated and crystallized from this aqueous solution a green compound which was proven to be $[Cr^{III}(H_2O)_4Cl_2]Cl \cdot 2H_2O$ by XR diffraction. Further study of this solvent effect is in progress.



Scheme 1.

As proposed in Scheme 1, the TBHP/CrO_3/Pyridine system involves at least four chemical equilibria, in which the Cr(VI)–oxo complex is the catalyst for the irreversible decomposition of the TBHP to *tert*-butanol and dioxygen, as was claimed elsewhere ([21]; see also Refs. [5–7]). We suggest that double ligation occurs when the pyridine:CrO_3 ratio is 2:1 or higher, altering the Lewis acidity of the complex. The *trans*-(**1a**–**d**)$_2$Cr(=O)$_2$(–OH)$_2$ complexes do not catalyze the decomposition, and therefore the rate slows down, depending on the relative strengths of K_2 and K_4. [1]

Our opinion is that complex formation explains the above observations better than the formation of a pyridinium dichromate (PDC) salt, for PDC is reported to be sparingly soluble in CH_2Cl_2 [23]. Indeed, UV–Vis measurements show that CrO_3/pyr species are soluble in CH_2Cl_2. Moreover, a CrO_3-diamine complex has already been envisaged by N'aït Ajjou et al. [24].

Table 3
Absorption maxima for CrO_3/pyr solutions in dry CH_2Cl_2

Entry	Pyr	[CrO_3] (mM)	[Pyr] (mM)	λ_1 (nm)	λ_2 (nm)
1	**1b**	2.32	4.66	241	363
2	**1c**	2.00	3.99	248	355
3	**1d**	2.32	4.64	243	367

[1] We considered the possible effect that the pyridine…HOOR hydrogen bond could have in our system [22]. Indeed, pyridine does form a strong hydrogen bond with TBHP, detectable by ^{1}H NMR (100% of the peroxidic hydrogen is shifted downfield from 7.3 ppm to 9.6 ppm in a 1:1 molar solution of TBHP and pyridine in $CDCl_3$). However, 2 mol% of pyridine cannot bond to more than 2% of the TBHP, so this factor was dismissed.

The acceleration effect of **4** and **5** was discovered by accident: reasoning that a 2:1 molecular ratio of pyridine:CrO_3 was needed to efficiently retard the TBHP decomposition, we presumed that **4**, being a bidentate ligand, would be an efficient retardant even in a 1:1 molecular ratio. We were intrigued upon finding that the opposite occurred, namely that **4** accelerated the reaction. Similar acceleration was observed when using **5**, indicating that the free-rotation of the pyridine rings was not a crucial factor. Appropriate blank reactions showed that **4** and **5** did not catalyze the decomposition in the absence of CrO_3.

We consequently hypothesized, that the 4-coordinated chromium atom in H_2CrO_4, changes to a 6-coordinated complex upon the addition of 2 equivalents of pyridine. For steric reasons, the pyridine ligands would favor the *trans* configuration. However, when compounds **4** and **5** were used, in which the distance between the two donor nitrogens was not sufficient to allow the formation of a stable *trans*-chelate, a *cis*-chelate was formed. This combination proved to be much more active than CrO_3. [2] Using semi-empirical calculations, we determined that inserting two extra carbon atoms between the two pyridine rings (as in compound **3**) should suffice to enable a stable *trans* configuration of the bipyridine–chromium chelate. Verily, **3** was found to be a formidable retardant even at a 1:1 molecular ratio of **3** to CrO_3. Experimental results for bidentate ligands are shown in Fig. 3.

We maintain that the above effects are the result of pyridine coordination to the Chromium atom rather than a change in the basicity of the reaction medium. If the pyridine was acting only as a buffer, without coordination to the Cr, then bipyridines such as **3** and **4** would be expected to retard the decomposition.

The above system is a complex one, containing both a catalytic cycle and a free-radical propagation step. These can be separately affected: addition of catalytic amounts of pyridines to the reaction mixture will prevent the formation of the TBHP–CrO_3 complex, thus retarding the catalytic cycle. Nevertheless, addition of catalytic amounts of a free-radical scavenger such as BHT to the reaction mixture will inhibit the free-radical propagation step. These two approaches were utilized by us to determine the role played by the various oxidative species in the CrO_3-catalyzed TBHP oxidation of olefins.

