Catalysis Letters Vol. 91, Nos. 3–4, December 2003 (© 2003)

On the similarity in catalytic activity of homogeneous and heterogeneous Cr(VI) catalysts in the decomposition of cyclohexyl hydroperoxide

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Received 3 July 2003; accepted 5 October 2003

Pyridinium dichromate, chromium trioxide and CrAlPO-5 showed a very similar selectivity pattern in the decomposition of cyclohexyl hydroperoxide. CrAPO-5 turned out to be a real heterogeneous catalyst, most likely acting via a similar mechanism to the homogeneous catalysts. Molecular modeling indicates that heterolytic decomposition of the intermediate cyclohexyl peroxychromate ester yields cyclohexanone and H_2CrO_4 via a cyclic transition state.

KEY WORDS: CrAlPO-5; cyclohexyl hydroperoxide decomposition; molecular modeling; cyclohexane oxidation.

1. Introduction

Cyclohexyl hydroperoxide (CHHP) is a common intermediate in the liquid-phase oxidation of cyclohexane [1–3] to cyclohexanone. Selective transformation of CHHP into cyclohexanone is an important issue to improve the performance of the cyclohexane oxidation process. Cr(VI) catalysts have been recognized as good catalysts with respect to the selective decomposition of secondary hydroperoxides into ketones [4]. Despite their desirable catalytic performance, to our knowledge homogenous Cr(VI) catalysts have not found application in the industrial production of cyclohexanone due to severe environmental constraints on Cr(VI) in purge streams. The heterogeneous catalyst CrAlPO-5 therefore seemed to be a good prospect for this problem, but later it was stated that leaching of active chromium was responsible for the observed selective catalysis [5,6], and thus the environmental problem would still be there. Since leaching of transition metal out of AlPOs is highly dependent on the exact conditions during the preparation of the heterogeneous catalyst, choice of organic structure-directing agents and the actual reaction, it was decided to reinvestigate the case using pyridinium dichromate (PDC), CrO_3 and CrAlPO-5 under identical reaction conditions.

2. Experimental

2.1. Synthesis and characterization of CrAlPO-5

The following gel composition was used for the synthesis of CrAlPO-5 : 0.96 Al : 1.5 H_3PO_4 : 0.04 Cr : 0.80 TEAOH : 40 H_2O. All chemicals were purchased from Aldrich and were used without further purification. The synthesis was carried out in Teflon-lined, stainless steel autoclaves. The gel was prepared using the above composition, first by dissolving 4.16 g of $Al(OH)_3$ in 9.60 g of H_3PO_4 (85%) and 16.25 g of H_2O. 0.8892 g of Cr(III) nitrate nonahydrate was dissolved in 9.85 g of H_2O and the resulting solution was added dropwise to the $Al(OH)_3$-H_3PO_4 solution. After 45 min, 18.6997 g of tetraethyl ammonium hydroxide (TEAOH) was added dropwise to the above mixture, and the resulting gel was stirred at room temperature for 1 h before the contents were transferred to a Teflon-lined, stainless steel autoclave and heated at 165 °C for 3 h. After crystallization, the solid product was separated by filtration, dried at 100 °C for 6 h, and calcined at 550 C for 12 h, in oxygen, to remove the organic template. The X-ray diffractogram (XRD) of the calcined CrAlPO-5 catalyst is shown in figure 1.

2.2. Preparation of CHHP solution

A solution of CHHP in cyclohexane, derived from a process stream, was extracted with an aqueous solution of $NaHCO_3$ to remove all acidic compounds. Then the organic solution was dried with $MgSO_4$. The final solution contained 2.61% of CHHP, 0.10% of cyclohexanone and 1.40% of cyclohexanol.

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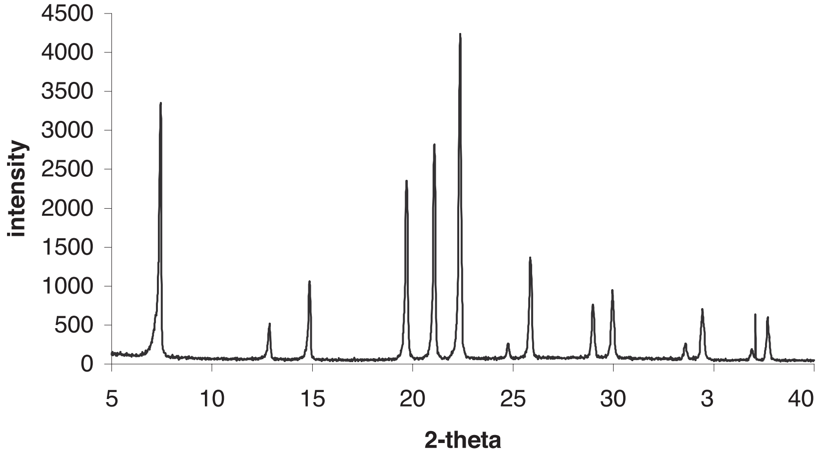

