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Effect of an Ionic Liquid on the Catalytic Performance of Thiocyanatodioxomolybdenum(VI) Complexes for the Oxidation of Cyclooctene and Benzyl Alcohol

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Abstract The complexes $(PPh_4)_2[Mo^{VI}O_2(NCS)_4]$ (**1**), $Mo^{VI}O_2(NCS)_2$(di-*t*Bu-bipy) (**2**) and $Mo_2^{VI}O_5(NCS)_2$(di-*t*Bu-bipy)$_2$ (**3**) (di-*t*Bu-bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) were studied as catalyst precursors for the oxidation of cyclooctene (Cy8) and benzyl alcohol (BzOH), using either dimethyl sulfoxide (DMSO) or *tert*-butyl hydroperoxide (TBHP) as oxidant. By dissolving complex **2** in the room temperature ionic liquid 1-butyl-3-methylpyridinium tetrafluoroborate, the catalytic performance with TBHP was improved (higher selectivity to the aldehyde and higher Cy8 conversions). For Cy8 oxidation, the unreacted substrate and products were easily extracted with *n*-hexane, and the ionic phase containing the catalyst could be reused without loss of catalytic performance.

Keywords Molybdenum · Thiocyanate · Dimethyl sulfoxide · *tert*-Butyl hydroperoxide · Ionic liquids

1 Introduction

High-valent molybdenum oxo compounds are of great importance as catalysts for oxygen atom transfer (OAT) reactions, both in nature as well as in industrial processes [1–4]. The first clear indication of molybdenum-mediated oxo transfer was the catalytic aerial oxidation of tertiary phosphines in the presence of the dithiocarbamate complex, $Mo^{VI}O_2(S_2CNEt)_2$ [5, 6]. This complex is also able to catalyse the OAT from dimethyl sulfoxide (DMSO) to triphenylphosphine, which is a frequently used model reaction [7, 8]. One of the simplest complexes that catalyses the oxidation of Ph_3P by DMSO is the thiocyanate complex, *cis*-$[Mo^{VI}O_2(NCS)_4]^{2-}$ (Chart 1). Arzoumanian and co-workers found that the tetraphenylphosphonium salt, $(PPh_4)_2[Mo^{VI}O_2(NCS)_4]$ (**1**), catalysed the model reaction approximately 20 times more efficiently than $Mo^{VI}O_2(S_2CNEt)_2$ [9]. In an attempt to improve the oxidising power of the anion $[Mo^{VI}O_2(NCS)_4]^{2-}$, the same group reacted **1** with various bipyridines and obtained, in the case of 4,4′-di-*tert*-butyl-2,2′-bipyridine, the neutral monomer $Mo^{VI}O_2(NCS)_2$(di-*t*Bu-bipy) (**2**) [10, 11] with exceptional OAT properties, not only towards phosphines, but also towards arylalkanes and alcohols [12, 13]. These oxidation reactions become catalytic in the presence of DMSO. During the reaction of **1** with di-*t*Bu-bipy, oxo-ligand redistribution gives rise to trace quantities of the μ-oxo dimer $Mo_2^{VI}O_5(NCS)_2$(di-*t*Bu-bipy)$_2$ (**3**). The direct synthesis and crystal structure of **3** were reported in 1999 [15], and ab initio theoretical calculations have been carried out recently [16].

The low cost and ready availability of DMSO make it quite attractive as an OAT agent. In addition, the side-product dimethyl sulfide is a weakly coordinating ligand and will not inhibit the catalyst as the reaction proceeds [17]. However, Me_2S would be unpleasant in large-scale applications [18]. To the best of our knowledge, the ability of **1**–**3** to catalyse the oxidation of alcohols in the presence of oxygen atom donors other than DMSO has not been reported. Nevertheless, there are several examples in the literature where oxomolybdenum(VI) complexes catalyse the oxidation of alcohols using oxidants such as hydrogen

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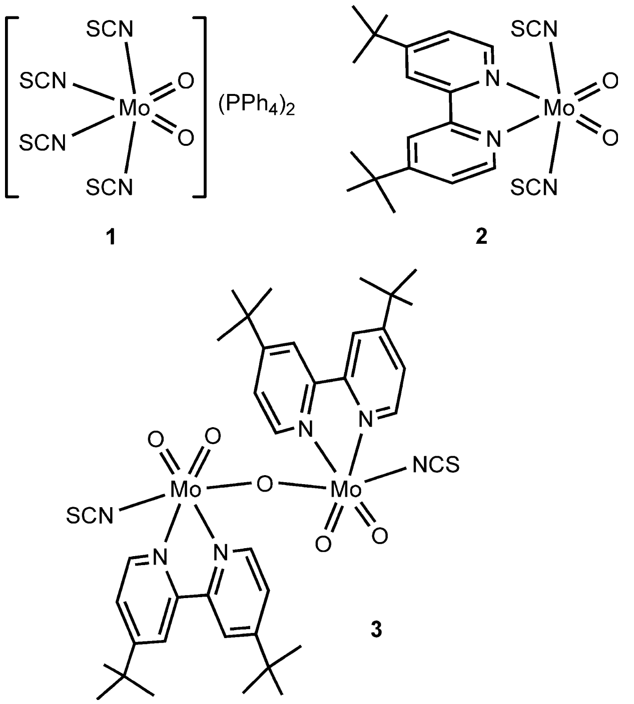

