Chromium(VI) oxide–*tert*-butyl hydroperoxide interactions: evidence for a *tert*-butylperoxychromium complex and its role in the catalytic oxidation of alcohols

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Based upon UV–visible and NMR spectroscopic studies in benzotrifluoride (BTF, α,α,α-trifluorotoluene) it has been shown that the purple colored species obtained from the reaction of *t*-BuOOH with CrO_3 is a *tert*-butylperoxychromium complex, preferably formulated as (*t*-BuOO)(HO)CrO_2. This complex, which is more stable in aromatic solvents than in haloalkanes, decomposes with time into *tert*-butylchromate. This transformation is greatly accelerated by the addition of benzyl alcohol. A catalytic cycle for the oxidation of alcohols is proposed.

Introduction

Previously we have reported on chromium(VI) oxide-catalyzed oxidation of alcohols by *tert*-butyl hydroperoxide in methylene chloride.[1–4] In 1987 we postulated that the active oxidative species was hydroxy(*tert*-butylperoxy)chromium complex (*t*-BuOO)(HO)CrO_2 (**1**).[2] Although we have not been able to characterize such a complex despite extensive UV and NMR studies, even at low temperatures,[5] we have recently demonstrated that the active oxidative species contain the *tert*-butyl moiety in their coordination sphere. We have not been successful, however, in determining whether the *t*-Bu moiety is connected to chromium through an oxygen atom or by a peroxo link to give *t*-BuOCr or *t*-BuOOCr units, respectively.[4] The difficulties arising during this characterization seem to be caused by the Cr-catalyzed decomposition of *t*-BuOOH, a reaction which is particularly rapid in the absence of an oxidizable substrate.[6] The decomposition products, *t*-BuOH and *t*-BuOO-*t*-Bu,[7,8] which are susceptible to reaction with chromium, as well as molecular oxygen (paramagnetic species), hamper the analysis and the reproducibility of the spectra. In contrast, *tert*-butylperoxo complexes[9] of vanadium,[10] molybdenum,[11] iron,[12] cobalt,[13] iridium,[14] titanium,[15] copper,[16] and palladium[17] have been identified; the characterization of such species, however, can also be difficult,[10a] particularly in the case of metal oxo compounds.[18] Recently, Sasson *et al.*[8] have reported on CrO_3-catalyzed oxygenation of olefins by *t*-BuOOH and have concluded that a CrO_3–*t*-BuOOH complex is formed during the reaction.

The report of Ogawa and Curran,[19] in which the use of benzotrifluoride (BTF, α,α,α-trifluorotoluene) as an alternative to the more toxic chlorocarbon solvents was recommended, led us to examine the CrO_3-catalyzed oxidation of alcohols by *t*-BuOOH in this solvent.[20] In the course of this study we observed that the use of BTF instead of CH_2Cl_2 slowed down the decomposition of *t*-BuOOH considerably. This encouraged us to monitor the CrO_3–*t*-BuOOH interactions in BTF by NMR and UV–visible spectroscopic techniques.

Results and discussion

Since complex reactions were expected and, in order to discriminate the *t*-BuOOCr type species from the other species present in the reaction mixture, it was necessary to know the relevant data for *t*-BuOH, *t*-BuOOH, *t*-BuOO-*t*-Bu and *tert*-butylchromate in BTF. The chemical shifts in NMR and the absorption positions in UV–visible[21] of these species are reported in Tables 1 and 2. When performing the NMR studies in BTF one drop of TMS–$CDCl_3$ was required as internal reference for the chemical shift determinations and to lock the deuterium signal.