Figure 1. X-Ray diffractogram of calcined CrAlPO-5 (0.04).

2.3. *Catalytic test*

CHHP decompositions were run in a 100-mL thermostated flask equipped with a Dean-Stark apparatus and a magnetic stirrer. A dry solution of 70 g of cyclohexane containing 2.61% of CHHP was refluxed (~81 °C) under nitrogen for several hours. The required amount of the catalyst was added at reflux temperature. Samples were taken at regular intervals. The CHHP conversion was determined by iodometric titration. The reaction products were analyzed by GLC after destroying remaining CHHP with excess triphenylphosphine. The catalytic activity was arbitrarily expressed as a pseudo-first-order rate constant after 10 min:

$$k(\text{min}^{-1}) = \ln([\text{CHHP}]_0/[\text{CHHP}]_{10})/10 \text{ min}$$

2.4. *Sample preparation for chromium analysis by high resolution ICP-MS*

The hot filtrate solution (after reaction) was evaporated to complete dryness. The remaining residue was treated with 5-mL aqua regia for 12 h at 90 °C. 5 mL of H_2O_2 (31%) was added, and the solution was stored overnight. This solution was diluted (approx. 25 times) with 3% HNO_3. The samples were finally analyzed with a high-resolution Thermo/Finnigan apparatus.

2.5. *Molecular modeling*

The Titan package [7] was used for all calculations. All structures underwent complete geometrical optimization on the B3LYP level (6-31G**), starting from PM3 structures. Energies were corrected for ZPE and temperature.

3. Results and discussion

3.1. *Pyridinium dichromate (PDC) and CrO_3*

Both PDC and CrO_3 were tested in the range of 0–1500 ppm. Generally, these catalysts show very similar behavior. Figure 2 summarizes the results.

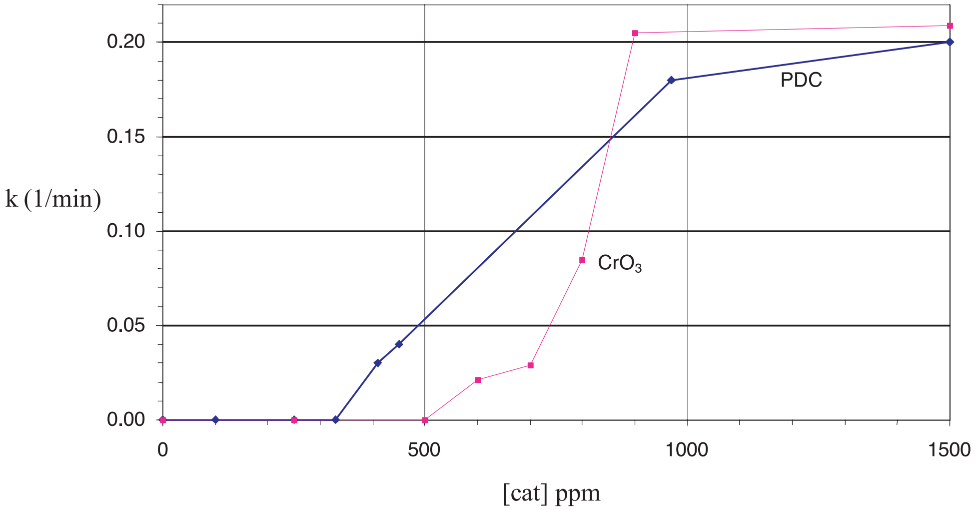

Figure 2. The relation between the concentration of CrO_3 and PDC, and their initial catalytic activity in the decomposition of CHHP.