Chart 1

peroxide (H_2O_2), molecular oxygen and *tert*-butyl hydroperoxide (TBHP) [19–22]. The first objective of the work described herein was therefore to compare DMSO, iodosobenzene (PhIO), H_2O_2 and TBHP as oxidants in the oxidation of benzyl alcohol and cyclohexanol with **1**–**3** as catalyst precursors. The second objective was to examine the role of **1**–**3** in the catalytic epoxidation of cyclooctene with TBHP. Brito et al. found that the analogous complexes $Mo^{VI}O_2(NCS)_2L$ and $Mo_2^{VI}O_5(NCS)_2L$ containing chiral oxazolines or (in the case of the dimer) 2,2′-bipyridine exhibit moderate activity as catalyst precursors for the epoxidation of cyclooctene, norbornene and (*R*)-limonene at room temperature, using TBHP in water as oxidant [23, 24]. These authors concluded that the presence of labile ligands like thiocyanate was required to give active catalytic systems. To the best of our knowledge, the only report of liquid-phase olefin epoxidation catalysed by complexes **1**–**3** concerns a reference to unpublished results for the reaction of styrene with **2** under UV irradiation and in the presence of Ph_2SO [13]. A theoretical study of ethylene oxidation in the presence of the dimeric complex **3** was recently reported [25].

In an effort to improve the recyclability of **1**–**3** for the liquid-phase catalytic oxidation reactions, we have studied a pyridinium-based ionic liquid as a solvent for the molybdenum complexes. This method provides a non-aqueous alternative for two-phase catalysis, in which the catalyst is “immobilised” and easily separated from the products [26–28]. Promising results have been reported for cyclooctene epoxidation using various room temperature ionic liquids (RTIL) as reaction solvents, TBHP [29, 30] or urea–hydrogen peroxide adduct [31] as oxidants, and molybdenum(VI) complexes as catalysts. Another report showed that the RTIL molybdate $[BMI]_2[Mo^{VI}O_2(NCS)_4]$ (BMI = 1-butyl-3-methylimidazolium) could be used as a self-supported catalyst in the biphasic oxidation of Ph_3P in the presence of DMSO [32]. In the present work, we demonstrate that the use of 1-butyl-3-methylpyridinium tetrafluoroborate, $[BMPy]BF_4$, as a solvent for complexes **1**–**3** greatly improves the catalytic performance in the oxidation of benzyl alcohol and the epoxidation of cyclooctene with TBHP.

2 Experimental

2.1 Materials and Methods

Microanalyses for CHN were carried out at the Department of Chemistry, University of Aveiro (by M.M. Marques). FTIR spectra using KBr pellets were obtained on a Mattson-7000 infrared spectrophotometer with 2 cm^{-1} resolution. Raman spectra were recorded on an RFS-100/S Bruker FT-spectrometer, using a Nd:YAG laser (Coherent compass-1064/500) with an excitation wavelength of 1,064 nm and 4 cm^{-1} resolution.

Diethyl ether and *n*-hexane (purity p.a., Riedel de Haën), anhydrous dichloromethane and anhydrous tetrahydrofuran (Aldrich), Na_2MoO_4 (Aldrich), KSCN (Panreac), HCl (Panreac, 37%), tetraphenylphosphonium chloride (Aldrich), 4,4′-di-*tert*-butyl-2,2′-bipyridine (Aldrich), $[BMPy]PF_6$ and $[BMPy]BF_4$ (Merck) were purchased from commercial sources and used as received. $(PPh_4)_2[Mo^{VI}O_2(NCS)_4]$ (**1**) [9], $Mo_2^{VI}O_5(NCS)_2$(di-*t*Bu-bipy) (**3**) [15] and MoO_2Cl_2(di-*t*Bu-bipy) (**4**) [33] were prepared according to literature procedures. Infrared and elemental analyses were in agreement with the expected formulations: For complex **1**, $\nu(NCS) = 2{,}098$ s, 2,054 s cm^{-1}; $\nu(Mo = O) = 920$ s, 883 s cm^{-1}; $C_{52}H_{40}N_4O_2P_2S_4Mo$ requires C 60.11, H 3.88, N 5.39, S 12.34; found C 60.01, H 4.01, N 5.18, S 12.52. For complex **3**, $\nu(NCS) = 2049$vs cm^{-1}; $\nu(bipy) = 1{,}612$ s, 1,546 m; $\nu(Mo = O) = 934$ s, 903vs cm^{-1}; $\nu(Mo–O–Mo) = 769$ s cm^{-1}; $C_{38}H_{48}N_6O_5S_2Mo_2$ requires C 49.35, H 5.23, N 9.09, S 6.93; found C 49.52, H 5.44, N 9.01, S 7.02. For complex **4**, $\nu(bipy) = 1{,}612$ s, 1,547 m; $\nu(Mo = O) =$ 940vs, 908vs cm^{-1}; $C_{18}H_{24}N_2Cl_2O_2Mo$ requires C 46.27, H 5.18, N 6.00; found C 46.40, H 5.33, N 5.91. $Mo^{VI}O_2(NCS)_2$(di-*t*Bu-bipy) (**2**) was prepared by the reaction of **1** with one equivalent of di-*t*Bu-bipy in dichloromethane at room temperature for 4 h [11]. Upon addition of diethyl ether to the resultant yellow solution, tetraphenylphosphonium thiocyanate was precipitated, filtered off, and compound **2** obtained as a yellow precipitate by addition of *n*-hexane to the filtrate. Selected IR (cm^{-1}): ν(Mo = O) 903vs, 934 s; ν(bipy) 1,413 s, 1,544 m, 1,614 s; ν(NCS) 2011vs. Selected Raman (cm^{-1}): ν(Mo = O) 902 m, 932vs; ν(bipy) 1,544 m, 1,612 m; ν(NCS) 2004vw, 2,045 m. $C_{20}H_{24}N_4O_2S_2Mo$ requires C 46.87, H 4.72, N 10.93, S 12.51; found C 46. 58, H 4.92, N 10.74, S 12.68.