The ^1H NMR spectrum of a 1 : 10 CrO_3–*t*-BuOH mixture (run 4) revealed a singlet at δ = 1.47 ppm which could be assigned to the *t*-Bu group of a *tert*-butyl chromate complex; this corresponds to a downfield shift $\Delta\delta_{H,t\text{-BuO}}$ with respect to free *t*-BuOH of 0.22 ppm. The ^{13}C NMR spectrum showed singlets at δ = 30.0 and 90.5 ppm which for this complex correspond to the following field shifts: $\Delta\delta_{C\text{-H},t\text{-BuO}} = -1.0$ ppm and $\Delta\delta_{C\text{-O},t\text{-BuO}} = 21.4$ ppm. An increase in the ratio of CrO_3–*t*-BuOH to 1 : 1 (run 5) led to a ^1H NMR spectrum exhibiting signals at δ = 1.40 and 1.44 ppm of similar intensities. The reaction of 2–3 equiv. of *t*-BuOH with CrO_3 is known to afford a complex, usually named *tert*-butylchromate,[22] but it has also been proposed that these conditions may lead to a mixture of (*t*-BuO)(HO)CrO_2 (**2**) and $(t\text{-BuO})_2CrO_2$ (**3**).[23] Indeed, both names, *tert*-butylchromate and di-*tert*-butylchromate, have been indiscriminately used for the complexes thus obtained.[24] We propose that the conditions of run 5 lead to a 1 : 1 mixture of **2** and **3** while essentially **3** is obtained in run 4. The chemical shifts attributed to the *t*-Bu group of the Cr-species and to *t*-BuOH in the different runs, however, showed a slight discrepancy. These observations led us to examine briefly the influence of the amount of $CDCl_3$ added to BTF on the chemical shifts of a 1 : 1 CrO_3–*t*-BuOH mixture. Actually, the signals were observed at δ = 1.18 to 1.27 ppm and at δ = 1.39 to 1.48 ppm for the *t*-Bu protons of the *t*-BuOH and *t*-BuOCr species,

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Table 1 NMR data in BTF at room temperature

Run	Compounds	^{1}H NMR $\delta_{\text{C-}H}$ (ppm)	^{13}C NMR $\delta_{\text{C-H}}$ (ppm)	$\delta_{\text{O-}C}$ (ppm)
1	*t*-BuOH	1.24	30.9	69.0
2	70% aq. *t*-BuOOH	1.20	25.3	80.7
3	*t*-BuOO-*t*-Bu	1.22	26.7	78.4
4	CrO_3 + 10 *t*-BuOH[b]	1.47, 1.25	30.0, 31.0	90.5, 69.1
5	CrO_3 + 1 *t*-BuOH[b]	1.44, 1.40, 1.18	30.0, 31.0	[c]

[a] Containing one drop of TMS–$CDCl_3$ (see text). [b] Spectra recorded after stirring for 2 h. [c] Intensity too low to be determined.

Table 2 UV–visible data in BTF at room temperature[21]

Run	Compounds	λ_{max}/nm
6	CrO_3[a]	375
7	CrO_3 + 1 H_2O[b]	379
8	CrO_3 + 1 *t*-BuOH[c]	386
9	CrO_3 + 1 *t*-BuOH[d]	383
10	CrO_3 + 2.5 *t*-BuOH[d]	379
11	CrO_3 + 6 *t*-BuOH[b]	378
12	CrO_3 + 1 *t*-BuOH + 1 H_2O[d]	384
13	CrO_3 + 6 *t*-BuOH + 6 H_2O[b]	377

[a] Spectra recorded after stirring for 1 week. [b] 5 min. [c] 30 min. [d] 3 h.

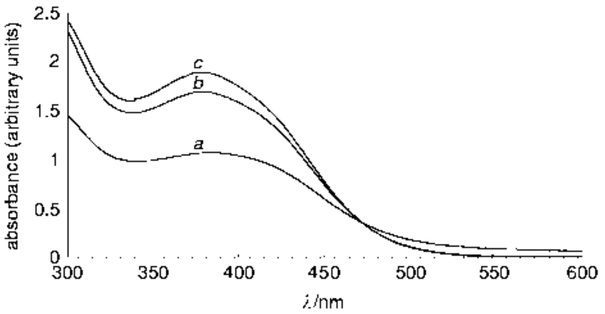


Fig. 1 UV–visible spectra of CrO_3–*t*-BuOH mixtures in BTF; CrO_3–*t*-BuOH = 1 : 1 (*a*), 1 : 2.5 (*b*), 1 : 6 (*c*).

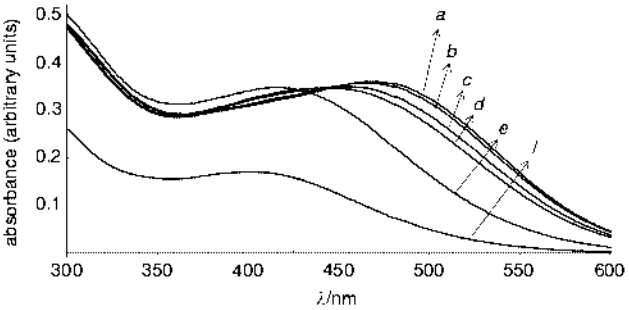


Fig. 2 Changes in the absorption spectrum of a 1 : 1 CrO_3–*t*-BuOOH mixture with time in BTF; 2 min (*a*), 10 min (*b*), 75 min (*c*), 135 min (*d*), 21 h (*e*), 41 h (*f*).