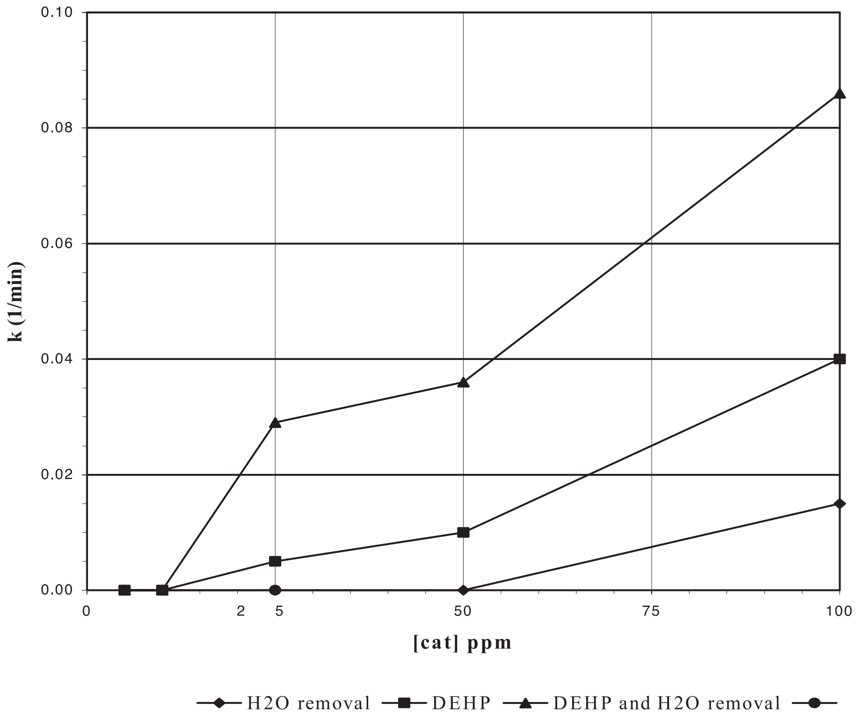

Figure 3. The influence of the addition of DEHP and water removal on the initial activity of PDC in the decomposition of CHHP.

Without azeotropic water removal, no initial activity was observed below 400 ppm. Between 400 and 1000 ppm, a more or less linear increase in activity was observed from $k = 0.03$ at 410 ppm to $k = 0.18\ \mathrm{min}^{-1}$ at 970 ppm in case of PDC. The catalytic activity of CrO_3 was observed from 600 ppm, with $k = 0.02\ \mathrm{min}^{-1}$ to the apparent maximum with $k = 0.205\ \mathrm{min}^{-1}$ at $[CrO_3]$ between 900 and 1500 ppm. It should be noted that, under these circumstances, no complete homogeneous solutions were obtained. The insoluble part of the catalysts turned from yellow-orange to brown-black.

Upon removal of azeotropic water, for PDC an initial activity with $k = 0.014\ \mathrm{min}^{-1}$ was observed at 100 ppm, but the catalyst was still not completely dissolved. To reach complete solubility, resulting in real homogeneous catalysis, diethyl hexyl phosphate (DEHP) was added in a tenfold molar excess relative to PDC. The results of these experiments are shown in figure 3. Even without azeotropic water removal, already some activity was observed at 25 ppm of PDC, while at 50 and 100 ppm, an activity of $k = 0.01$ and $0.04\ \mathrm{min}^{-1}$ respectively was observed, albeit rapidly decreasing. However, upon the addition of DEHP and azeotropic water removal, already at 25 ppm of PDC an activity of $k = 0.03\ \mathrm{min}^{-1}$ was observed, increasing to $k = 0.086\ \mathrm{min}^{-1}$ at 100 ppm.

Iodometric titration of the reaction mixture after 1 h indicated an overall CHHP conversion of 92%, corresponding with $k_{60} = 0.04\ \mathrm{min}^{-1}$. GLC analysis of the reaction mixture after destruction of the remaining CHHP yielded 2.10% cyclohexanone and 1.60% cyclohexanol, in good agreement with the observed conversion. This value also indicates almost complete selectivity of the decomposition toward cyclohexanone. The deactivation of the homogeneous Cr(VI) seemed to be a general phenomena, probably linked to the amount of water, and the presence of cyclohexanol.