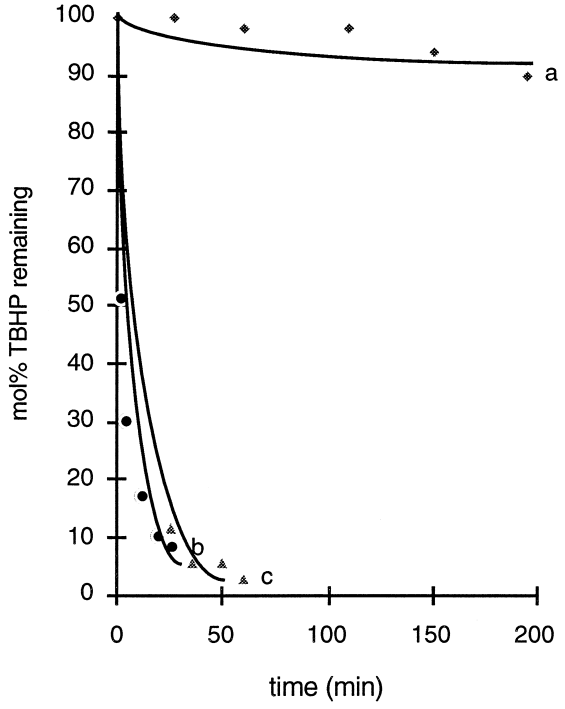


Fig. 3. TBHP decomposition with bipyridines. Conditions: 20 mmol TBHP (70% aq), 10 ml CH_2Cl_2, 22°C, 1 mol% CrO_3. (a) 1 mol% **3**. (b) 1 mol% **4**. (c) 1 mol% **5**.

2.2. CrO_3-catalyzed oxidations of olefins by TBHP

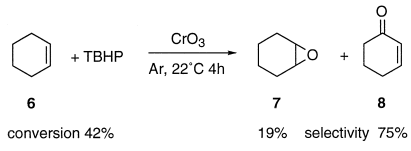
The classic oxidation of olefinic substrates containing allylic hydrogens is thought to follow two possible pathways: Allylic oxidation (ene reaction), and direct attack on the double bond (1,2 addition) [8]. When using oxygen-

[2] In several cases, *cis* chelates based on **4** and **5** were reported to have strong catalytic effects [25,26].

transfer reagents, such as TBHP or PhIO, the metal can serve as a relay for the transfer of the oxygen atom from the hydroperoxide to the olefin via an oxometal intermediate [27,28].

The dismutation of TBHP in the presence of transition-metal catalysts to produce *t*-BuOH and O_2 has been documented ([29]; see also p. 38 of Ref. [9]). We have observed that the oxygenation can be carried out both by O_2 and by the peroxo-oxygen atom in the TBHP molecule. Therefore, in order to make significant comparisons when employing TBHP as an oxidant, an inert Ar atmosphere was used.

In a typical experiment, molar equivalents of cyclohexene **6** and 70% aq. TBHP were stirred in 1-Chloronaphthalene under Ar for 4 h at 22°C, in the presence of 1–5 mol% of CrO_3 (Eq. (7)). Blank reactions showed that the solvent and the internal standard (naphthalene) were inactive at 22°C [30]. The main products were cyclohexene oxide **7** and 2-cyclohexene-1-one **8**, together with 2–5% of cyclohexenyl dimer and traces of 2-cyclohexene-1-ol.



(7)

As we have shown above, the free-radical decomposition of TBHP can be inhibited by the addition of a phenolic radical scavenger such as BHT [31], while addition of a pyridine derivative can tamper with the catalytic cycle. Performing the oxidation reaction in the presence of a catalytic amount of BHT showed a significant (2–5 h) induction period for the formation of **8** (Fig. 4) while no induction period was observed for the formation of **7**. Indeed, catalytic amounts of BHT increased the overall yield of **7** (Fig. 5).

Further proof of the non-radical nature of the epoxidation reaction was obtained through the epoxidation of (*Z*)-stilbene (Eq. (8)). We have found that under the reaction conditions, the

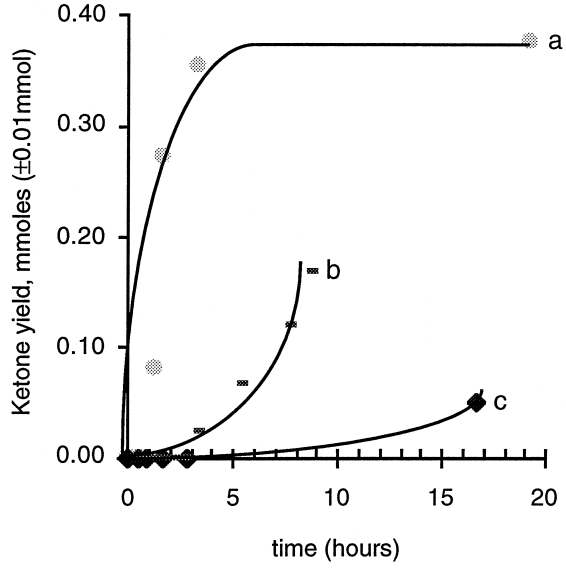
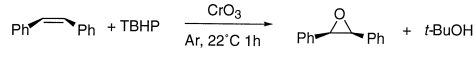