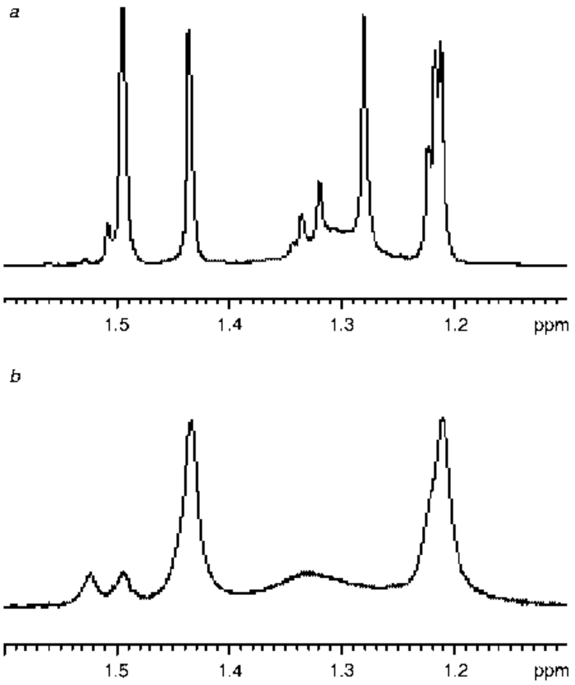


Fig. 3 500 MHz ^{1}H-NMR spectra of a 1 : 1 CrO_3–*t*-BuOOH mixture in BTF; after 15 min (*a*), after 20 h (*b*).

respectively, when the concentration of $CDCl_3$ was increased. This observation seemed to suggest some interactions between $CDCl_3$ and these species. Since there are some vacancies in the inner coordination sphere of the complex we suspect a weak coordination of $CDCl_3$ to chromium. Coordination of halogenated solvents to transition metals is well documented[25,26] but hydrogen bonding in the second sphere of coordination between $CDCl_3$ and inner-sphere ligands may also be envisaged.[27]

Chromium oxide is only slightly soluble in BTF but the solution shows a weak UV band centered at 375 nm (run 6).[28] By addition of one equiv. of H_2O (run 7) or *t*-BuOH (runs 8 and 9) to the CrO_3–BTF heterogeneous mixture the dissolution of CrO_3 was enhanced and led to a red shift of the UV band. An increase in the amount of *t*-BuOH from 1 to 6 equiv. induced a slight blue-shift of λ_{max}. The UV spectra from runs 8, 10 and 11 are reported in Fig. 1. From the literature data mentioned earlier[22,23] and the above NMR observations we propose that curve *a* corresponds mainly to the absorption of a *ca.* 1 : 1 mixture of **2** and **3**. while curve *c* shows the absorption of **3** suggesting the λ_{max} value of **2** to be above 386 nm. We cannot, however, exclude other minor chromium species being present in runs 10 and 11, their general formula being $(t\text{-BuO})_x(\text{HO})_y\text{CrO}_{3-0.5(x+y)}$ where $x + y = 4$ or 6. From runs 9 and 12, and 11 and 13, it appears that the λ_{max} value is fairly independent of small amounts of water, and the formation of some $(\text{HO})_z\text{CrO}_{3-0.5z}$ (z = 2, 4, 6)[8] species cannot be excluded under these conditions.

Having these results in hand the reaction of *t*-BuOOH with CrO_3 in BTF was studied, a reaction in which the solution develops a purple color. The UV–visible spectrum of a 1 : 1 mixture of these components exhibited a λ_{max} at *ca.* 470 nm (Fig. 2, curve *a*) which suffered a blue-shift with time. The UV evolution indicated initially a clear isosbestic point at λ = 448 nm suggesting an initial selective reaction; this point, however, was not preserved for prolonged reaction times. After 41 h (Fig. 2, curve *f*), the UV–visible spectrum was most similar to the one depicted previously (Fig. 1, curve *a*) and attributed to a mixture of **2** and **3**. The ^{1}H and ^{13}C NMR spectra of 1 : 1 mixtures of CrO_3 and *t*-BuOOH were also recorded (Figs. 3 and 4). Because of the time required for the preparation of the NMR samples and the acquisition of the data we suspect that the signals obtained were not solely due to the primary formed