3.2. *CrAlPO-5*

In a first experiment 0.59 g of the 4% CrAlPO-5 was added to 69.5 g of the CHHP solution at 81 °C. Water was removed by azeotropic distillation. Iodometric titration of the sample after 10 min indicated a conversion of 19%, corresponding with $k_{10} = 0.021\ \mathrm{min}^{-1}$. GLC analysis yielded 0.51% cyclohexanone and 3.21% cyclohexanol, again in good agreement with the titration, and again indicating almost complete selectivity of the decomposition toward cyclohexanone. After 3 h, the conversion was 58%, corresponding with $k_{180} = 0.0048\ \mathrm{min}^{-1}$.

The experiment was stopped, the catalyst was filtered off on a preheated filter at reaction temperature, and the remaining liquid was immediately refluxed again under the same conditions. No further conversion could be measured after another 24 h. Furthermore, the filtrate was evaporated to dryness, and the remainder was treated with aqua regia, and H_2O_2, in order to dissolve all possible chromium species. The sample was analyzed by high-resolution ICP-MS. Chromium was clearly detected in an absolute amount of 12 719 ng, corresponding to 0.18-ppm chromium in solution, or 0.05% leaching, relative to CrAlPO-5. Interestingly, ICP-MS of the final filtrate showed an even lower value of 2880 ng. These two low but different chromium values might

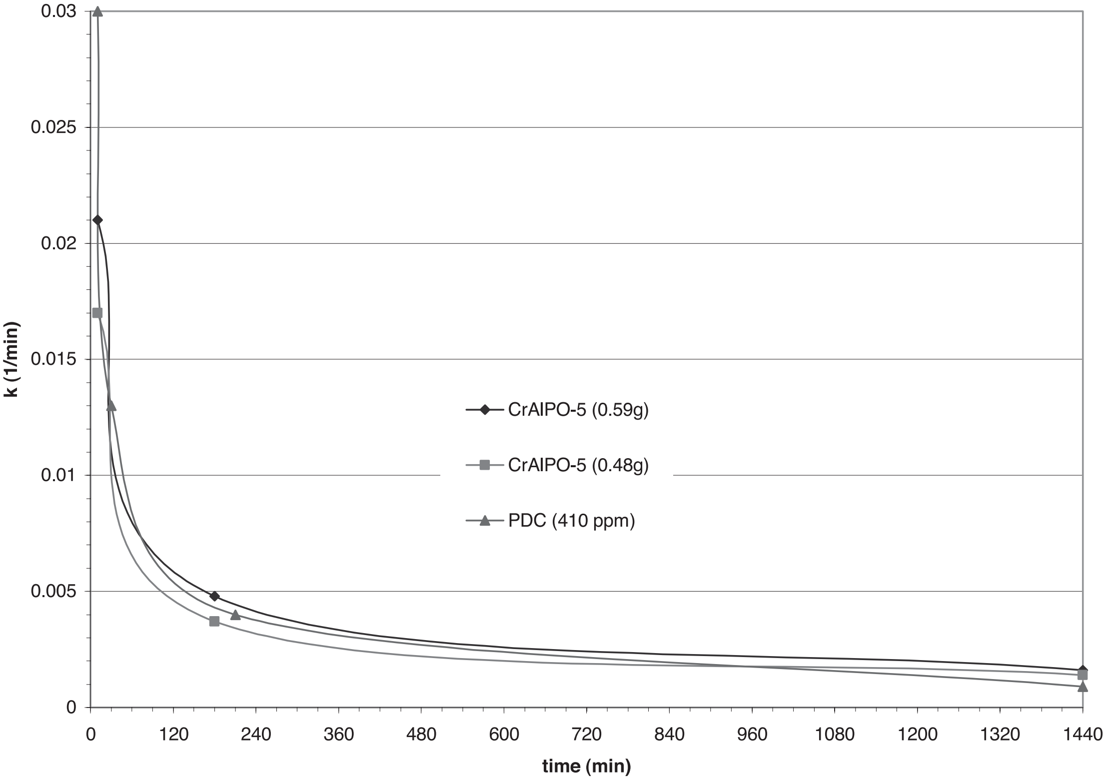

Figure 4. Plot of the catalytic activity versus time for two samples of CrAlPO-5 (0.04) and 410 ppm of PDC.

indicate either the presence of some very small particles in the sample (that might have escaped through the filter paper on hot filtration) or loosely bound chromium. The used catalyst was added to a fresh amount of 69.5 g of CHHP. After a reaction time of 24 h, the conversion was 91%, corresponding with $k_{1440} = 0.0016\ \mathrm{min}^{-1}$. A second experiment with 0.48 g CrAlPO-5 catalyst gave very similar results.

