

Homogeneous oxidation of methyl isobutyrate with oxygen catalysed by metal complexes: polyoxometalates versus metalloporphyrins and metallophthalocyanines

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Abstract

Two types of homogeneous oxidation of methyl isobutyrate (MIB) with O₂ catalysed by transition metal complexes aiming at methyl α -hydroxyisobutyrate (MHIB) have been studied: (1) low-temperature (30–50 °C, 1 bar O₂) co-oxidation with isobutyraldehyde (IBA); (2) high-temperature (100–140 °C, 10 bar O₂) direct oxidation. As the catalysts, Keggin-type polyoxometalates (PMo_{12–n}V_nO₄₀; *n* = 1–3) and (PW₁₁MO₃₉; M = Ni(II), Co(II), Cu(II), Fe(III), and Ru(III)) as well as metalloporphyrins and metallophthalocyanines of Co(II), Ni(II), Cu(II), Fe(II, III), Mn(III), and Ru(III) have been used. The complexes of Fe(II, III), Co(II), and Ru(III) have been found to be the most active catalysts. The co-oxidation occurs with a fairly good efficiency, allowing up to 0.55 mol MIB to be converted per 1 mol IBA reacted at 50 °C and a molar ratio [MIB]:[IBA] = 5:1. About a half of IBA is non-productively consumed to isobutyric acid (IBAcid; up to 95% yield) and acetone. MIB appears to be mainly converted to methyl α -hydroperoxyisobutyrate (MHPIB), the maximum selectivity to MHIB being only 15%. The high-temperature direct oxidation of MIB is found to be more efficient providing 24% selectivity to MHIB at 19% MIB conversion (120 °C). The drawback to this route is the formation of a large amount of IBAcid (39–59% selectivity) and acetone (25–46%). All three types of complexes studied perform quite similarly as the catalysts for these reactions. The important result is that in the low-temperature co-oxidation, the complexes with organic ligands (porphyrins and phthalocyanines) are more active than the corresponding polyoxometalates, whereas the opposite is observed in the high-temperature oxidation. This is in agreement with the views on polyoxometalates as robust, oxidation-resistant analogs of metal complexes with macrocyclic ligands.

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1. Introduction

Methyl methacrylate is an important commodity chemical which is produced worldwide on a commer-

cial scale. There are several routes to methyl methacrylate, the production via acetone cyanohydrin still being the dominant one [1]. A prospective alternative method involves the oxidative dehydrogenation of isobutyric acid to methacrylic acid which proceeds efficiently in the gas phase over solid heteropoly acid catalysts [2]. Direct liquid-phase oxidation of methyl isobutyrate (MIB) to methyl α -hydroxyisobutyrate (MHIB)

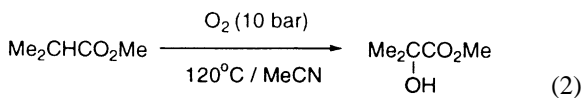
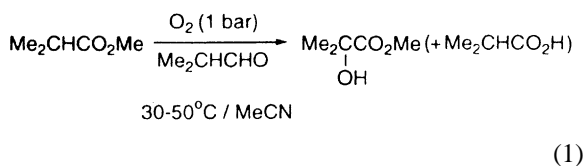
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followed by the easy dehydration of MHIB to methyl methacrylate has attracted interest [3,4]. For this oxidation, oxygen [4] or hydroperoxides [3] as oxidants and metal complexes or metal oxides as catalysts have been used; the catalytic oxidation with oxygen appears to be the most attractive.

The present work concerns with the homogeneous metal-catalysed oxidation of MIB to MHIB with oxygen. Two modes of oxidation are attempted: (1) low-temperature (30–50 °C, 1 bar O₂) co-oxidation with isobutyraldehyde (IBA; Eq. (1)); (2) high-temperature (100–140 °C, 10 bar O₂) direct oxidation (Eq. (2)).



