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Direct and efficient transformation of gaseous alkanes into carboxylic acids catalyzed by vanadium containing heteropolyacids

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Abstract

The vanadium containing heteropolyacids $H_4[PMo_{11}VO_{40}] \times 34H_2O$ (**HPA-1**), $H_5[PMo_{10}V_2O_{40}] \times 32H_2O$ (**HPA-2**) and $H_6[PMo_9V_3O_{40}] \times 34H_2O$ (**HPA-3**) act as highly active catalysts for the direct transformation of light C_1–C_3 alkanes into the corresponding carboxylic acids in the presence of CO and in the $K_2S_2O_8/CF_3COOH$ system. Propionic acid (ca. 70% yield), *iso*- and *n*-butyric acids (ca. 65% overall yield), and acetic acid (ca. 20%) are the major products obtained from the carboxylation of ethane, propane and methane, respectively, with vanadium playing a main catalytic role. The effects of the catalyst amount have been studied and overall turnover numbers (TONs) up to ca. 12×10^3 (for the ethane and propane conversions) or up to 3×10^3 (for the methane carboxylation to acetic acid) have been achieved for very high alkane-to-catalyst molar ratios which also promote the selectivity towards acetic acid.

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1. Introduction

Heteropolyacids (HPA) (or polyoxometalates) and their various derivatives have found broad applications in both industrial and preparative chemistries [1–17] due to their (i) unique physical and catalytic properties, (ii) ability to work in different multiphase systems and (iii) easiness and cheapness of their preparation. A number of the HPA catalyzed processes has been commercialized, and many interesting and promising examples of their catalytic application for various types of transformations in both homo- and heterogeneous systems are currently under study [6–15]. A considerable attention has been paid to the use of HPAs as catalysts for the oxidative functionalization of inert alkanes in connection with the continuously growing interest on such a type of transformations, particularly in view of the availability and low cost of alkanes [6,10,18]. Hence, several HPA based catalysts have been applied, e.g. to liquid phase oxidation of linear and cycloalkanes to alcohols and ketones in the presence of O_2 or oxygen containing compounds [19,20], oxydehydrogenation of light alkanes to olefins [21–23], and gas phase oxidation of propane and isobutane into acrylic and methacrylic acids, respectively [24–29]. However, the instability of the HPA catalysts under the harsh reaction conditions usually required for the activation of alkanes constitutes a main drawback. Thus, there is a strong motivation to soften the reaction conditions by searching for new alternative systems and/or optimisation of current HPA-based methods of alkanes transformations.

Some examples of mild oxidation of alkanes with HPAs have been recently reported and include: (i) homogeneous oxidation of *cyclo*- and *n*-octane, adamantane and ethane by hydrogen peroxide mainly to alkylhydroperoxides catalyzed by vanadium-containing polyphosphomolybdates $[PMo_{11}VO_{40}]^{4-}$ and $[PMo_6V_5O_{39}]^{12-}$ [30], (ii) oxidation of methane to various oxygenated products such as methylformiate and methyltrifluoroacetate catalyzed by $[PMo_{11}VO_{40}]^{4-}$ in a trifluoroacetic anhydride/H_2O_2 system [31], and (iii) aerobic oxidation of methane to methanol and partially to acetaldehyde catalyzed by a supported bipyridinylplatinum–polyoxometalate $H_5[PV_2Mo_{10}O_{40}]$ in aqueous solution [32].

The use of vanadium containing HPAs towards the partial oxidation of methane to methyl trifluoroacetate [33] or acetic acid [34] (formed only in the presence of CO) was reported by Fujiwara and co-workers, in the system comprising

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trifluoroacetic acid (TFA) and $K_2S_2O_8$. However, the obtained yields (based on methane) were rather low and, in the case of acetic acid formation, did not exceed 1% with a maximum TON of 31. Moreover, the use of the HPAs as catalysts for this type of alkane transformation was limited to methane, whereas other alkanes like ethane and propane remained untested.

Recently we have reported [35] an efficient catalytic carboxylation by CO of gaseous and liquid alkanes into carboxylic acids under relatively mild conditions, in which vanadium containing catalysts, especially *amavadin* (a natural bare V^{IV} complex present in some *Amanita* fungi), exhibit the highest activity among the other metal catalysts. In this connection, there is a justified interest to test, for this type of reaction, vanadium containing heteropolyacids which, in addition, possess excellent oxidative properties due to the reducibility of vanadium atoms [8].