3.3. Loss of catalytic activity

The rapid loss of activity of the homogeneous Cr(VI) catalysts and CrAlPO-5 seemed to be strongly related to the amount of water in the system. Figure 4 shows the rapid decrease in the activity of the two samples, namely, CrAlPO-5 and PDC, the latter under conditions without azeotropic water removal. In the case of CrAlPO-5, water will still remain in the polar pores, and cannot be removed easily by simple azeotropic water removal. As can be easily calculated, under these conditions the activity of the homogeneous and the heterogeneous catalysts are very similar on a molar basis. 0.59 g of 4% CrAlPO-5 in 70 g of solution corresponds to 340 ppm of chromium in solution, which is fairly analogous to the 410 ppm of chromium in PDC.

3.4. Discussion and molecular modeling

Cr(VI) reagents easily form esters and (mixed) anhydrides [8]. In dilute solutions, the monomeric chromate ion is present, but as concentration increases the dichromate ion dominates. This tendency might explain why both PDC and CrO_3 exhibit such a remarkable catalytic response as a function of their concentration. Below 400 and 500 ppm, PDC and CrO_3 respectively did not show catalytic activity at all. Above approximately 900 ppm, a maximum activity was observed probably due to the maximum solubility of dimeric species in the reaction mixture. The range in between could then be explained as a gradual increase in solubility of dimeric chromate species, including the ester of CHHP and chromic acid. In the presence of hydroxylic compounds, chromium (VI) is essentially present as the ester of chromic acid. Figure 5 illustrates the reversible ester formation of CHHP and

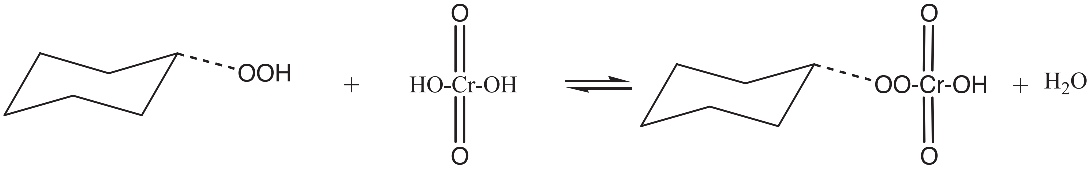

Figure 5. The equilibrium formation of cyclohexyl peroxychromate from CHHP and chromic acid.

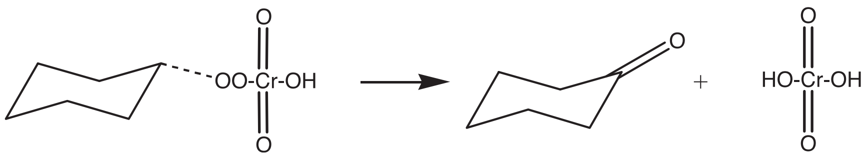

Figure 6. The irreversible formation of cyclohexanone from cyclohexyl peroxychromate.

chromic acid. No attempts were made to model the mechanism of the actual ester formation because it is uncertain where to start from, and, under these circumstances, bulk water removal seems to be the rate-controlling factor.

By azeotropic removal of water, formed as a result of the esterification, the availability of catalytically active species increased, already at a much lower concentration. The catalytic activity of Cr(VI) was further enhanced by the addition of an organic soluble ligand, diethyl hexyl phosphate (DEHP), in a tenfold excess relative to chromium. Transesterification with (di)chromic acid, leading to enhanced chromium solubility, offers an attractive explanation for the effect of DEHP. So, it seemed rather plausible to propose the cyclohexyl peroxychromate ester as a reactive intermediate. The following decomposition of the cyclohexyl peroxychromate is illustrated in figure 6.

A heterolytic mechanism was proposed [4], mainly because of the high selectivity toward ketone, but it was never accurately described. Because the kinetics of the systems that were hitherto investigated were difficult to determine, owing to phase and transport phenomena, a molecular modeling study was carried out so as to develop a better insight in the overall reaction scheme. A suitable candidate for the transition state of the decomposition of cyclohexyl peroxychromate was selected and the thermodynamics of the overall reactions were determined as well.