In reaction (1), isobutyric acid (IBAcid) as a byproduct is formed. The IBAcid itself could be converted into methacrylic acid, which justifies the choice of IBA as the coreductant. As the catalysts, a range of Keggin-type polyoxometalates are studied in comparison with metalloporphyrins and metallophthalocyanines. Polyoxometalates have been widely used as catalysts for selective oxidation in liquid phase, including co-oxidation with aldehydes [5–7]. Mechanism of the co-oxidation of organic compounds with aldehydes catalysed by polyoxometalates has been studied [8,9]. Regarding the liquid-phase oxidation, transition metal-substituted polyoxometalates are frequently considered as close analogs of metal complexes with macrocyclic organic ligands, e.g. porphyrins, but with an important advantage of being more oxidation-resistant than the organic complexes [5–7]. Thus, the comparison of catalytic performances of polyoxometalates versus metalloporphyrins and metallophthalocyanines in reactions (1) and (2) is one of the objectives of this work.

2. Experimental

2.1. Materials

Acidic sodium heteropoly salts Na₂H₂[PMo₁₁VO₄₀], Na₃H₂[PMo₁₀V₂O₄₀], and Na₄H₂[PMo₉V₃O₄₀] were prepared by the literature method [10]. The corresponding heteropoly acids H_{3+n}[PMo_{12-n}V_nO₄₀] (*n* = 1–3) were prepared by ion-exchange of the sodium salts with Amberlyst-15. Transition metal-substituted polyoxometalates (TBA)₄H[PW₁₁Ni^{II}(H₂O)O₃₉], (TBA)₄H[PW₁₁Cu^{II}(H₂O)O₃₉], (TBA)₄H[PW₁₁Co^{II}(H₂O)O₃₉], (TBA)₄[PW₁₁Ru^{III}(H₂O)O₃₉], and (TBA)₄[PW₁₁Fe^{III}(H₂O)O₃₉], where TBA is tetrabutylammonium, were synthesised as described elsewhere [11]. Iron(II) phthalocyanine and metalloporphyrins (TPP)Cu(II), (TPP)Ni(II), (TPP)Mn(III)Cl, (TPP)Co(II), and (TPP)Fe(III)Cl, where TPP is 5,10,15,20-tetraphenyl-21H,23H-porphine, were purchased from Aldrich. Phthalocyanines (PC) of Cu(II), Ni(II), and Co(II) were purchased from Fluka. The metallophthalocyanines and metalloporphyrins were used as received. All heteropolyoxometalates were dried at 100 °C under vacuum. The catalysts were kept in a desiccator over P₂O₅. All organic reagents and solvents were 99% pure from Acros or Aldrich and used without further purification except isobutyraldehyde which was used freshly distilled and kept in a refrigerator.

2.2. Co-oxidation of methyl isobutyrate and isobutyraldehyde

The reaction was carried out in a closed 50 ml three-necked round-bottomed flask, with the side arms sealed with rubber septa. The flask was maintained at a constant temperature using an oil bath and had an intense magnetic stirring. Typically, the reaction mixture was made up of 1.0 μmol of metal complex catalyst dissolved in 6.0 ml of acetonitrile added with 10 mmol of methyl isobutyrate. Oxygen (10 ml/min) was bubbled through the stirred mixture in the flask for 10 min until the flask was saturated with oxygen. Then the flask was sealed and the temperature was set to 30 or 50 °C. The reaction was started by injecting 2.0 mmol of isobutyraldehyde into the mixture with a syringe through the septum. The amount of O₂ in the flask was more than two-fold excess to that

required for complete oxidation of the isobutyraldehyde to isobutyric acid. Samples of the reacting mixture (0.5 ml) were taken in appropriate time intervals with a syringe through the septum and analysed by GC (a Varian CP-3380 gas chromatograph equipped with a Varian 8200 autosampler, an FID detector, and a 25 m BP1 capillary column). Decane was used as an internal standard. Products were identified by GC–MS using authentic samples. Measured were IBA and MIB conversions and product yields; from these, selectivities were calculated.

The co-oxidation of cyclohexane was carried out similarly, using 10 mmol of cyclohexane instead of methyl isobutyrate.