2.2 Liquid-Phase Oxidation of Alcohols and Olefins Using **1–3** as Catalyst Precursors

The liquid-phase catalytic reactions were carried out at atmospheric pressure in a reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath. The substrates used were cyclohexanol (Cy6OH), benzyl alcohol (BzOH) and cyclooctene (Cy8), and the oxygen donors were DMSO, PhIO, aqueous H_2O_2 (30%) and TBHP in decane (5.5 M). Unless otherwise stated, the reactions were carried out without additional solvent. The course of the reaction was monitored using a Varian 3800 GC equipped with a capillary column (DB-5, 30 m × 0.25 mm for the reactions of cyclooctene and CP WAX 52CB, 30 m × 0.53 mm for oxidation of alcohols) and a flame ionisation detector. The products were quantified using *n*-nonane or undecane as internal standards (added after the reaction). The products were identified by GC-MS (Trace GC 2000 Series (Thermo Quest CE Instruments)—DSQ II (Thermo Scientific)), using He as the carrier gas.

3 Results and Discussion

3.1 Liquid-Phase Oxidation of Alcohols

*3.1.1 Catalytic Performance of **1–3** Using DMSO as Oxidant*

The catalytic performance of **1–3** was investigated for the oxidation of cyclohexanol and benzyl alcohol at 80 °C with DMSO as the oxidant and no additional solvent. Substrate:oxidant:MC (MC = molybdenum(VI) complex) molar ratios of 9.6:0.7:0.01 and 9.3:0.7:0.01 were used for BzOH and Cy6OH. Under these conditions, which are equivalent to those used by Arzoumanian et al. for the oxidation of alcohols with **2** [12], the reactions of Cy6OH and BzOH gave cyclohexanone and benzaldehyde as the only reaction products, with no further oxidation to acids. Control experiments for both substrates showed that no reaction occurred in the absence of **1–3**. When no oxidant was added, the reactions of BzOH and CyOH in the presence of **1–3** were very slow, giving turnover numbers (TON) at 24 h in the range of 1–5 $\mathrm{mol_{sub}\ mol_{MC}^{-1}}$.

The reaction of Cy6OH with DMSO in the presence of **1–3** was very sluggish and the results were similar to those obtained in the absence of DMSO (Table 1, entries 2/5/8). The three complexes were much more active in the oxidation of BzOH, giving TONs in the range of 10–14 $\mathrm{mol_{BzOH}\ mol_{MC}^{-1}}$ at 3 h and 44–46 $\mathrm{mol_{BzOH}\ mol_{MC}^{-1}}$ at 24 h, with benzaldehyde yields (based on DMSO) of 14–19 and 63–66% (Table 1, entries 1/3/7). The higher reaction rates achieved in the presence of an oxidant relative to those achieved in its absence indicate that the conversion into benzaldehyde is an oxidative dehydrogenation (OD) reaction. In contrast to that reported for the oxidation of Ph_3P with DMSO in the presence of **1** and **2** [12], where the neutral complex **2** was more active than the anionic complex **1**, both complexes give similar results with BzOH as the substrate. Possibly, for these complexes, the reaction mechanism of OD of alcohols is different from that for the OAT reaction to Ph_3P with DMSO. The benzaldehyde yield of 17% at 3 h for **2** is in line with the 11% yield at 1 h reported by Arzoumanian et al. for the same reaction system and conditions [12]. Increasing the amount of DMSO in this system to give an initial substrate:oxidant molar ratio of 1:1 led to a nearly threefold increase in TON, with benzaldehyde as the only product (Table 1, entry 4). Conversely, for Cy6OH, no improvement in the reaction rate was observed by increasing the amount of oxidant (entry 6). These results are consistent with earlier observations about the difficulty in oxidising aliphatic alcohols like Cy6OH relative to benzylic alcohols like BzOH [12].