Computationally cheap PM3 semiempirical calculations often provide a reasonable account for chemical structures, including organometallics. However, reaction energetics are unreliable. B3LYP DFT calculations provide a good account for both structure and energetics, but are computationally more expensive. Therefore, a survey was made using PM3 calculations to obtain good starting structures for B3LYP calculations. The first step was to systematically examine a series of cyclohexyl peroxychromate conformers as suitable candidates for the transition state. The result of a series of calculations, in which the CO-OCr dihedral angle is varied, is shown in figure 7.

Starting with an *anti*-conformation of the chromate and the cyclohexyl group along the O–O axis, at a dihedral angle at −180°, the chromate was turned in a series of steps toward the cyclohexyl ring. As expected,

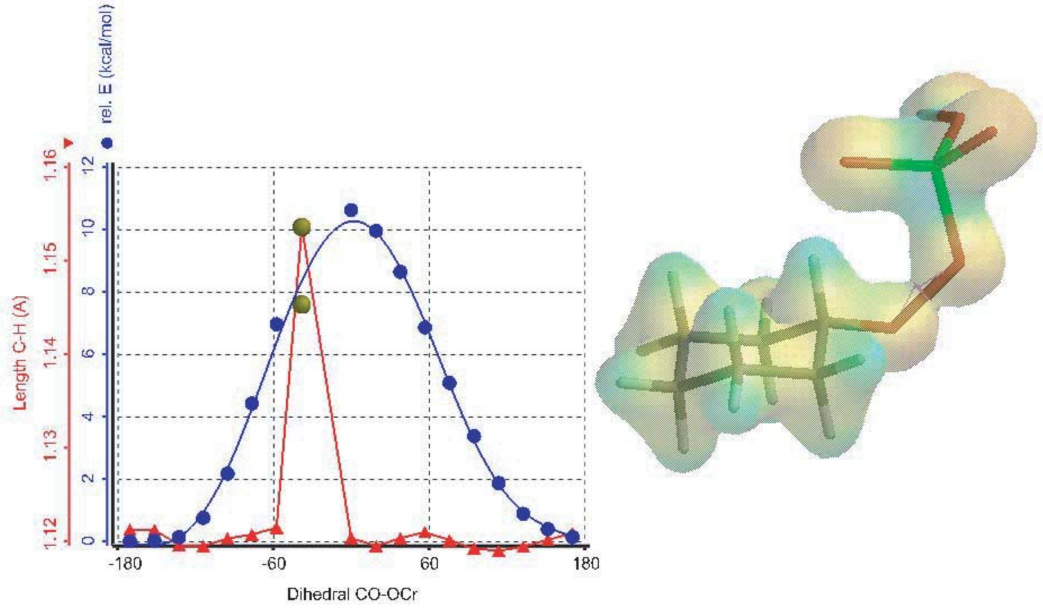

Figure 7. Energy profile of cyclohexyl peroxychromate conformers subject to the dihedral constraint CO-OCr dihedral angle. Calculations were performed on the PM3-level. The conformer shown on the right, with its elongated α-CH-bond (red curve) as indicated in the graph with golden markers, was chosen as the candidate transition state.

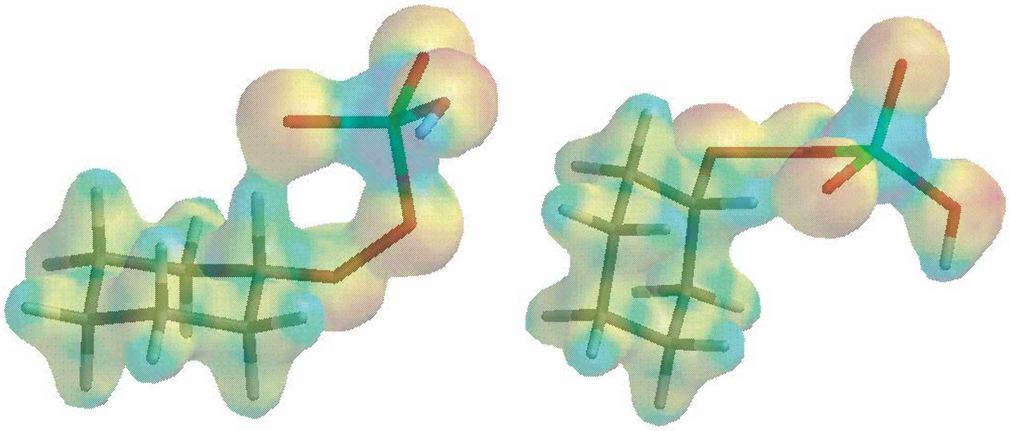

Figure 8. Two views of the transition state of the decomposition of cyclohexyl peroxychromate, (a) showing proton transfer to the chromate oxygen , and (b) the chair geometry of the transition state. Calculation: B3LYP (6-31G**); surface: density bond; property: electrostatic potential. There is one imaginary frequency at 921.19 cm^{-1}.