2.3. Oxidation of methyl isobutyrate in autoclave

The reaction was carried out in a 50 ml stainless steel Parr autoclave equipped with magnetic stirring. The reaction mixture contained 0.5–5 μ mol of catalyst and 10 mmol of methyl isobutyrate dissolved in 6.0 ml

of acetonitrile. The autoclave, while stirred, was pressurised to 10 bar with O₂, heated to 120 °C with an oil bath and kept at this temperature for 4 h. Then it was cooled in an ice bath, depressurised and opened. The products were analysed by GC.

3. Results and discussion

3.1. Co-oxidation of methyl isobutyrate and isobutyraldehyde

A number of polyoxometalates, metalloporphyrins, and metallophthalocyanines (20 in total) were tested in the co-oxidation of methyl isobutyrate (MIB) and isobutyraldehyde (IBA) with O₂ (Eq. (1)) at 30 °C and a molar ratio MIB:IBA = 5:1 (Table 1). Under such conditions, the reaction mainly involves the oxidation of IBA (42–76% conversion) to isobutyric acid (IBAcid, 10–76% yield), with MIB conversion being only 1.2–4.3%. Without catalyst, reaction (1) occurs

Table 1
Co-oxidation of methyl isobutyrate (MIB) and isobutyraldehyde (IBA) with O₂ in acetonitrile^a

Catalyst	IBA conversion (%)	IBAcid yield (%) ^b	MIB conversion (%)
None	15 (22)	6.0 (20)	0.2 (0.3)
H ₄ [PMo ₁₁ VO ₄₀]	77 (81)	32 (57)	1.8 (3.2)
H ₄ [PMo ₁₁ VO ₄₀] ^c	–	0	0
H ₅ [PMo ₁₀ V ₂ O ₄₀]	57	22	1.8
H ₆ [PMo ₉ V ₃ O ₄₀]	52	19	1.9
Na ₂ H ₂ [PMo ₁₁ VO ₄₀]	65	25	1.5
Na ₃ H ₂ [PMo ₁₀ V ₂ O ₄₀]	42	9.0	1.0
Na ₄ H ₂ [PMo ₉ V ₃ O ₄₀]	46	11	1.2
(TBA) ₄ H[PW ₁₁ Ni ^{II} (H ₂ O)O ₃₉]	57	10	2.4
(TBA) ₄ H[PW ₁₁ Cu ^{II} (H ₂ O)O ₃₉]	65	16	2.1
(TBA) ₄ H[PW ₁₁ Co ^{II} (H ₂ O)O ₃₉]	80 (96)	55 (70)	3.1 (4.3)
(TBA) ₄ [PW ₁₁ Ru ^{III} (H ₂ O)O ₃₉]	82	42	3.0
(TBA) ₄ [PW ₁₁ Fe ^{III} (H ₂ O)O ₃₉]	89 (90)	51 (64)	4.2 (4.4)
(TPP)Cu(II)	57	32	2.3
(TPP)Ni(II)	62	39	2.1
(TPP)Mn(III)Cl	76	54	3.4
(TPP)Co(II)	89 (97)	65 (74)	4.2 (5.0)
(TPP)Fe(III)Cl	94 (100)	76 (85)	4.3 (6.2)
(PC)Cu(II)	63	35	2.8
(PC)Ni(II)	76	33	2.4
(PC)Co(II)	87 (99)	62 (65)	3.9 (5.1)
(PC)Fe(II)	90 (92)	63 (68)	3.7 (5.4)

^a Reaction in a 50 ml glass vessel; 2.0 mmol IBA; 10 mmol MIB; 6.0 ml MeCN; [Cat] 0.14 mM; 1 bar O₂; at 30 °C, 6 h. Values in parenthesis are results at 50 °C.

^b Yield based on IBA charged.

^c Blank run: no IBA added.

too, but much slower, with IBA and MIB conversion of 15 and 0.2%, respectively. In the absence of IBA, no MIB conversion was observed. The complexes of Fe(II), Fe(III), Co(II), and Ru(III) and the heteropoly acid $H_4[PMo_{11}VO_{40}]$ were found to be the most active catalysts. Complexes of Cu(II), Ni(II), Mn(III), as well as heteropoly acids and salts ($PMo_{12-n}V_n$; $n = 2, 3$) were less efficient.