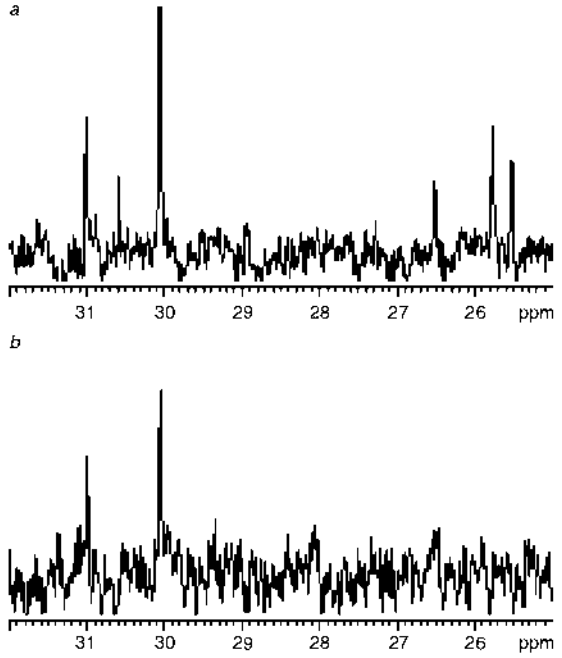


Fig. 4 500 MHz ^{13}C-NMR spectra of a 1 : 1 CrO_3–*t*-BuOOH mixture in BTF; after 15 min (*a*), after 20 h (*b*).

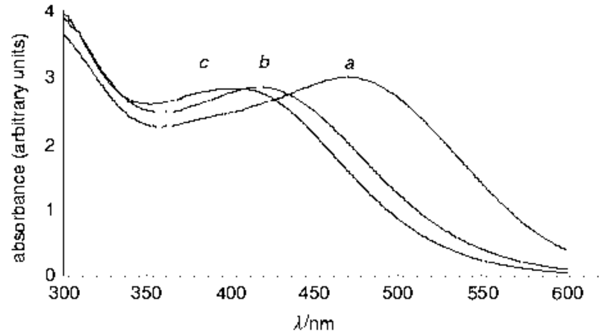


Fig. 5 The absorption spectrum of a 1 : 10 CrO_3–*t*-BuOOH mixture in BTF solution after 5 min (*a*), 17 h (*b*), 45 h (*c*).

chromium adducts; in fact, the spectrum evolved with time. Based upon the assignments reported in Table 1 the main signals in the ^{1}H NMR spectrum shown in Fig. 3*a* could be assigned to the methyl groups of *t*-BuOH + *t*-BuOO-*t*-Bu (δ at *ca.* 1.21 ppm), *t*-BuOOH (δ = 1.28 ppm), *t*-BuOCr (δ = 1.43 ppm) and *t*-BuOOCr (δ = 1.49 ppm); the evolved ^{1}H NMR spectrum (Fig. 3*b*) showed the disappearance of the peaks at δ = 1.28 and 1.49 ppm while two new peaks at δ = 1.21 and 1.43 ppm appeared, both with broadening indicating the presence of paramagnetic species. Since the peak at δ = 1.49 ppm (Fig. 3*a*) disappeared with time we conclude this peak to be due to *t*-BuOOCr rather than *t*-BuOCr; this signal corresponds to a downfield shift $\Delta\delta_{\mathrm{H},t\text{-BuOO}}$ of 0.21 ppm with respect to free *t*-BuOOH. The ^{13}C NMR spectra showed poor resolution and were less informative. The peaks observed in the methyl area after approximately 15 min (Fig. 4*a*) were tentatively attributed to the primary carbons of *t*-BuOOH, δ = 25.5 ppm; *t*-BuOO-*t*-Bu, δ = 26.5 ppm; *t*-BuOCr, δ = 30.1 ppm (field shift: $\Delta\delta_{\mathrm{C\text{-}H},t\text{-BuO}} = -0.9$ ppm); *t*-BuOOCr, δ = 30.6 ppm (field shift: $\Delta\delta_{\mathrm{C\text{-}H},t\text{-BuO}}$ = 5.1 ppm) and *t*-BuOH, δ = 31.0 ppm; after 20 h, only the peaks due to *t*-BuOCr and *t*-BuOH could be detected (Fig. 4*b*) indicating degradation of the peroxo species during this period of time. The peaks corresponding to the tertiary carbon atoms had intensities too low to be analyzed. The various NMR spectra contained additionally some minor bands which have not been assigned. From these UV and NMR experiments we presume that **1** was first transformed into **2** with subsequent formation of a mixture of **2** and **3**.