Hence, the present work aims to explore the application of various vanadium containing heteropolyacids as catalysts for the single-pot transformations of gaseous alkanes (in particular ethane and propane) to industrially significant carboxylic acids (i.e. propionic and butyric acids), thus providing a contribution to the development of the important field of alkane C–H bond activation. The formation of trifluoroacetate esters, namely at low CO pressures, has also been detected but is not within the scope of the current study and was not investigated in detail.

2. Experimental

The catalysts **HPA-1**, **HPA-2** and **HPA-3** (the numbering corresponds to the number of V ions per Keggin unit) were prepared according to published methods [36]. Methane, ethane, propane (AlphaGaz), carbon monoxide (Air Products) and dinitrogen gases (Air Liquid Portugal), $H_3PO_4 \cdot 12MoO_3 \times 24H_2O$, i.e. $H_3[PMo_{12}O_{40}]$ (The British Drug Houses), potassium peroxodisulfate (Fluka), trifluoroacetic acid (Aldrich), $CBrCl_3$ (Fluka), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Aldrich), Ph_2NH (Fluka), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Aldrich), *n*-heptanoic (Aldrich) and *n*-butyric acid (Aldrich) were obtained from commercial sources and used as received.

In a typical experiment the reaction mixtures were prepared as follows. To a mixture of 20.0–0.042 μmol of the catalyst with 4.00 mmol (1.08 g) $K_2S_2O_8$, contained in a 13.0 mL stainless steel autoclave, were added 5.0 mL of CF_3COOH (TFA). Then the autoclave was closed and flushed with dinitrogen three times for replacing the air inside and finally pressurized with CH_4 (5–10 atm), C_2H_6 (5–10 atm) or C_3H_8 (8.5 atm), and CO (0–30 atm). The reaction mixture was vigorously stirred for 20 h at 80 °C using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed and opened. The product analysis was undertaken as follows. To 1.0 mL of the reaction mixture were added 5.0 mL of diethyl ether and 90 μL of internal standard (*n*-butyric acid for the carboxylation of CH_4 and C_2H_6, *n*-heptanoic acid for the carboxylation of C_3H_8). The obtained mixture was stirred, then filtered off and analyzed by gas chromatography (GC) using a Fisons Instruments GC 8000 series gas chromatograph with a DB WAX fused silica capillary column (P/N 123-7032) and the Jasco-Borwin v.1.50 software. In some cases, the products were also identified by GC–MS, ^1H and $^{13}C\text{-}\{^1H\}$ NMR techniques using a Trio 2000 Fisons spectrometer with a coupled Carlo Erba (Auto/HRGC/MS) gas chromatograph and a Varian UNITY 300 NMR spectrometer, respectively. Blank experiments were performed for all tested alkanes in the presence of CO and $K_2S_2O_8$, and confirmed that no carboxylic acid formation was detected unless the catalyst was used.

3. Results and discussion

Three Keggin-type heteropolyacid compounds $H_4[PMo_{11}VO_{40}] \times 34H_2O$ (**HPA-1**), $H_5[PMo_{10}V_2O_{40}] \times 32H_2O$ (**HPA-2**) and $H_6[PMo_9V_3O_{40}] \times 34H_2O$ (**HPA-3**) with different vanadium content were used as catalysts or catalysts precursors for the carboxylation of gaseous alkanes (i.e. CH_4, C_2H_6 and C_3H_8) to form the corresponding carboxylic acids. The results of these studies are summarized in Tables 1–3 and Figs. 1 and 2. The tested catalysts showed a very high activity in the abovementioned reaction leading to the maximum overall yield of carboxylic acids of 80% (based on the alkane, or ca. 60% based on $K_2S_2O_8$) and TON value of 12.4×10^3, thus displaying an unprecedented efficacy of HPAs in the field of mild functionalization of gaseous alkanes. The presence of the catalyst is essential for the formation of carboxylic acids since in its absence the reaction does not proceed.