The most active systems were also tested at 50 °C. These gave 81–100% IBA conversion and 57–85% IBAAcid yield, with MIB conversion being of 3.2–6.2% (Table 1). Fig. 1 shows the time course for reaction

(1) at 50 °C. The activity of the catalysts is in the order: $(TPP)Fe(III)Cl > (PC)Co(II) > (TPP)Co(II) \approx PW_{11}Co(II) > (PC)Fe(II) \approx PW_{11}Fe(III) > H_4[PMo_{11}V]$. Thus, the metalloporphyrins and metallophthalocyanines are more active than polyoxometalates, although the difference between them is not large.

Table 2 shows the effect of [MIB]:[IBA] ratio and catalyst concentration on the co-oxidation catalysed by iron complexes. Increasing [IBA] up to [MIB]:[IBA] = 1:1 causes a slight increase in the conversion of IBA and MIB as well as in the yield of

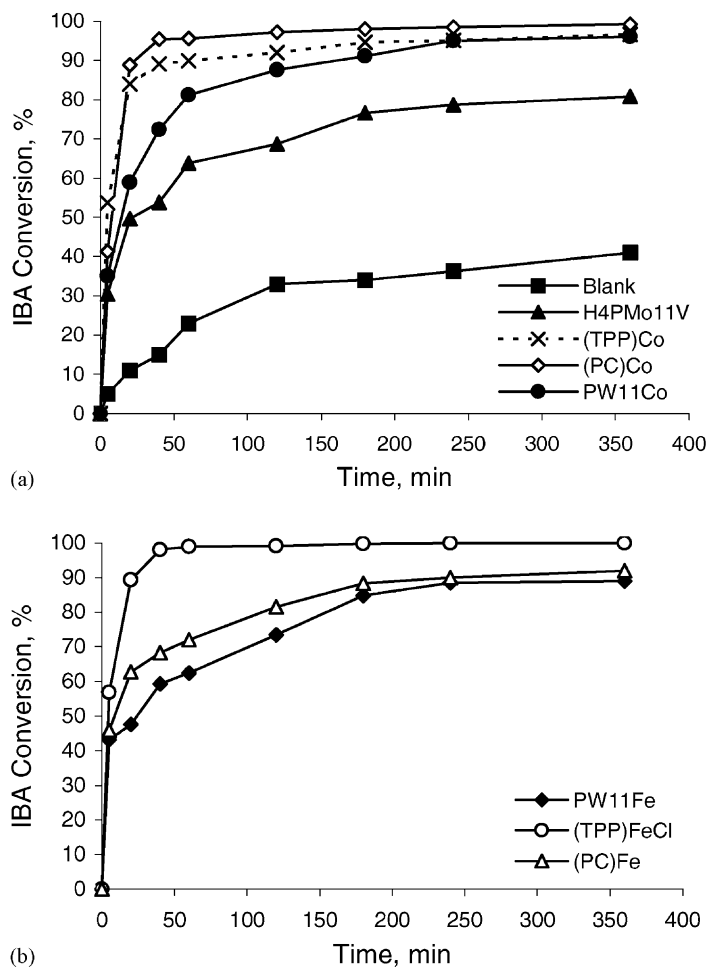


Fig. 1. Conversion of isobutyraldehyde vs. time for the co-oxidation of isobutyraldehyde and methyl isobutyrate in acetonitrile at 50 °C (2.0 mmol IBA, 10 mmol MIB, 6.0 ml MeCN, [Cat] 0.14 mM, 1 bar O_2). (a) Reaction catalysed by cobalt and vanadium complexes; (b) reaction catalysed by iron complexes.