The results obtained for the systems BzOH/DMSO/**1–3** contrast with those reported for $MoO_2Cl_2(DMSO)_2$, performed with continuous bubbling of oxygen in DMSO under reflux, where no reaction of BzOH was detected [21]. On the other hand, $MoO_2(acac)_2$ is able to catalyse the selective oxidation of BzOH to benzaldehyde (at 100 °C) using DMSO both as oxidant and solvent [18]. To check whether molecular oxygen could play a role in the oxidation of BzOH in the presence of DMSO and **2**, the micro-reactor containing the reaction mixture BzOH/DMSO/**2** (9.6:9.6:0.01) was purged with nitrogen before heating to the reaction temperature of 80 °C. Conversion at 24 h was 11% compared to 14% when the reaction was performed under air, suggesting that molecular oxygen does not play a major role in the OD of BzOH with these complexes.

In an attempt to characterise the major species present during the catalytic reactions involving **2**, an experiment was performed where DMSO and **2** were mixed in a molar ratio of 0.7:0.01 and heated at 80 °C for 6 h. The FTIR spectrum of the resultant solution showed one medium intensity absorption band characteristic of thiocyanate groups (2,065 cm^{-1}), two weak bands in the Mo = O stretching region (902 and 932 cm^{-1}), and one weak band

Table 1 Liquid-phase oxidation of benzyl alcohol (BzOH) and cyclohexanol (Cy6OH) using **1**–**3** as catalyst precursors

Entry	Sub/Ox/MC[a]	Sub:Ox:MC[a] (mole ratio)	T[b] (°C)	TON[c]	Yield[d] (%)	Select[e] (%)
1	BzOH/DMSO/**1**	9.6:0.7:0.01	80	14/44	19/63	100/100
2	Cy6OH/DMSO/**1**	9.3:0.7:0.01	80	3/5	4/7	100/100
3	BzOH/DMSO/**2**	9.6:0.7:0.01	80	13/46	17/66	100/100
4	BzOH/DMSO/**2**	9.6:9.6:0.01	80	–/132	–/14	0/100
5	Cy6OH/DMSO/**2**	9.3:0.7:0.01	80	3/4	4/5	100/100
6	Cy6OH/DMSO/**2**	9.3:9.3:0.01	80	3/5	4/6	100/100
7	BzOH/DMSO/**3**	9.6:0.7:0.01	80	10/45	14/65	100/100
8	Cy6OH/DMSO/**3**	9.3:0.7:0.01	80	3/3	4/3	100/100
9	BzOH/PhIO/-	2.5:0.3:0	80	–	60/78	100/100
10	BzOH/PhIO/**2**	2.5:0.3:0.02	80	10/15	68/74	100/75
11	BzOH/PhIO/-	2.5:0.3:0	55	–	–/58	0/100
12	BzOH/PhIO/**2**	2.5:0.3:0.02	55	–	–/55	0/100
13	BzOH/TBHP/-	9.6:0.7:0	55	–	20/32	100/100
14	BzOH/TBHP/**2**	9.6:0.7:0.01	55	20/70	29/78	100/78
15	BzOH/TBHP/-	9.6:0.7:0[f]	55	–	0/52	0/79
16	BzOH/TBHP/**2**	9.6:0.7:0.01[f]	55	9/70	13/90	100/89

[a] Sub, substrate; Ox, oxidant; MC, molybdenum complex

[b] Reaction temperature

[c] Turnover number calculated for 3 and 24 h reaction ($\mathrm{mol_{Sub}\ mol_{MC}^{-1}}$)

[d] Yield to the carbonyl product (benzaldehyde from BzOH, cyclohexanone from Cy6OH) for 3 and 24 h reaction, calculated as (moles of carbonyl product/moles of oxidant) × 100

[e] Selectivity to the carbonyl product (benzaldehyde from BzOH, cyclohexanone from Cy6OH) for 3 and 24 h reaction

[f] 1.8 mmol of BzOH and 100 μL of $[\mathrm{BMPy}]\mathrm{BF}_4$ as solvent

for a molybdenum μ-oxo group (770 cm^{-1}). The ν(NCS) band is shifted to higher frequency relative to that for **2** (2,011 cm^{-1}). The similarity between these bands and those exhibited by the μ-oxo dimer **3** (770, 905, 940 and 2,065 cm^{-1}) leads to the conclusion that dimerisation of the monomer **2** is likely to occur under the catalytic reaction conditions used for the oxidation of BzOH.