3.1. Conversion of ethane into propionic and acetic acids

The carboxylation of ethane in the presence of carbon monoxide, under typical reaction conditions, leads to the formation of propionic acid as the main product with a high yield, reaching 70% (based on ethane). Acetic acid is also formed as a result of partial oxidation of ethane, but in a smaller amount. However, in the absence of CO, acetic acid becomes the major product reaching the considerable yield of ca. 36, 20 or 35% for **HPA-1**, **HPA-2** or **HPA-3**, respectively (Table 1, entries 7, 9 and 12), while ethyl trifluoroacetate is also detected in an amount comparable with that of acetic acid. In the presence of CO, only the traces of $CF_3COOC_2H_5$ have been revealed. Propionic acid is also formed in these cases (without CO) but in a rather low yield of ca. 3%, as a result of propane carboxylation by TFA [35a]. Acetic acid is also the main product for sufficiently low catalyst amounts (see below).

The effect of the catalyst amount on the yields of carboxylic acids was studied in detail for the **HPA-1** catalyst (Table 1, Fig. 1). There is an optimum ethane-to-catalyst molar ratio of ca. 300, which corresponds to the maximum total yield of carboxylic acids of ca. 77% and the maximum yield of propionic acid (70%) (Fig. 1, Table 1, entry 3). The corresponding TONs are 235 and 215. Higher values of that ratio lead to a smooth decrease of those yields, although providing a growth of the TONs. Thus, the increase of the ethane-to-catalyst molar ratio from 306 to 2448 results in the total yield lowering from 77 to 37% with the overall TON rise

Table 1
Conversion of ethane into propionic and acetic acids[a]

$$C_2H_6 + CO \xrightarrow[TFA,K_2S_2O_8]{HPA} C_2H_5COOH + CH_3COOH$$

Entry	Catalyst	Catalyst amount (µmol)	pC_2H_6[b] (atm)	pCO[b] (atm)	Yield[c] (%)			TON[d]		
					Propionic acid	Acetic acid	Total	Propionic acid	Acetic acid	Total
1	**HPA-1**	20.0	10	30	62.7	5.6	68.3	96	9	105
2		20.0	10	25	48.7	8.8	57.5	75	13	88
3		10.0	10	30	70.3	6.5	76.8	215	20	235
4		5.00	10	30	64.4	5.9	70.3	394	36	430
5		2.50	10	30	54.9	5.1	60.0	670	62	732
6		1.25	10	30	24.9	12.4	37.3	609	303	912
7		2.50	5	0	2.8	36.3	39.1	17	222	239
8		0.042	10	30	–	4.8	4.8	–	3.6×10^3	3.6×10^3
9	**HPA-2**	2.50	10	30	62.4	5.8	68.2	765	71	836
10		2.50	5	0	3.2	20.2	23.4	20	124	144
11		0.042	10	30	–	8.2	8.2	–	5.9×10^3	5.9×10^3
12	**HPA-3**	10.0	10	30	61.9	5.9	67.8	190	18	208
13		2.50	10	30	58.2	8.5	66.7	712	104	816
14		2.50	5	0	2.9	35.2	38.1	18	216	234
15		0.042	10	30	8.8	8.1	16.9	6.46×10^3	12.4×10^3	12.4×10^3
16	$H_3[PMo_{12}O_{40}]$	2.50	10	30	0	4.6	4.6	–	56	56

[a] Reaction conditions (unless stated otherwise): $K_2S_2O_8$ (4.00 mmol), CF_3COOH (5 mL), 80 °C, 20 h, in an autoclave (13 mL capacity).

[b] Measured at 25 °C (amounts of C_2H_6 or CO gases correspond to 0.306 mmol atm^{-1}).

[c] Molar yield (%) based on C_2H_6, i.e. moles of either acetic or propionic acid per 100 moles of ethane (determined by GC); molar yields (%) based on $K_2S_2O_8$, if required, can be estimated (except for runs 7, 10 and 14) as total yields × 0.765, e.g. 59% for run 3; for runs 7, 10 and 14, it can be estimated as total yields × 0.38, e.g. 15% for run 7.