Table 2

Co-oxidation of methyl isobutyrate and isobutyraldehyde with O₂ catalysed by iron complexes in acetonitrile at 50 °C^a

Catalyst	[Cat] (mM)	IBA conversion (%)	IBAcid yield ^b (%)	Acetone yield ^b (%)	MIB conversion (%)	MHIB yield ^c (%)
(TPP)Fe(III)Cl	0.14	100 (100)	85 (90)	3.2 (5.2)	6.2 (9.3)	0.2 (0.3)
(TPP)Fe(III)Cl	0.56	100	95		11	0.6
(PC)Fe(II)	0.14	92 (100)	68 (90)	2.9 (3.6)	5.4 (7.5)	0.7 (0.8)
(PC)Fe(II)	0.56	100	95		6.5	1.0
(TBA) ₄ [PW ₁₁ Fe ^{III} (H ₂ O)O ₃₉]	0.14	90 (95)	64 (74)	2.0 (3.6)	4.4 (6.7)	0.3 (0.4)
(TBA) ₄ [PW ₁₁ Fe ^{III} (H ₂ O)O ₃₉]	0.56	100	92		9.4	0.6

^a Reaction in a 50 ml glass vessel; 10 mmol MIB; [MIB]:[IBA] = 5:1; 6.0 ml MeCN; 1 bar O₂; at 6 h. Values in parenthesis are results at [MIB]:[IBA] = 1:1.

^b Yield based on IBA charged.

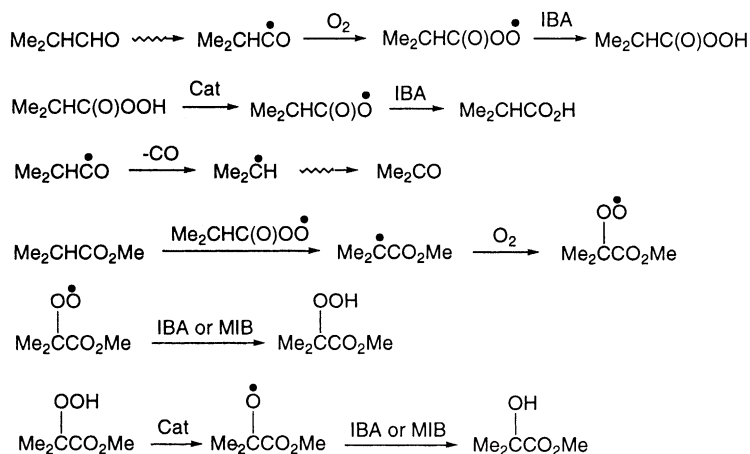
^c Yield based on MIB charged.

products—IBAcid, acetone and MHIB. A four-fold rise in catalyst concentration causes the same effect, but more pronounced. For the most active catalyst, (TPP)Fe(III)Cl, the efficiency of MIB co-oxidation is 55% (at 50 °C, [Cat] = 0.56 mM and [MIB]:[IBA] = 5:1), i.e. 0.55 mol of MIB is converted per 1 mol of IBA reacted. IBA is converted into IBAcid (95% yield) and acetone [8]. The yield of MHIB is low, i.e. only 0.2–1.0% (Table 2). This corresponds to the selectivity of MIB oxidation of 3–15%.

The mechanism of co-oxidation with aldehydes is well known [12,13]. For reaction (1), it may be represented by Scheme 1, excluding termination steps. Apparently, MIB is mainly converted to methyl α-hydroperoxyisobutyrate (MHPIB). The presence of peroxocompounds (supposedly perisobutyric acid

(PIBAcid) and MHPIB) among the products of reaction (1) was confirmed by iodometric titration. GC analysis indicated the presence of MHPIB, however quantitative analysis was unreliable. Tertiary hydroperoxides are known to be much more stable towards homolytic cleavage than primary and secondary hydroperoxides [13]. This is probably the reason for the yield of MHIB being so low.

For comparison, we tested the co-oxidation of cyclohexane with the most active Fe(II, III) and Co(II) catalysts under similar conditions at 50 °C (Table 3). The conversions of cyclohexane were 1.1–2.2%. This means that the tertiary C–H bond in MIB is 40–60 times more reactive than the secondary C–H bond in cyclohexane towards the formation of the corresponding hydroperoxides, as expected [12,13]. On



Scheme 1.