Fig. 4. BHT effect on **8** yields. Conditions: 1.00 mmol **6**, 1.00 mmol TBHP, 0.025 mmol CrO_3, Ar atmosphere, 4 gr 1-Chloronaphthalene, 22°C. (a) no BHT. (b) 5 mol% BHT. (c) 10 mol% BHT.

configuration of the substrate was retained in the epoxide. Thus, (*Z*)-stilbene afforded only (*Z*)-stilbene oxide, whereas in a free-radical reaction some (*E*) epoxide would be expected. This result differs from the report of Muzart et al., but their experimental conditions were different from the present work [32].



(8)

When the reaction was performed in the presence of catalytic amounts of **1d**, two effects were observed: the epoxidation and the allylic oxidation reactions were slower, but, while the yield of the ketone **8** was largely unaffected by the presence of **1d**, the yield of the epoxide **7** was significantly lower compared to the control reaction containing no **1d**. This phenomenon was particularly distinct (Fig. 6) when the **1d**:CrO_3 ratio was 2:1 or higher. These findings agree with the observations of Agarwal et al., who used a pyridine:CrO_3 ratio of 60:1 in the

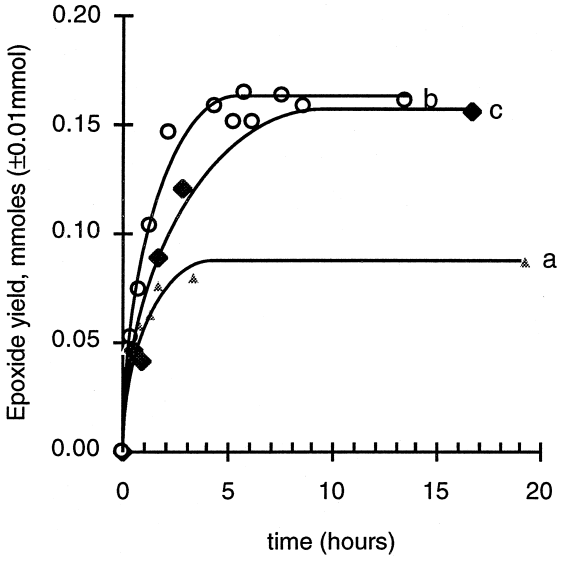
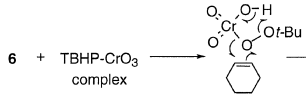


Fig. 5. BHT effect on **7** yields. Conditions: 1.00 mmol **6**, 1.00 mmol TBHP, 0.025 mmol CrO_3, Ar atmosphere, 4 gr 1-Chloronaphthalene, 22°C. (a) no BHT. (b) 5 mol% BHT. (c) 10 mol% BHT.

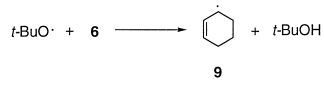
oxidation of cyclohexene, albeit under different reaction conditions [30].

We therefore propose that when employing TBHP as the oxidant, the catalytic epoxidation and allylic oxidation reactions follow different paths. The allylic oxidation follows a free-radical pathway, while the epoxidation is an oxygen-transfer reaction. The epoxidation reaction could occur via the activation of the peroxidic oxygens (Eq. (9)). [3] For efficient catalysis along this path, proposed by Sheldon in 1973 [21], the metal center would have to be both a strong Lewis acid and a weak oxidant. Indeed, CrO_3, being a strong Lewis acid, is not an efficient epoxidation catalyst in this system because it is a strong oxidant and therefore catalyzes the decomposition of the TBHP. In this case, the suggested ligand exchange from TBHP to pyridine would suffice to arrest the epoxidation.



(9)

The allylic hydrogen, on the other hand, can be abstracted by either the *t*-BuO· or the *t*-BuOO· free radicals (Eqs. 10 and 11) that are formed in the decomposition of TBHP.