[d] Turnover number (moles of acetic or/and propionic acids per mol of catalyst).

from 235 to 912 (Fig. 1). The maximum TON (670) towards propionic acid is reached for the ethane/catalyst molar ratio of ca. 1200, whereas a further sufficient increase of this ratio promotes the selectivity towards acetic acid (Fig. 1) and can even result in the suppression of the formation of propionic acid. Hence, a TON of 3.6×10^3 towards acetic acid, without detection of propionic acid, is reached for the very low catalyst amount of 0.042 µmol (ethane/catalyst molar ratio of 72.9×10^3; entry 8, Table 1), although corresponding to the low yield of 4.8%.

Table 2
Conversion of propane into butyric and acetic acids[a]

$$C_3H_8 + CO \xrightarrow[TFA,K_2S_2O_8]{HPA} (CH_3)_2CHCOOH + C_3H_7COOH + CH_3COOH$$

Entry	Catalyst	Catalyst amount (µmol)	Yield[b] (%)				TON[c]			
			Isobutyric acid	*n*-Butyric acid	Acetic acid	Total	Isobutyric acid	*n*-Butyric acid	Acetic acid	Total
1	**HPA-1**	20.0	43.3	21.2	1.3	65.8	56	28	2.0	86
2		2.50	23.7	11.2	3.5	38.4	246	116	37	399
3		0.084	0.3	–	4.1	4.4	87	–	1.2×10^3	1.3×10^3
4	**HPA-2**	20.0	31.3	16.7	–	48.0	42	22	–	64
5		10.0	21.8	10.0	1.5	33.3	57	26	4.0	87
6		2.50	35.0	24.6	–	59.6	364	256	–	620
7		0.084	0.9	2.4	9.5	12.8	268	712	2.8×10^3	3.8×10^3
8	**HPA-3**	2.50	26.8	13.9	1.9	42.9	278	144	21	443
9		0.084	21.4	8.8	7.0	37.2	6.5×10^3	2.7×10^3	2.1×10^3	11.3×10^3
10		0.042	4.3	1.6	5.5	11.4	2.6×10^3	970	3.3×10^3	6.9×10^3
11	$H_3[PMo_{12}O_{40}]$	2.50	0.6	–	8.6	9.2	6.0	–	88	94

[a] Reaction conditions (unless stated otherwise): C_3H_8 (8.5 atm), CO (30 atm), $K_2S_2O_8$ (4.00 mmol), CF_3COOH (5.0 mL), 80 °C, 20 h, in an autoclave (13 mL capacity). Propane and CO gases measured at 25 °C (amounts of C_3H_8 or CO gases correspond to 0.306 mmol atm^{-1}).

[b] Molar yield (%) based on C_3H_8, i.e. moles of products per 100 moles of propane (determined by GC); molar yields (%) based on $K_2S_2O_8$, if required, can be estimated as total yields × 0.65, e.g. 43% for run 1.

[c] Turnover number (moles of products per mol of catalyst).

Table 3
Conversion of methane into acetic acid[a]

$CH_4 + CO \xrightarrow[\text{TFA},K_2S_2O_8]{\text{HPA}} CH_3COOH$

Entry	Catalyst	Catalyst amount (μmol)	pCH$_4$[b] (atm)	pCO[b] (atm)	Yield of acetic acid[c] (%)	TON[d]
1	**HPA-1**	2.50	10	30	18.3	224
2		20.0	10	30	17.0	26
3	**HPA-2**	2.50	10	30	15.2	186
4	**HPA-3**	2.50	10	30	19.9	244
5		0.084	10	30	8.4	3.0×10^3
6		2.50	5	10	20.1	85
7	$H_3[PMo_{12}O_{40}]$	2.50	10	30	0.0	–

[a] Reaction conditions (unless stated otherwise): $K_2S_2O_8$ (4.00 mmol), CF_3COOH (5 mL), 80 °C, 20 h, in an autoclave (13 mL capacity).

[b] Measured at 25 °C (amounts of CH_4 or CO gases correspond to 0.306 mmol atm^{-1}).

[c] Molar yield (%) based on CH_4, i.e. moles of acetic acid per 100 moles of methane (determined by GC); molar yields (%) based on $K_2S_2O_8$, if required, can be estimated (except for run 6) as molar yields based on $CH_4 \times 0.765$, e.g. 15% for run 4 or 8% for run 6.

[d] Turnover number (moles of acetic acid per mol of catalyst).