the highest energy conformer (+10.6 kcal/mol) was observed in the eclipsed conformation at 0^0. Thereafter, the curve goes almost symmetrically down to arrive at the *anti*-conformation again at +180°. Apart from the relative energy, the C–H distance of the α-carbon of the peroxy ester is also listed. It shows a distinct elongation between –60 and 0° of the CO-OCr dihedral angle, indicative of a possible hydrogen transfer to a chromate oxygen. In fact, the conformers with a dihedral angle of –18.9 and –0.1° "decompose" into cyclohexanone and chromic acid on geometry optimization. Thus, a candidate for the transition state was easily selected. The transition state was optimized on the B3LYP level, using the PM3 transition state geometry as input. The transition State is shown in figure 8.

The geometry of the transition state can be described as a chair. The O–O distance is 1.632 Å, the C–O distance is 1.343 Å, and the C–H distance is 1.225 Å. The process is rather concerted with C–H, and O–O bond breaking, and O–H bond formation taking place simultaneously. The hydrogen is transferred as a proton. The activation energy at 80 °C is 15.6 kcal/mol. Figure 9 gives an overview of the reaction energetics of both cyclohexyl peroxychromate ester formation from CHHP

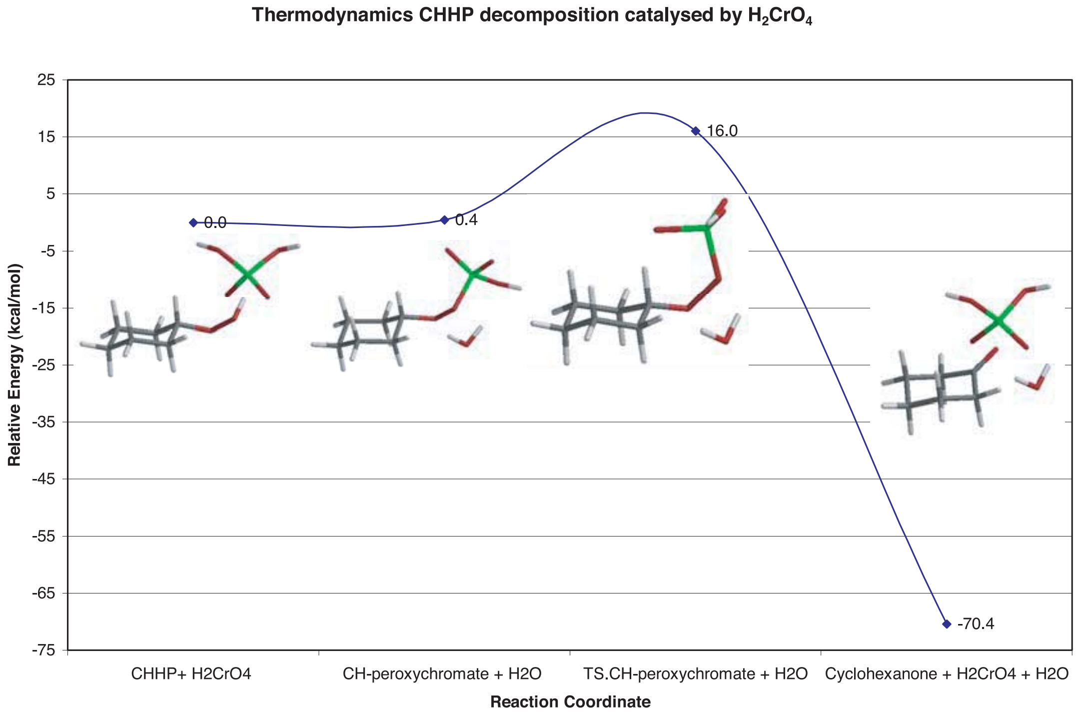

Figure 9. Energy profile (DFT, B3LYP) of the CHHP decomposition into cyclohexanone and water via the formation of cyclohexyl peroxychromate. The activation energy is 15.6 kcal/mol at 81 °C.

and H_2CrO_4, and its decomposition into cyclohexanone and H_2CrO_4. It should be noted that a very similar transition state was proposed for the oxidation of an alcohol by Cr(VI) [9,10], but attempts to establish such a transition state, using molecular modeling, have failed so far.