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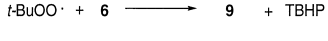


(11)

The resultant cyclohexenyl radical **9** can react with O_2 (Eq. 12) or, as was recently reported by Bravo et al., with the *t*-BuOO·

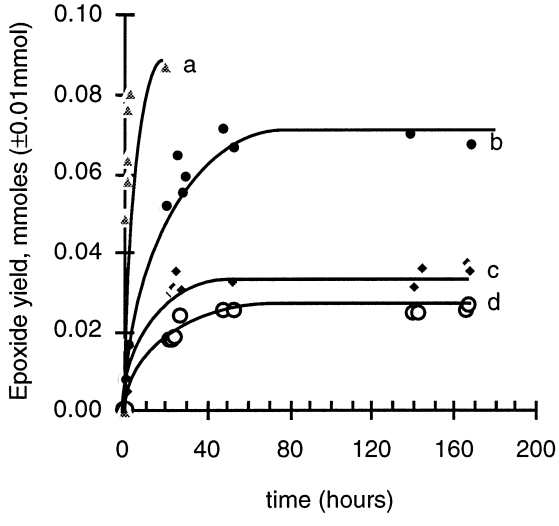
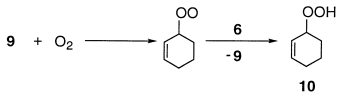


Fig. 6. Effect of **1d**:CrO_3 ratio on **7** yields. Conditions: 1.00 mmol **6**, 1.00 mmol TBHP, 0.025 mmol CrO_3, Ar atmosphere, 4 gr 1-Chloronaphthalene, 22°C. (a) 0 (no **1d**). (b) 1:1. (c) 2.65:1. (d) 5:1.

[3] The fact that both the epoxidation of **6** and the decomposition of TBHP can be retarded by *trans* complexation of two pyridines to the chromium atom, can also be explained if the epoxide forms via the metallocyclic Sharpless intermediate, with the CrO_3 analogous to chromyl chloride [33]. Such organometallic bonding would be less likely to form with the pyridine-bonded complex, where the ligands would cause a steric interference.

(Eq. 13) to form the hydroperoxide **10**, or a mixed peroxide **11**, respectively [34].



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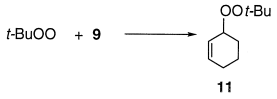

(13)

It is possible that the mixed peroxide would form preferentially when using copper catalysts, as was shown recently by us in the case of benzylic oxidations with TBHP [35]. As **11** was not detected in our system, we propose that Eq. 12 predominates in the presence of CrO_3, where **10** is oxidized to **8**.

3. Conclusion

The nature and the orientation of the ligands surrounding the chromium atom play a vital part in the Cr-catalyzed oxidation of olefins by TBHP. The epoxidation reaction is dependent on the formation of a TBHP–CrO_3 complex. Conversely, allylic oxidation, a free-radical process, occurs also in the absence of such a complex. The immediate environment of the chromium atom also influences the rate of the decomposition of TBHP. Retardation of this decomposition can be achieved by blocking either the catalytic cycle or the free-radical formation. We suggest that pyridine derivatives coordinate to the chromium catalyst, arrest the catalytic cycle, and simultaneously lower of the yield of the epoxide. Thus, when employing certain pyridines as co-catalysts, the oxygenation can be shifted from epoxidation towards allylic oxidation.

4. Experimental section

4.1. General

All of the solvents and the reagents were obtained from commercial sources and were used without further purification. ^{1}H NMR spectra were measured on a Bruker 300 MHz instrument. δ shift values are reported in ppm relative to TMS. GC analysis was performed on an HP-5890 series II gas chromatograph with a 95%-dimethyl–5%-diphenyl packed column and a FID. GCMS analysis was performed on an HP G1800B gas chromatograph with a similar column and an EID.

4.2. Caution!

Although relatively safe to work with, TBHP, like almost all substances containing peroxidic bonds, has to be handled cautiously. Container should be kept at 10–20°C, to avoid layer separation. Concentrations above 95% purity should be avoided. Strong acids should not be added to high-strength TBHP solutions. Extreme care should be taken when adding metal catalysts (we have had a minor explosion when adding $RuCl_3$ to a 70% TBHP soln). It is safer to add TBHP to CrO_3 than vice versa. Small-scale reactions are preferable.

4.2.1. General procedure for decomposition of TBHP

A mixture of 20 mg (0.2 mmol) of powdered CrO_3 and appropriate molar amounts of amine (e.g., 158 mg pyridine for 2 mmol) in 10 ml CH_2Cl_2 was stirred at 25°C for 1 min, after which 2.54 g (20 mmol) of 70% aqueous TBHP were added. Peroxide content was monitored by iodometric titration [36].