Comparable behaviours are exhibited by the **HPA-2** and **HPA-3** catalyst. Hence, in the case of **HPA-3**, a fourfold decrease of the catalyst amount, from 10.0 to 2.50 μmol (the latter corresponding to the ethane-to-catalyst molar ratio of 1224), results in the preservation of the total yield (ca. 67%) and an overall TON increase from 208 to 816 (Table 1, entries 12 and 13). For **HPA-2**, an identical total yield (ca. 68%) and a similar overall TON (836) are observed for such an ethane-to-catalyst molar ratio (Table 1, entry 9). The highest overall TONs of 12.4×10^3 for **HPA-3** and 5.9×10^3 for **HPA-2** (corresponding to similar amounts of propionic and acetic acid or to only acetic acid, respectively) are achieved at the much lower catalyst amount of 0.042 μmol, although with a substantial yield drop, mainly for propionic acid (Table 1, entries 15 and 11).

The catalytic activities of the tested heteropolyacids for typical conditions (Fig. 2) are comparable (although being slightly higher for **HPA-2** and **HPA-3**) and thus do not depend markedly on the vanadium content. However, for very low catalyst amounts, the activity increases in the order of the V-content (**HPA-3** > **HPA-2** > **HPA-1**).

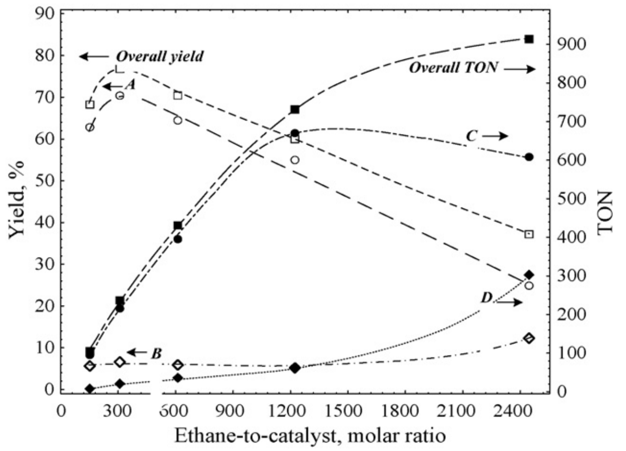

Fig. 1. Effect of the **HPA-1** catalyst amount on the yield of propionic (curve A) and acetic (curve B) acids and on the TONs towards propionic (curve C) and acetic (curve D) acids formation from ethane. The corresponding overall curves (A + B, C + D) are also shown. For reaction conditions see Table 1.

It is noteworthy to mention that no carboxylation reaction, i.e. no formation of propionic acid, is observed in the absence of vanadium in the heteropolyacid. Thus, the reaction catalyzed by $H_3[PMo_{12}O_{40}]$, (Table 1, entry 16) proceeds just with the formation of acetic acid as the result of ethane oxidation catalyzed by molybdenum. Therefore, the relevant vanadium role in C–C bond formation is evident.

3.2. *Carboxylation of propane into butyric acids*

Propane can be efficiently transformed into *iso*- and *n*-butyric acids with a total yield up to 65% in the presence of CO (typically at 30 atm pressure) and a heteropolyacid as catalyst (Table 2). The yield of isobutyric acid, under typical conditions, is often about twice that of *n*-butyric acid (e.g. 43% versus 21%, entry 1), thus indicating that the unique secondary carbon atom in the propane molecule undergoes an easier carboxylation than the other two primary C-atoms. Acetic acid is also formed during this reaction as a result of C–C bond cleavage and partial