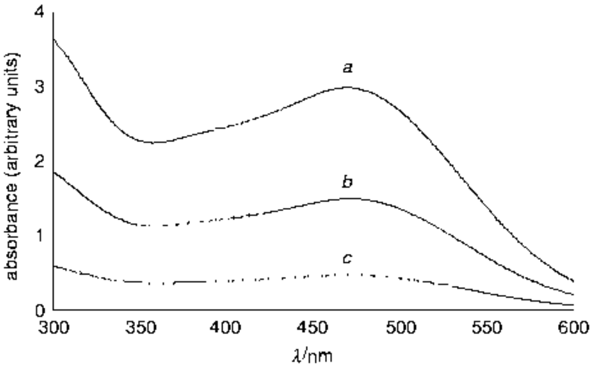
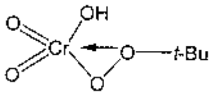


Fig. 6 UV–visible spectra of CrO_3–*t*-BuOOH mixtures in BTF recorded after shaking for 2 min; CrO_3 : *t*-BuOOH = 1 : 10 (*a*), 1 : 5 (*b*), 1 : 1 (*c*).

The use of a large excess of *t*-BuOOH caused an instantaneous dissolution of CrO_3 and the rate of the evolution of the UV–visible spectrum was strongly reduced (Fig. 5). Different mixtures containing CrO_3 and from 1 to 10 equiv. of *t*-BuOOH exhibited initial $\lambda_{\max}$ values at 471 ± 1 nm (Fig. 6) corresponding to a red shift of *ca.* 96 nm. This led us to conclude that this $\lambda_{\max}$ is characteristic of a *tert*-butylperoxychromium complex. As shown earlier the $\lambda_{\max}$ values of (t-BuO)(HO)CrO_2 and (t-BuO)$_2CrO_2$ differ by at least 8 nm, the latter species being formed by a reaction of *t*-BuOH with the former. Apparently, the different *t*-BuOOH–CrO_3 mixtures led essentially to the same Cr-complex since $\lambda_{\max}$ was not significantly altered when 1 to 10 equiv. of *t*-BuOOH were added. This complex, equally well observed with 1 equiv. as with 10 equiv. of *t*-BuOOH, can most likely be formulated as (t-BuOO)(HO)CrO_2 rather than (t-BuOO)$_2CrO_2$. In fact, complexes containing only one alkylperoxo ligand have been frequently reported while (ROO)$_n$M-type complexes ($n > 1$) have been suggested[11,18a,29] but rarely characterized.[10e,14,15]

The red shifts of $\lambda_{\max}$ induced by addition of *t*-BuOH or *t*-BuOOH to CrO_3 are very different. This suggests that both oxygen atoms of the OO-*t*-Bu ligand may coordinate simultaneously to chromium (Scheme 1). We have already proposed η^2-coordination of this ligand to be able to rationalize the mechanisms of chromium-catalyzed oxidation of methylene groups in allylic, propargylic and benzylic compounds by *t*-BuOOH[1,30] and chromium-catalyzed homolytic scission of organic peroxides by *t*-BuOOH.[31] Such a dicoordination of *t*-BuOO, which has been demonstrated by an X-ray crystallographic study of (pyridine-2,6-dicarboxylate)VO(OO-*t*-Bu)·H_2O,[10b] has also been proposed for titanium[15] and vanadium[9a,10b,10c,10e] complexes on the basis of NMR field shifts: $\Delta\delta_{\mathrm{H},t\text{-BuOO}}$ = 0.09–0.6 ppm, $\Delta\delta_{\mathrm{C\text{-}H},t\text{-BuOO}}$ = 0.25–5 ppm; the magnitude of these $\Delta\delta$ values indicating the strength of the M←O-(t-Bu) bond, *i.e.* the bidentate character of OO-*t*-Bu. The values observed for the present Cr-complexes; $\Delta\delta_{\mathrm{H},t\text{-BuOO}}$ = 0.21 ppm and $\Delta\delta_{\mathrm{C\text{-}H},t\text{-BuOO}}$ = 5.1 ppm, appear to be consistent with the ones assigned for dicoordination. Similar field shifts of *tert*-butylperoxo- and *tert*-butyloxotitanium complexes have also led to the conclusion of η^2-coordination of the OO-*t*-Bu ligand.[15] In the present case similar field shifts in ^{1}H NMR ($\Delta\delta_{\mathrm{H},t\text{-BuOO}}$ = 0.21 ppm, $\Delta\delta_{\mathrm{H},t\text{-BuO}} \approx 0.24$ ppm) were observed while those for ^{13}C NMR ($\Delta\delta_{\mathrm{C\text{-}H},t\text{-BuOO}}$ = 5.1 ppm, $\Delta\delta_{\mathrm{C\text{-}H},t\text{-BuO}} = -1.0$ ppm) were clearly different. Although the UV and NMR results point toward a dicoordination of OO-*t*-Bu to Cr, the coordination mode of this ligand still remains uncertain since the instability of the complex has prevented an X-ray analysis.