4.2.2. General procedure for oxidation of cyclohexene

A solution of 0.0821 g (1 mmol) of **6**, 0.1287 g (1 mmol) of 70% TBHP, 0.0025 g (0.025

mmol) of CrO_3, and 0.05 gr of naphthalene (internal standard) in 4 g of 1-Chloronaphthalene was stirred under Ar at 22°C for 4 h. The inorganic matter was filtered on silica and the filtrate was analyzed by GC and GCMS to obtain 0.52 mmol of **6**, 0.08 mmol of **7**, and 0.35 mmol of **8**. GC/GCMS conditions: 40°C for 6 min, 20°C/min slope, 80°C for 5 min, 20°C/min slope, 240°C for 1 min. Typical retention times (min): **6** 4.93; **7** 9.46; **8** 12.03; 2-cyclohexene-1-ol 10.74; naphthalene 12.64; cyclohexenyl dimer 19.77. Retention times and MS analysis were identical to commercial samples.

4.2.3. Oxidation of stilbenes

A solution of 0.1802 g (1 mmol) of (*Z*)-stilbene, 0.1287 g (1 mmol) of 70% TBHP, 0.005 g (0.05 mmol) of CrO_3 and 0.05 g of naphthalene (internal standard) in 3 gr of benzene was stirred under Ar at 22°C for 1 h. The inorganic matter was filtered on silica and the filtrate was analyzed by GC. GC conditions: 160°C for 3 min, 20°C/min slope, 240°C for 3 min. Retention times (min): naphthalene 2.77; (*Z*)-stilbene 5.34; (*Z*)-stilbene oxide 5.96. The retention time of the (*E*) epoxide (obtained both by similar oxidation of (*E*)-stilbene and commercially) was 7.49 min.

4.2.4. Calculations of ΔH_f° values for cis- and trans-complexes

Each structure was built in SPARTAN® [37], using standard bond lengths and angles. Geometrical and energetical optimization was performed with the semi-empirical engine using the PM3 (tm) method (which supports d-functions for transition metals). The following values (kcal/mol) were obtained: *trans*-(**1a**)$_2$Cr(=O)$_2$(–OH)$_2$: −178; *trans*-(**1d**)$_2$Cr(=O)$_2$(–OH)$_2$: −149; *cis*-**3**-Cr(=O)$_2$(–OH)$_2$: −86; *trans*-**3**-Cr(=O)$_2$(–OH)$_2$: −30; *cis*-**4**-Cr(=O)$_2$(–OH)$_2$: −184; *trans*-**4**-Cr(=O)$_2$(–OH)$_2$: +149; *cis*-**5**-Cr(=O)$_2$(–OH)$_2$: −170; *trans*-**5**-Cr(=O)$_2$(–OH)$_2$: +98.

4.2.5. Isolation of $[Cr^{III}(H_2O)_4Cl_2]Cl \cdot 2H_2O$

10.00 g of 70% TBHP was treated as in Eq. (1). with 1.00 g CrO_3. No pyridines were added. After 12 h the phases were separated and the aqueous phase was washed (3×10 ml CH_2Cl_2) and filtered. The filtrate was left to crystallize under reduced pressure at 5°C for 15 d. A layer of dark-green crystals formed. The crystals were filtered by suction at 5°C (60 mg yield). Single-crystal XR diffraction analysis showed monoclinic structures (lit. values [38]): $a_0 =$ 12.053 (12.055), $b_0 = 6.835$ (6.840), $c_0 =$ 11.645 (11.648), and $\beta = 94.160$ (94.169).

4.2.6. ^1H NMR measurements of TBHP and TBHP–CrO_3

1 mmol of 70% TBHP was extracted into 3 ml of $CDCl_3$. The organic phase was separated and dried over $MgSO_4$, and the ^1H NMR spectrum was recorded. Results: 1.23 ppm, 9H, s; 6.22 ppm, 1H, s. 1 mmol of CrO_3 was added to the same sample, and the spectrum was immediately recorded again (the subsequent formation of paramagnetic O_2 in the tube causes a severe signal disturbance). Results: 1.33 ppm, 9H, s; 4.00 ppm, 1H, s.

Acknowledgements

We thank Dr. Shmuel Cohen for performing the XR diffraction analysis of $[Cr^{III}(H_2O)_4Cl_2]Cl \cdot 2H_2O$, and Ms. Shahar Keinan for calculating the semi-empirical ΔH_f° values.

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