3.1.2 *Influence of the Type of Oxidant on the Catalytic Performance of* **2**

The catalytic performance of **2** for the oxidation of BzOH was tested using PhIO, TBHP and H_2O_2 as oxidants. PhIO oxidises BzOH to benzaldehyde in non-catalytic reactions [34]. For example, Paraskevopoulou et al. reported a BzOH conversion of 19% for the reaction of equimolar amounts of BzOH and PhIO in CH_2Cl_2 at room temperature for 24 h [34]. Accordingly, with an initial BzOH:PhIO molar ratio of about 8.3, we found that the oxidation of BzOH at 80 °C took place to a significant extent in the absence of a catalyst, giving benzaldehyde as the only product in 78% yield (based on PhIO) at 24 h (Table 1, entry 9). Iodobenzene was detected as a side-product of the decomposition of PhIO. When **2** was included in the starting mixture (0.8 mol% with respect to BzOH), benzaldehyde yield was similar (entry 10), and dibenzyl ether was formed as a by-product in ca. 25% selectivity. The formation of dibenzyl ether in the presence of $Al(OH)_3$ containing molybdenum species was previously attributed to the reaction of benzyl alcohol over acid sites [35]. Hence, in the case of **2**, the Lewis acidity of the $\mathrm{Mo^{VI}}$ centre may be responsible for this side reaction. Decreasing the reaction temperature to 55 °C gave benzaldehyde as the only product in similar yields with or without **2** in the starting mixture (Table 1, entries 11/12). When aqueous H_2O_2 (30%) was used as the oxidant, no reaction took place in the presence of **2**. Based on these results, PhIO and H_2O_2 are not attractive oxidants for OD reactions using **2** as a catalyst precursor.

As found for PhIO, TBHP in decane (5.5 M) oxidises BzOH to benzaldehyde in non-catalytic reactions (Table 1, entry 13). With an initial BzOH:TBHP molar ratio of 9.6:0.7, the oxidation proceeded selectively at 55 °C to give benzaldehyde in 32% yield (based on TBHP) after 24 h. In contrast to the results with PhIO, the reaction was faster with complex **2** present in the starting mixture (entry 14), giving benzaldehyde as the only reaction product in 29% yield after 3 h (based on TBHP). The yield reached 78% after 24 h, at which point all of the oxidant was consumed and benzyl-*tert*-butyl ether was present as a by-product. Control experiments carried out in the absence of substrate showed (by iodometric titration) no significant decomposition of TBHP after 24 h at 55 °C. When the reaction was carried out in the presence of equimolar amounts of substrate and the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol, no decrease in the reaction rate was observed, suggesting that the reaction mechanism does not involve free radicals. The activation of TBHP may take place via complexation to the molybdenum complex, followed by proton abstraction of BzOH to give benzaldehyde, *tert*-butanol and water. Comparing the results obtained with DMSO at 80 °C or TBHP at 55 °C (Table 1, entries 3/14), and the same BzOH:oxidant:**2** molar ratio, the TON and benzaldehyde yield at a given residence time were higher when TBHP was used as the oxidant, but selectivity to benzaldehyde was lower (for residence times longer than 3 h).

With Cy6OH as substrate no improvement in catalytic activity was observed when PhIO or TBHP were used instead of DMSO.

3.1.3 Ionic Liquid-Standing Complex 2

When [BMPy]BF$_4$ was used as a solvent for the system BzOH/TBHP/**2** (9.6:0.7:0.01) at 55 °C, the TON at 24 h was 70 mol$_{\mathrm{BzOH}}$ mol$_{\mathrm{MC}}^{-1}$, which is unchanged from that observed in the absence of the ionic liquid (Table 1, entries 14/16). Although benzyl-*tert*-butyl ether was still formed as a by-product, the selectivity to the carbonyl product was higher, giving 90% benzaldehyde yield at 24 h compared with 78% in the absence of [BMPy]BF$_4$. Without a catalyst, the BzOH/TBHP/RTIL reaction system gave considerably lower TON and benzaldehyde yield at 24 h, with benzyl benzoate formed as the only by-product in 21% selectivity (entry 15). When TBHP was used in excess relative to the substrate (BzOH:TBHP:**2** molar ratio = 1.8:2.7:0.018), BzOH conversion at 24 h was 38% (Fig. 1) with 70% selectivity to benzaldehyde; the by-products were benzyl-*tert*-butyl ether (10% selectivity), dibenzyl ether (13% selectivity) and benzyl benzoate (7%). Under similar conditions but in the absence of **2**, the reaction was slower, giving 11% conversion at 24 h, and the products were benzaldehyde (65% selectivity) and benzyl benzoate (35% selectivity) (Fig. 1).

3.2 Liquid-Phase Oxidation of Cyclooctene

*3.2.1 Catalytic Performance of **1–3** Using TBHP as Oxidant*

The catalytic activity of **1–3** was studied in the oxidation of cyclooctene at 55 °C using TBHP in decane (5.5 M) as oxidant, no additional solvent, and a Cy8:TBHP:MC molar ratio of 1.8:2.7:0.018. Under these conditions, **1** is poorly soluble (yellow solid in suspension), **2** is completely soluble (yellow solution) and **3** is partially soluble (yellow mixture). The reaction does not take place to a measurable extent without a molybdenum complex. With **1–3** present in the starting mixture, olefin conversions were 25–52% at 6 h and 31–64% at 24 h (Table 2, entries 1/3/5). The reaction rates for the neutral complexes **2** and **3** bearing the bipyridine ligand were higher than that for the ionic, less soluble complex **1**. When the reaction using **2** was performed in the presence of TBHP in water (70%), the kinetic profile of cyclooctene conversion (not shown) was practically coincident with that obtained for the reaction using TBHP in decane. For **2** and **3**, 1,2-epoxycyclooctane was the only reaction product up to about 45 and 25% conversion, respectively, and thereafter epoxide selectivity decreased to 80 and 94% at ca. 50% conversion (Table 2). In the case of **1**, epoxide selectivity decreased drastically from 99% at 11% conversion to 3% at 31% conversion. The by-products included 1,2-cyclooctanediol and 1-(*tert*-butylperoxy)-2-cyclooctene.