Scheme 1

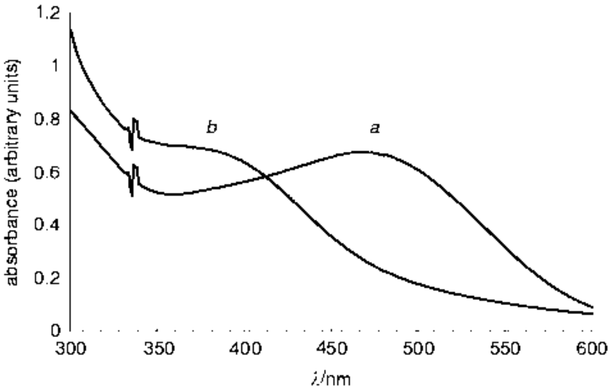


Fig. 7 UV–visible spectra of a 1 : 1 CrO_3–*t*-BuOOH mixture in BTF recorded after shaking for 2 min (*a*) and immediately after addition of 2 equivalents of $PhCH_2OH$ (*b*).

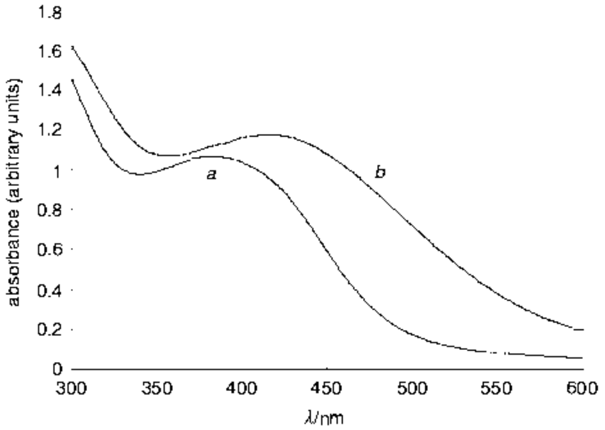


Fig. 8 UV–visible spectra of a 1 : 1 CrO_3–*t*-BuOH mixture in BTF recorded after shaking for 30 min (*a*) and immediately after addition of 6 equivalents of *t*-BuOOH (*b*).

We have previously commented on CrO_3-catalyzed oxidation of benzyl alcohol by *t*-BuOOH in CH_2Cl_2[3a] and BTF[20] in which benzaldehyde and benzoic acid are formed. It was therefore of interest to study the influence of this oxidizable substrate on the evolution of the UV–visible spectrum of these reactions. The treatment of a 1 : 1 mixture of CrO_3 and *t*-BuOOH with this alcohol (2 equiv.) induced a rapid change of the spectrum (Fig. 7, curve *a* and curve *b*); the new λ_{max}, located at *ca.* 381 nm, corresponds to the formation of the *tert*-butyl chromate complex (see Fig. 1 and Table 1). In contrast to Fig. 2, curve *a* and curve *f*, the present blue-shift is not accompanied by a decrease in ε, presumably due in part to the formation of benzaldehyde (λ_{max} = 323 nm, ε = 27 dm^3 mol^{-1} cm^{-1} in BTF). This experiment confirms that the *tert*-butylperoxychromium complex has oxidative properties towards alcohols.