Table 3

Co-oxidation of cyclohexane and isobutyraldehyde with O₂ in acetonitrile at 50 °C^a

Catalyst	IBA conversion (%)	Cyclohexane conversion (%)	Cyclohexanol yield (%) ^b	Cyclohexanone yield (%) ^b
(TPP)Fe(III)Cl	82	2.2	0.7	1.3
(PC)Fe(II)	88	1.1	0.4	0.6
(TBA) ₄ H[PW ₁₁ Co ^{II} (H ₂ O)O ₃₉]	89	1.5	0.6	0.8
(PC)Co(II)	93	1.6	0.7	0.7

^a Reaction in a 50 ml glass vessel; 2.0 mmol IBA; 10 mmol C₆H₁₂; 6.0 ml MeCN; [Cat] 0.14 mM; 1 bar O₂; at 6 h.^b Yield based on cyclohexane charged.

the other hand, the total selectivity to cyclohexanol and cyclohexanone is 87–93% compared to 3–15% for the oxidation of MIB to MHIB. This indicates that the tertiary hydroperoxide MHPIB is an order of magnitude less reactive than the secondary cyclohexyl hydroperoxide.

3.2. Direct oxidation of methyl isobutyrate

Direct oxidation of MIB with O₂ (Eq. (2)) was attempted at higher temperatures (100–140 °C) and 10 bar oxygen pressure without adding IBA. The

results at 120 °C are shown in Table 4. In this system, the MIB conversion varies from 3.1 to 11%. Again, Fe(II, III), Co(II), and Ru(III) complexes are the most active catalysts. The products obtained are MHIB, IBAcid, and acetone, IBAcid being the main product (39–59% selectivity). The IBAcid is likely to be formed by acid-catalysed hydrolysis of MIB with water that is made in the oxidation, as well as traces of water that may be present in the initial system. Only about 0.1 wt.% water in the reaction mixture would be sufficient for making that amount of IBAcid.

Table 4

Oxidation of methyl isobutyrate with O₂ in acetonitrile at 120 °C^a

Catalyst	MIB conversion (%)	Selectivity (%)		
		MHIB	IBAcid	Acetone
H ₄ [PMo ₁₁ VO ₄₀]	3.8	0	47	32
H ₅ [PMo ₁₀ V ₂ O ₄₀]	3.9	0	49	28
H ₆ [PMo ₉ V ₃ O ₄₀]	4.5	0	47	31
Na ₂ H ₂ [PMo ₁₁ VO ₄₀]	3.8	0	47	34
Na ₃ H ₂ [PMo ₁₀ V ₂ O ₄₀]	3.6	0	53	25
Na ₄ H ₂ [PMo ₉ V ₃ O ₄₀]	3.1	0	39	32
(TBA) ₄ H[PW ₁₁ Ni ^{III} (H ₂ O)O ₃₉]	7.8	12	54	31
(TBA) ₄ H[PW ₁₁ Cu ^{II} (H ₂ O)O ₃₉]	7.5	12	57	28
(TBA) ₄ H[PW ₁₁ Co ^{II} (H ₂ O)O ₃₉]	6.9	15	59	25
(TBA) ₄ [PW ₁₁ Ru ^{III} (H ₂ O)O ₃₉]	8.4	17	51	30
(TBA) ₄ [PW ₁₁ Fe ^{III} (H ₂ O)O ₃₉]	11	14	50	30
(TPP)Cu(II)	6.9	8.7	42	38
(TPP)Ni(II)	7.1	9.8	45	41
(TPP)Mn(III)Cl	7.4	11	42	46
(TPP)Co(II)	8.8	9.1	47	42
(TPP)Fe(III)Cl	9.4	13	46	39
(PC)Cu(II)	5.3	9.4	53	34
(PC)Ni(II)	6.8	8.8	47	41
(PC)Co(II)	7.2	13	50	37
(PC)Fe(II)	8.4	12	46	38

^a Reaction in a 50 ml stainless steel autoclave; 10 mol MIB; 6.0 ml MeCN; [Cat] 0.14 mM; 10 bar O₂; at 120 °C, 4 h.