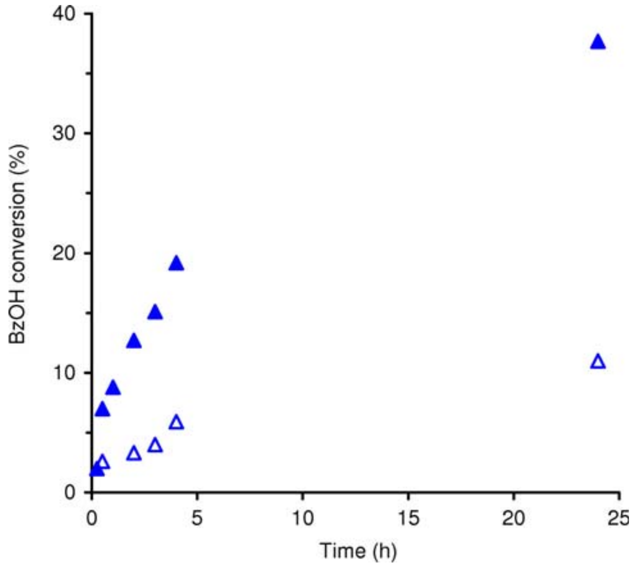

Fig. 1 Kinetic profile of the reaction of benzyl alcohol with TBHP using [BMPy]BF$_4$ as solvent, without a catalyst (Δ) or with **2** present in the starting mixture (▲). Reaction conditions: 55 °C, BzOH:TBHP:**2** molar ratio = 1.8:2.7:0.018, 1.8 mmol of BzOH, 100 μL of [BMPy]BF$_4$

The stability of each catalyst was investigated by recharging the reaction mixture at 24 h with the same amounts of oxidant and substrate used initially, and monitoring the reaction for a further 24 h. For **2** and **3**, the initial TOFs increased between the first and second runs, and epoxide selectivity decreased (especially for **2**; Table 2, entries 3/4 and 5/6). As shown in Fig. 2, the kinetic curves after 30 min are practically coincident for **2**, whereas for **3** the reaction in the second run is slower. For

Table 2 Liquid-phase oxidation of cyclooctene using **1**–**4** as catalyst precursors and, optionally, an ionic liquid [BMPy]*X* ($X = BF_4^-$, PF_6^-)[a]

Entry	Sample	TOF[b] (mol mol_{MC}^{-1} h^{-1})	Conv.[c] (%)	Select.[d] (%)
1	**1**/run 1	46	25/31	8/3
2	**1**/run 2	<1	20/32	65/13
3	**2**/run 1	81	45/50	100/80
4	**2**/run 2	101	41/59	63/59
5	**3**/run 1	76	52/64	94/94
6	**3**/run 2	91	38/56	85/85
7	**4**/run 1	112	79/90	100/100
8	**4**/run 2	28	50/77	100/100
9	**1**-[BMPy]BF_4/run 1	97	60/67	65/54
10	**1**-[BMPy]BF_4/run 2	50	57/74	92/92
11	**2**-[BMPy]PF_6	52	16/22	51/50
12	**2**-[BMPy]BF_4/run 1	57	57/74	87/83
13	**2**-[BMPy]BF_4/run 2	56	55/78	95/88
14	**3**-[BMPy]BF_4/run 1	62	70/85	94/93
15	**3**-[BMPy]BF_4/run 2	31	68/86	96/94

[a] Reaction conditions for entries 1–8:1.8 mmol cyclooctene, 2.7 mmol TBHP, 18 μmol **1**–**4**, no additional solvent. For reactions 9–15, the ionic liquids [BMPy]BF_4 (100 μL) or [BMPy]PF_6 (100 mg) were added