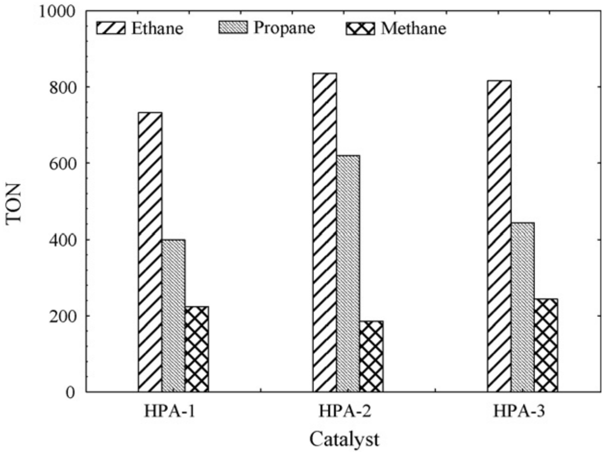

Fig. 2. Comparison of catalytic activities (overall TONs) of heteropolyacids for the conversion of alkane (ethane, propane and methane) into carboxylic acids. Reaction conditions: C_2H_6 (10 atm), C_3H_8 (8.5 atm), CH_4 (10 atm), CO (30 atm), catalyst (2.5 μmol), $K_2S_2O_8$ (4.0 mmol). For the other reaction conditions see Tables 1–3.

oxidation. However, the yield of CH_3COOH does not exceed 3.5%, under typical conditions. Isopropyl trifluoroacetate is also formed in considerable yield (up to 25% based on propane), thus becoming the main product at low CO pressure or in the absence of CO. However, the *n*-propyl ester $CF_3COOCH_2CH_2CH_3$ was not observed in accord with the higher reactivity of the secondary carbon atom of propane towards esterification in comparison with the primary carbon atoms.

The catalytic system exhibits a rather high activity even for considerably small amounts of catalyst. Thus, the decrease of this amount from 20.0 to 2.50 μmol (corresponding to a propane-to-catalyst molar ratio variation from 130 to 1040) leads to an overall TON growth from 86 to ca. 400 in the case of **HPA-1** (with a lowering of the total carboxylic acids yield from ca. 66 to 38%; Table 2, entries 1 and 2) or from 64 to 620 for **HPA-2** (with the overall yield increase from 48% to ca. 60%; Table 2, entries 4 and 6). The **HPA-3** catalyst also exhibits a high activity with a total yield of ca. 43% and an overall TON of 443 at the propane-to-catalyst molar ratio of 1040 (Table 2, entry 8). The highest overall TON values of 1.3×10^3, 3.8×10^3 and 11.3×10^3 for **HPA-1**, **HPA-2** and **HPA-3**, respectively, are observed at a rather low catalyst amount (0.084 μmol, corresponding to the propane-to-catalyst molar ratio of 32.5×10^3) (Table 2, entries 3, 7 and 9). This order of activity follows the V-content of the catalyst (**HPA-3** > **HPA-2** > **HPA-1**) but, under typical reaction conditions (Fig. 2), the highest overall activity is displayed by **HPA-2** (TON of 620, while **HPA-1** and **HPA-3** show similar TON values of ca. 400).

Vanadium has a key role in the propane carboxylation reaction since almost no butyric acids are formed and acetic acid is the main product in the reaction catalyzed by $H_3[PMo_{12}O_{40}]$ (Table 2, entry 11).

3.3. Carboxylation of methane into acetic acid

The catalytic carboxylation of methane into acetic acid was also achieved in the presence of CO by using the various vanadium containing HPAs (Table 3). They exhibit comparable activities, leading to typical acetic acid yields of 15–20% with TONs of 224–244 (Table 3, entries 1, 3 and 4; Fig. 2). The known [33] formation of methyl trifluoroacetate (at low CO pressure or in the CO absence) was also confirmed. As observed in the previous reactions, lowering the catalyst amount results in a TON increase and this becomes ca. 3.0×10^3 for the reaction catalyzed by **HPA-3** for the low catalyst amount of 0.084 μmol (i.e. at the high methane-to-catalyst molar ratio of 36.4×10^3) (Table 3, entry 5). The obtained yields and TONs (under our reaction conditions) are much higher than those reported previously [34] for methane carboxylation with such a type of catalysts (i.e. 0.56–0.64% yields of CH_3COOH with TONs of 22–24 for **HPA-1**, **HPA-2** and **HPA-3**). Nevertheless, as expected, the carboxylation of methane proceeds less efficiently than those of the less inert ethane and propane gases.

Similarly to the ethane and propane carboxylations, the role of vanadium in the formation of acetic acid is crucial, since without this metal in the heteropolyacid catalyst no carboxylation reaction is observed (Table 3, entry 7, for $H_3[PMo_{12}O_{40}]$).