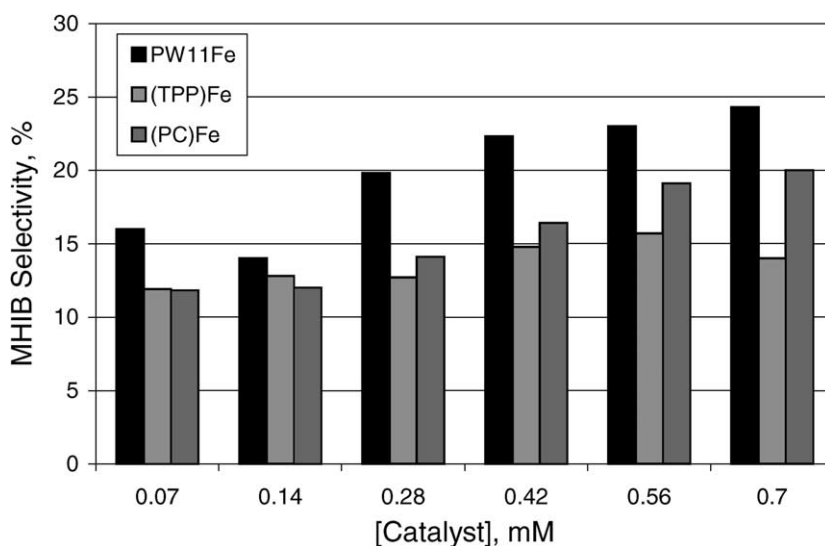


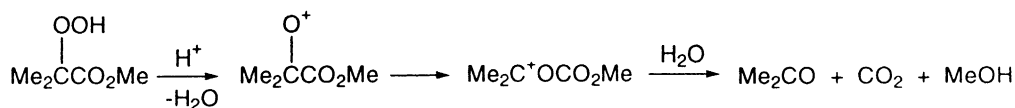
Fig. 2. Selectivity to methyl α -hydroxyisobutyrate vs. catalyst concentration for the oxidation of methyl isobutyrate in acetonitrile at 120 °C catalysed by iron complexes (10 mmol MIB, 6.0 ml MeCN, 10 bar O₂, 4 h).

MHIB, the product of selective oxidation of MIB, forms with a selectivity up to 17% at 120 °C. In contrast to the low-temperature co-oxidation, in the high-temperature direct oxidation of MIB to MHIB, transition metal-substituted polyoxometalates are the superior catalysts to porphyrins and phthalocyanines. The order of activity for the most active catalysts is as follows: PW₁₁Ru(III) > PW₁₁Co(II) > PW₁₁Fe(III) > (TPP)Fe(III)Cl \approx (PC)Co(II) > PW₁₁Ni(II) \approx PW₁₁Cu(II) \approx (PC)Fe(II). This is in agreement with the views on polyoxometalates as robust, oxidation-resistant analogs of metal complexes with macrocyclic ligands (e.g. metalloporphyrins) [5–7]. As found here, all the three types of complexes studied act quite similarly as oxidation catalysts. However, under more forcing oxidising conditions, the more stable transition metal-substituted

As shown for Fe(II, III) complexes, the selectivity to MHIB increases significantly with a 10-fold increase in catalyst concentration (0.07–0.7 mM; Fig. 2) and so does the MIB conversion. This is the case for all three types of complexes studied, i.e. polyoxometalates, porphyrins and phthalocyanines, PW₁₁Fe(III) being clearly in the lead, reaching a selectivity to MHIB of 24% at 19% MIB conversion.

The mechanism of MHIB formation is likely to involve a homolytic initiation at the tertiary C–H bond of MIB, generating *tert*-alkyl radical, followed by its transformation to MHPIB and further to MHIB, as shown in Scheme 1.

Acetone is another product that is obtained in this system with a significant selectivity (25–46%; Table 4). It may be formed by acid-catalysed heterolytic decomposition of MHPIB (the Hock cleavage of the O–O bond) [14]:



polyoxometalates show better catalytic performances than the corresponding metalloporphyrins or phthalocyanines.