The addition of *t*-BuOOH (*ca.* 6 equiv.) to a filtered[32] solution of the 1 : 1 (*t*-BuO)(HO)CrO_2–(*t*-BuO)$_2CrO_2$ mixture, obtained from run 9, Table 2, induced a red-shift of λ_{max} (Fig. 8). This seems to imply a reaction between *t*-BuOOH and the Cr-mixture and indicates the formation of *t*-BuOOCr species. Exchange reactions of *t*-BuOOH with alkoxyvanadium,[9a,10b,10d,10e] hydroxycobalt[13b,13c] and hydroxycopper[16] units, also forming *tert*-butylperoxy–metal complexes, have been reported. Therefore, an *in-situ* generation of **1** and/or (*t*-BuOO)(*t*-BuO)CrO_2 (**4**) can be envisaged. Indeed, the starting **2** + **3** mixture was at best partially transformed to **1** since the new λ_{max} value (417 nm, Fig. 8, curve *b*) was much lower than had previously been observed (λ_{max} = 471 nm). Interestingly, indan-1-ol was readily oxidized (*ca.* 20 equiv. per Cr) in BTF using *t*-BuOOH (4 equiv. per indan-1-ol) and a filtered[32] 1 : 1 mixture of **2** and **3**; by stirring this mixture at room temperature for 3 h, a yield of 80% indan-1-one was obtained. This latter experiment reflects that *tert*-butylchromate can be involved in CrO_3-catalyzed oxidation of alcohols by *t*-BuOOH. These observations lead us to propose Scheme 2 for this catalytic reaction. In this Scheme, which involves the alkoxy-*tert*-butylperoxychromium complex **A** for the key oxidation step, the Cr(VI) oxidation state is preserved for the different Cr-intermediates and two possible pathways mediate the regeneration of **1**; pathway *a* was suggested in our original report.[2] Through pathway *b* the formation of the ketone leads to a concomitant formation of CrO_3 and *t*-BuOH in a solvent cage; a reaction between these two species will then give rise to **2** and thus the active oxidizing species **1** and **4**, **4** being transformed into **A** through an exchange reaction. We believe that both pathways, *a* and *b*, are operative under our experimental conditions. Since η^2-coordination of *t*-BuOO to Cr (Scheme 1) has not been firmly established, Scheme 2 is presented with only monocoordination of this ligand. However, η^2-coordination will presumably decrease the O–O bond strength of the peroxydic ligand[33] and thus facilitate its cleavage.

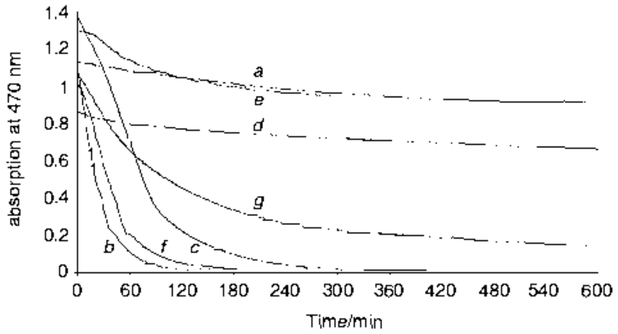
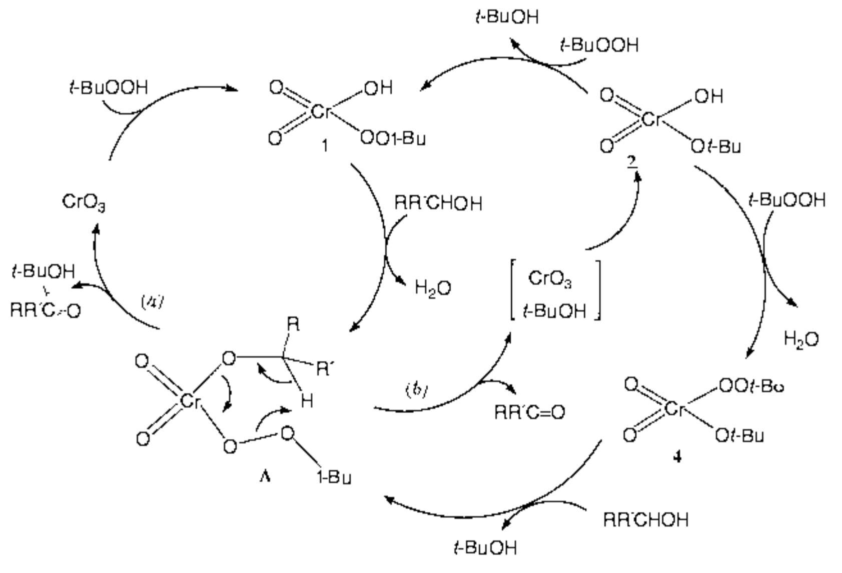


Fig. 9 Evolution at 470 nm of the UV–visible spectra of 1 : 3 CrO_3–*t*-BuOOH mixture with time in various solvents; BTF (*a*), dichloromethane (*b*), chloroform (*c*), benzene (*d*), hexane (*e*), 9 : 1 dichloromethane + BTF (*f*), 1 : 9 dichloromethane + BTF (*g*).