From figure 9, it can be concluded that the ester formation is indeed an equilibrium process at 80 °C with an equilibrium constant of 0.6 (reaction energy of +0.4 kcal/mol). Thus, DFT calculations fully support the explanation put forward above that bulk azeotropic water removal enhances catalytic activity by shifting the ester equilibrium. Furthermore, the decomposition to cyclohexanone is highly exothermic: –70.4 kcal/mol.

It is tempting to speculate that CrAlPO-5 might react via the same mechanism as the homogeneous Cr(VI) catalyst, owing to the presence of at least a fraction of Cr(VI) in the AlPO, and also the similarity in selectivity pattern and the deactivation behavior. An obvious way to enable such a mechanism would be the substitution of a phosphate, rather than an Al^{3+}, by a chromate. Molecular modeling calculations show that at least the size of these two anions are very similar: V-phosphate = 80.86 [3], and V-chromate = 80.81[3]. The difference in charge can easily be accommodated with an additional OH^-. Especially in the very polar AlPO-environment (reversible) deactivation by water stuck to the pores could explain the first stage of rapid loss of activity. Slow oxidation of the relatively nonpolar cyclohexanol might explain the ongoing slow deactivation of both the homogeneous and the heterogeneous catalysts.

Finally, it should be kept in mind that even in the presence of DEHP, homogeneous Cr(VI) only starts to show activity at 25 ppm. This value is in sharp contrast with our observed results even at the highest amount of (soluble) chromium analyzed in the filtrate by ICP-MS, which corresponds to 0.18 ppm in solution. This augurs well with the absence of catalytic activity in the hot filtrate after removal of the heterogeneous catalyst. These values are also approximately six times lower than that reported by Lempers and Sheldon [11,12]. Hence, it seems very unlikely that the activity of CrAlPO-5 is due to leaching of the catalytically active chromium species.

4. Conclusion

On the basis of the experimental data, it can be concluded that homogeneous Cr(VI) catalysts decompose CHHP into cyclohexanone via esterification to cyclohexyl peroxychromate, followed by intramolecular elimination of chromic acid. DFT calculations on the B3LYP level fully support this view. The CrAlPO-5 used in this study behaved like a true heterogeneous catalyst, showing a similar selectivity and deactivation pattern as the homogeneous Cr(VI) catalysts.

Acknowledgments

We thank the EPSRC (UK) for a rolling grant to John Meurig Thomas and Bayer AG, Leverkusen, Germany for their financial support to Robert Raja.

References

[1] R. Raja and P. Ratnasamy, Catal. Lett. 48 (1997) 1.
[2] M. Dugal, G. Sankar, R. Raja and J.M. Thomas, Angew. Chem., Int. Ed. Engl. 39 (2000) 2310.
[3] R. Raja, G. Sankar and J.M. Thomas, J. Am. Chem. Soc. 121 (1999) 11926.
[4] M. Constantini, E. Fache and L. Gilbert, (Rhone-Poulenc Chimie) French Patent FR 2 744 719-A1 (1996).
[5] J.D. Chen, J. Dakka and R.A. Sheldon, Appl. Catal. A 108 (1994) L1–L6.
[6] R.A. Sheldon, in *3rd World Congress on Oxidation Catalysis*, (Elsevier Science, Amsterdam, 1997) p. 151–175.
[7] Titan was obtained from Wavefunction Inc. (Irvine, CA).
[8] F.A. Carey and R.J. Sundberg, in *Advanced Organic Chemistry Part B* (Plenum, 1979) p. 481–485.
[9] J. Muzart, Chem. Rev. 92 (1992) 113.
[10] J. Muzart, Tetrahedron Lett. 28 (1987) 2133.
[11] H.E.B. Lempers and R.A. Sheldon, J. Catal. 175 (1998) 62.
[12] R.A. Sheldon, M. Wallau, I.W.C.E. Arends and U. Schuchadt, Acc. Chem. Res. 31 (1998) 485.