The acid catalyst could be IBAcid as well as the metal complexes. This is supported by the total absence of MHIB among the products when the reaction

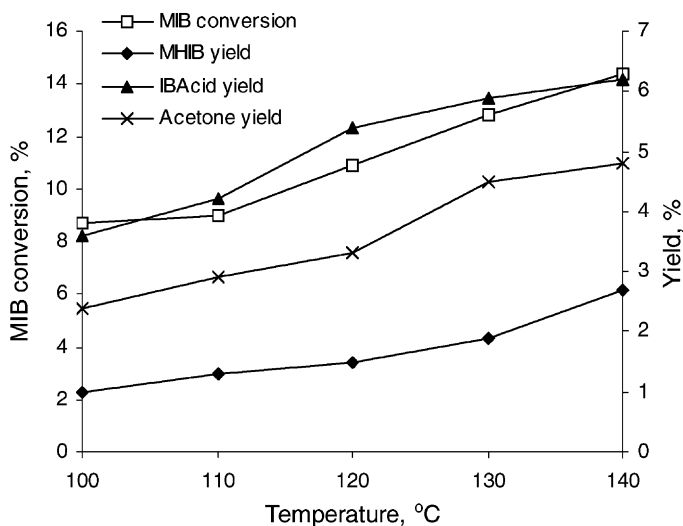


Fig. 3. Effect of temperature on the oxidation of methyl isobutyrate in acetonitrile catalysed by $(\text{TBA})_4[\text{PW}_{11}\text{Fe}^{\text{III}}(\text{H}_2\text{O})\text{O}_{39}]$ (10 mmol MIB, 6.0 ml MeCN, 10 bar O_2 , at 4 h).

was carried out with strong Brønsted acids–heteropoly acids and their acid salts ($\text{PMo}_{12-n}\text{V}_n$; Table 4). Adding a base to the system might inhibit this unwanted reaction.

The MIB conversion as well as the yields of MHIB, IBACid, and acetone moderately increase with temperature in the range of 100–140 °C, the selectivities remaining almost unchanged. Fig. 3 shows the temperature effect for $\text{PW}_{11}\text{Fe}(\text{III})$; similar results were obtained for $(\text{TPP})\text{Fe}(\text{III})\text{Cl}$ and $(\text{PC})\text{Fe}(\text{II})$.

4. Conclusion

Two types of homogeneous oxidation of MIB to MHIB with O_2 catalysed by transition metal complexes have been studied: (1) low-temperature (30–50 °C, 1 bar O_2) co-oxidation with IBA (Eq. (1)); (2) high-temperature (100–140 °C, 10 bar O_2) direct oxidation (Eq. (2)). As the catalysts, polyoxometalates, metalloporphyrins and metallophthalocyanines have been used, the complexes of Fe(II, III), Co(II), and Ru(III) being the most active catalysts. The co-oxidation occurs with a fairly good efficiency, allowing up to 0.55 mol MIB to be converted per 1 mol IBA reacted at 50 °C and a molar ratio $[\text{MIB}]:[\text{IBA}] = 5:1$. About a half of IBA is

non-productively consumed to IBACid (95% yield) and acetone. However, MIB appears to be mainly converted to the relatively stable MIB α -hydroperoxide, the maximum selectivity to MHIB being only 15%. The high-temperature direct oxidation of MIB is found to be more efficient providing 24% selectivity to MHIB at 19% MIB conversion (120 °C). The drawback to this route is the formation of a large amount of IBACid (39–59% selectivity) and acetone (25–46%). As regards the influence of the type of metal complex on its catalytic activity and stability, all three types of complexes studied perform quite similarly as the catalysts for reactions (1) and (2). The important result is that in the low-temperature co-oxidation, the complexes with organic ligands (porphyrins and phthalocyanines) are more active than the corresponding transition metal-substituted polyoxometalates, whereas the opposite is observed in the high-temperature oxidation. This is in agreement with the views on polyoxometalates as robust, oxidation-resistant analogs of metal complexes with macrocyclic ligands (e.g. metalloporphyrins) [5–7]. Consequently, under more forcing oxidising conditions, the more stable transition metal-substituted polyoxometalates show better catalytic performances than the corresponding metalloporphyrins or phthalocyanines.

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