[b] Turnover frequency calculated at 15 min reaction

[c] Cyclooctene conversion at 6 and 24 h reaction

[d] Epoxide selectivity at 6 and 24 h reaction

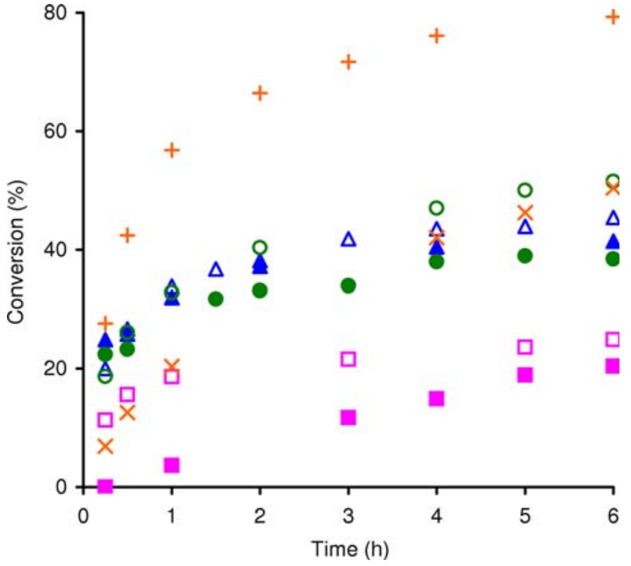

Fig. 2 Kinetic profiles of cyclooctene oxidation at 55 °C with TBHP and no additional solvent, using **1** (□), **2** (Δ), **3** (○) and **4** (+) as catalyst precursors. The second reaction runs (labelled as ■, ▲, ● and ×, respectively) were carried out after recharging the reaction mixtures at 24 h with olefin and oxidant

the anionic complex **1**, although the initial TOF in the second run was much lower than that in the first run (Table 2, entries 1/2), similar olefin conversions were reached in both runs for reaction times of 6 h or longer (Fig. 2). Epoxide selectivity increased from the first to the second run, in contrast to that observed for **2** and **3**.

In order to examine the effect of the axial thiocyanate ligands on the catalytic performance of **2** for the liquid-phase oxidation of cyclooctene, the reaction was carried out in the presence of MoO_2Cl_2(di-*t*Bu-bipy) (**4**), under similar conditions. The catalytic activity of **4** was higher than that for **2**, giving 90% olefin conversion at 24 h and 100% epoxide selectivity (Table 2, entry 7). Unlike complex **2**, the epoxide selectivity did not change in the second run, and a significant drop in activity occurred (entry 8, Fig. 2). Previous studies with complexes of the type MoO_2Cl_2L bearing bipyridine ligands (L) have consistently indicated that neither the Mo–Cl bonds nor the Mo–N bonds are disrupted during catalytic olefin epoxidation using TBHP in decane as the oxidant [36, 37]. The available experimental and theoretical evidence indicates that the complexes undergo an equilibrium reaction with excess TBHP to give seven-coordinate Mo^{VI} η^1-alkylperoxo complexes; attempts to isolate these species have been unsuccessful, with the starting compound always being recovered unchanged [36, 37]. For complex **4**, the fact that the selectivity to the epoxide is always 100% for both catalytic runs is consistent with the complex being stable under the reaction conditions. The loss in activity between the first and second runs is probably due to the accumulation of *tert*-butyl alcohol (a by-product) in the reaction mixture, which competes with TBHP for coordination to the Mo^{VI} centre [38, 39].

For complex **2**, the results for the two catalytic runs suggest that the starting complex undergoes a chemical transformation under the applied oxidising conditions. In an attempt to characterise the nature of the species formed during the course of the reactions, complex **2** was treated with a 150-fold excess of TBHP in decane (5.5 M) for 6 h at 55 °C. At the end of the reaction a yellow precipitate had formed, which was filtered, washed with pentane and dried at room temperature. The infrared spectrum of this solid (**2***) was very different from that for complex **2**, and in fact indicated the presence of the oxobisperoxo complex $MoO(O_2)_2$(di-*t*Bu-bipy). Thus, although strong bands characteristic of coordinated di-*t*Bu-bipy ligands were present (at 1,412 and 1,617 cm^{-1}), no bands due to thiocyanate ligands were observed in the range 2,000–2,100 cm^{-1}. The new bands at 942 [s, $\nu(Mo = O)$], 875 (sh), 862 [s, ν(O–O)], 658, 589 and 530 (m, $\nu[Mo–O(O_2)]$) are all characteristic of $MoO(O_2)_2L_n$ complexes bearing either two monodentate ligands or one bidentate ligand (L) [40–42]. These seven-coordinate molybdenum peroxo complexes are active catalysts for the epoxidation of olefins with TBHP, especially when L is a neutral bidentate *N,N*-ligand such as a substituted pyrazolylpyridine [40, 43, 44]. Mechanistic studies have indicated that the oxidising agent coordinates to the Mo^{VI} centre, undergoes a proton transfer to one of the peroxo ligands and is activated for oxygen transfer by η^2-coordination [45]. A catalytic run carried out with the solid **2*** under conditions equivalent to those used for the fresh catalyst precursor **2** (Table 2) revealed a similar performance for the oxidation of cyclooctene. Thus, after 6 h, a conversion of 45% was reached, which is the same as that obtained with **2** in the first run. The epoxide selectivity decreased slightly from 100% at the beginning of the reaction to 93% at 6 h.