The visual observation that *t*-BuOOH is significantly less prone to CrO_3-induced decomposition in BTF than in CH_2Cl_2 led us to examine briefly the stability of the *in situ* CrO_3–*t*-BuOOH complex in some solvents. In Fig. 9, curves *a* and *b*, is shown the decrease in the absorption at 470 nm with time in BTF and CH_2Cl_2, respectively. Addition of some BTF to CH_2Cl_2 (ratio 1 : 9) reduced only slightly the rate of decomposition (curve *f*) from that observed in pure CH_2Cl_2 (curve *b*). Addition of some CH_2Cl_2 to BTF (ratio 1 : 9), however, caused a notable rate increase from pure BTF (curve *g*). A high rate of decomposition was also observed in $CHCl_3$ (curve *c*) while in benzene[34] and hexane (curves *d* and *e*) the decomposition of the *tert*-butylperoxychromium complex was of the same order of magnitude as in BTF. The limited stability of this complex in the chlorinated solvents, solvents which are essentially acidic in nature, may suggest that these solvents do not afford the necessary stabilization by coordination. The notable difference in the selectivity with the nature of the solvent, BTF as compared with CH_2Cl_2, for the oxidation of icos-1-en-3-ol by the CrO_3–*t*-BuOOH catalytic system[35] led us to assume that BTF is coordinated to the Cr-species.[36] BTF is known to act predominantly as a donor solvent and only as a very weak acceptor.[37] The higher stability of alkylperoxocobalt complexes in aromatic solvents than in chlorinated solvents has also been reported.[13d,38] The rapid destruction of the CrO_3–*t*-BuOOH complex in BTF by addition of acetic acid or trifluoroacetic acid may be further evidence for the lower stability of this complex in $CHCl_3$ and CH_2Cl_2 due to their acidic properties. However, numerous cases are known of degradation of metal complexes in CH_2Cl_2 and particularly $CHCl_3$ being induced by coordination of the halogenated solvent molecules.[38,39] The stability in hexane (Fig. 9, curve *e*), only slightly less than in aromatic solvents, seems to indicate that alkanes may interact



Scheme 2

weakly with this kind of coordinatively unsaturated solvent by their CH bonds, hydrogen bonds[26] or by agostic interactions.[40,41] Based upon the apparent stability of the chromium complex in hexane as shown in Fig. 9, the oxidation of indan-1-ol was examined under the usual experimental conditions.[2,20] The starting alcohol was found to be completely consumed in 23 h and indan-1-one was isolated in 46% yield. Although this yield is lower than that obtained in BTF (81%)[20] and CH_2Cl_2 (77%)[2] it is apparent that Cr(VI)-catalyzed oxidation by t-BuOOH may be also carried out in alkanes.

Conclusion

The results obtained in the present study provide evidence for the generation of a *tert*-butylperoxychromium complex from CrO_3 and t-BuOOH, a complex which can preferably be formulated as (t-BuOO)(HO)CrO_2. This complex is more stable in aromatic solvents than in chlorinated solvents. Its instability, however, presently prevents a rigorous determination of its structure. The results are consistent with this complex being the active species in the oxidation of alcohols by t-BuOOH in the presence of CrO_3.

Experimental

Purification of BTF

The sample from Rhodia appeared as a clear, colourless liquid. After treatment with CaH_2 (2 g l^{-1}) overnight, the solvent was filtered and distilled from fresh CaH_2 (1 g l^{-1}). The purified solvent was stored at +4 °C in darkness.

Anhydrous t-BuOOH[42,43]

70% t-BuOOH (10 ml) from Aldrich was added to BTF (10 ml) in a separating funnel and the mixture was swirled but not shaken to avoid the formation of an emulsion. The organic phase was separated and dried over $MgSO_4$. The concentration of the solution, 4.9 M, was determined by ^1H NMR.

NMR measurements

In a typical experiment the appropriate amount of t-BuOH or t-BuOOH was added to CrO_3 (1 mg, 0.01 mmol) in BTF (10 ml). Samples containing t-BuOH were stirred until dissolution and were stored at room temperature while samples containing t-BuOOH were used immediately. The ^1H and ^{13}C NMR spectra of the BTF solutions, *ca.* 700 µl, containing a small amount (10–20 µl) of TMS–$CDCl_3$, were recorded at 20 °C with a Bruker 500 MHz FT NMR instrument. The range of the measurements was from 0.5 to 6.5 ppm for ^1H NMR and from 0 to 100 ppm for ^{13}C NMR, embracing the aliphatic region but outside the range of the signals due to BTF to avoid saturation.

UV–visible measurements

In a typical experiment the appropriate amount of t-BuOH or t-BuOOH was added to CrO_3 (2 mg, 0.02 mmol) in BTF (4 ml). Samples containing t-BuOH were stirred up to 3 h before measurements were performed while samples containing t-BuOOH were usually measured immediately. The experiments were carried out at 20 °C using a UVIKON 941 PLUS spectrophotometer equipped with 1 cm cuvettes.

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