3.2.2 *Ionic Liquid-Standing Complexes **1–3***

The effect of using the ionic liquids $[BMPy]PF_6$ and $[BMPy]BF_4$ in the epoxidation of cyclooctene at 55 °C was investigated for **2** as catalyst precursor and TBHP as oxidant. The apparent poor solubility of **2** in $[BMPy]PF_6$ under the catalytic reaction conditions resulted in a solid–liquid mixture being obtained. For $[BMPy]BF_4$, a biphasic liquid–liquid mixture was obtained with a top layer composed of olefin and decane, and a bottom layer composed of the ionic liquid, decane, TBHP and **2**. Although the initial TOFs were similar for both ionic liquids, after 30 min olefin conversion and epoxide selectivity were much higher for $[BMPy]BF_4$ than for $[BMPy]PF_6$, giving values of 74 and 83% after 24 h (Table 2, entry 12). These results are better than those obtained without solvent, where a conversion of only 50% was reached at 24 h (Table 2, entry 3; compare Fig. 2 with Fig. 3). The ionic liquid $[BMPy]BF_4$ also had a very clear promotional effect on the catalytic performance with complexes **1** and **3**, principally when the residence time was greater than 1 h (Table 2, entries 1/9 and 5/14; Figs. 2, 3). With complex **1** as catalyst precursor, the epoxide selectivity with ionic liquid was much higher than that without solvent (entries 1/9).

The catalytic systems containing $[BMPy]BF_4$ were recycled at the end of the first run (24 h) by extracting cyclooctene and products with *n*-hexane (3 × 1 mL), which is immiscible with the ionic phase. GC analysis confirmed the absence of cyclooctene and products in the ionic phase. For each system, the kinetic profiles for the two consecutive runs are practically coincident for reaction times longer than 1 h (Fig. 3). Comparing the results for the two runs at 6 and 24 h (Table 2, entries 9/10, 12/13 and 14/15), epoxide selectivity either remains unchanged (**3**), increases slightly (**2**) or increases significantly (**1**). The slight increase in epoxide selectivity observed for **2** in the second run contrasts with the significant decrease observed in the absence of the RTIL (Table 2, entries 3/4).

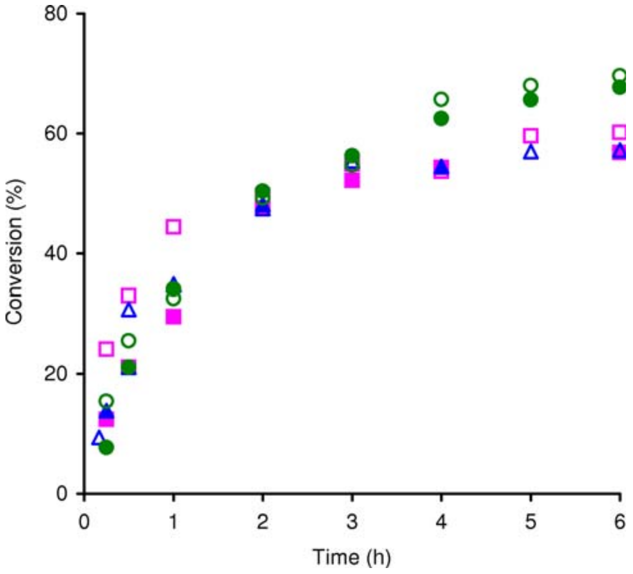

Fig. 3 Kinetic profiles of cyclooctene oxidation at 55 °C with TBHP as oxidant, $[BMPy]BF_4$ as solvent, and **1** (□), **2** (Δ) and **3** (○) as catalyst precursors. The solid symbols (■, ▲, ●) show the profiles of the second runs carried out using the recycled ionic phases containing the Mo complexes

4 Conclusions

The catalytic systems comprising the complexes $(PPh_4)_2[Mo^{VI}O_2(NCS)_4]$, $Mo^{VI}O_2(NCS)_2$(di-*t*Bu-bipy) and $Mo_2^{VI}O_5(NCS)_2$(di-*t*Bu-bipy)$_2$, and the oxidants DMSO or TBHP, are capable of selectively oxidising benzyl alcohol to benzaldehyde with moderate activity. Surprisingly, in the presence of DMSO, the three systems exhibit very similar catalytic performance. The similar activities for the two complexes containing the bipyridine ligand may be explained by the dimerisation of the monomeric complex under the reaction conditions used. With TBHP in decane as the oxidant and $Mo^{VI}O_2(NCS)_2$(di-*t*Bu-bipy) as catalyst precursor (and no additional solvent), preliminary experiments carried out in the absence of a substrate indicate that TBHP is likely to promote the de-coordination of the labile thiocyanate ligands under the reaction conditions used, possibly leading to an oxobisperoxo species. The dioxomolybdenum(VI)/TBHP system is more active (at 55 °C) than the dioxomolybdenum(VI)/DMSO systems (at 80 °C) for the oxidation of benzyl alcohol, although benzyl-*tert*-butyl ether was formed. The selectivity to the aldehyde was improved by using the ionic liquid [BMPy]BF_4 as a solvent for the molybdenum complex. Although so far limited to the oxidation of cyclooctene, the present work has demonstrated that the addition [BMPy]BF_4 to the systems comprising the thiocyanatodioxomolybdenum(VI) complexes and TBHP results in improved efficiency for the epoxidation reaction, both in terms of cyclooctene conversion and epoxide selectivity. Furthermore, these systems can be easily recycled without loss of performance.

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