3.4. Mechanistic considerations

It is known [6,8,37] that HPAs can undergo various structural transformations in their catalytic systems, depending on the working conditions (reaction medium, temperature, presence of O_2 and H_2O, etc.), thus acting as precursors for active species. The isolation and identification of the latter in our carboxylation systems were unsuccessful. However, as shown above, the presence of vanadium in the HPA catalyst is essential for the occurrence of carboxylation. Hence, oxovanadium centres are expected to play a key role, what is consistent with the reported [31b] behaviour of a somehow related system (i.e. trifluoroacetic anhydride/H_2O_2, 80 °C, 24 h), in the oxidation of methane to various oxygenated products (such as methylformiate and methyltrifluoroacetate) catalyzed by $[PMo_{11}VO_{40}]^{4-}$, which proceeds with the decomposition of the latter in the presence of H_2O_2 to give $[PMo_{11}O_{39}]^{7-}$ and $VO(O_2)^+$, which is stable in strong acidic medium. This oxoperoxovanadium cation was proposed [31b] to be responsible for the formation of oxygenated products via a radical chain mechanism. A radical process is also believed to occur in our system, namely involving both C-centered and O-centered radicals since the yields of carboxylic acids are fully suppressed when the reactions are carried out in the presence of either a C- or an O-centered radical trap [38], such as $CBrCl_3$, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT) or Ph_2NH.

The C-radical $R^\bullet$ can be formed by H-atom abstraction from the alkane (RH) by the sulfate radical $SO_4^{-\bullet}$ (or its protonated $HSO_4^\bullet$ form) derived from thermolytic decomposition of $K_2S_2O_8$ [39,40]. This is confirmed by radical trapping experiments that reveal the formation of various bromo- and chloroalkanes (e.g. CH_3CH_2Br, CH_3CHBr_2, CH_3CH_2Cl and CH_3CHCl_2 for ethane carboxylation, and $(CH_3)_2CHBr$, $CH_3CH_2CH_2Br$, $(CH_3)_2CHCl$ and $CH_3CH_2CH_2Cl$ for propane carboxylation), when the reaction is performed in the presence of $CBrCl_3$ and $K_2S_2O_8$. These organoalkanes are also formed in the absence of the HPA catalyst what indicates the key role of $K_2S_2O_8$ (in contrast to the catalyst metal centres) for the generation of the organo-radicals $R^\bullet$.

Carbonylation of $R^\bullet$ leads to the acyl radical $RCO^\bullet$ that, upon reaction with a peroxo-V catalyst, yields the $RCOO^\bullet$ radical which, by H-abstraction from the alkane or TFA, converts into carboxylic acid, as proposed [35g] to proceed for the methyl radical on the basis of theoretical calculations. CO_2 is detected in the gaseous phase, being expected from CO oxidation or decomposition ($K_2S_2O_8$ promoted [18c,34,41] or thermal [42]) of TFA. However, our *carboxylation* processes do not appear to proceed via free alcohol or free olefin, since they are not converted into carboxylic acids (with one more C atom than in the alkane) in our systems in the presence of CO. Nevertheless, we cannot rule out the possibility of involvement of some free alcohols and aldehydes in the *oxidation* of alkanes since, when used as substrates, they can be oxidized to the corresponding carboxylic acids (e.g. ethanol and acetaldehyde are converted to acetic acid, but not to propionic acid). However, neither free alcohol nor aldehyde (or ketone) were detected along the reaction. Organohydroperoxides ROOH (formed from coupling of the radical $R^\bullet$ with traces of O_2) can be involved in the formation of alcohols and ketones (that ultimately can lead to carboxylic acids), but we also did not detect the presence of hydroperoxides by using Shul'pin's method [43] (addition of PPh_3 prior to the GC analysis to convert ROOH into the corresponding alcohol). Under our reaction conditions, they possibly undergo decomposition. O_2 inhibits the formation of carboxylic acids, conceivably acting as a $R^\bullet$ radical trap [38b].

4. Conclusions

Highly efficient carboxylations, by CO in the $K_2S_2O_8$/TFA system, of gaseous alkanes (ethane, propane and methane) into the corresponding carboxylic acids catalyzed by vanadium containing heteropolyacids, $H_4[PMo_{11}VO_{40}] \times 34H_2O$ (**HPA-1**), $H_5[PMo_{10}V_2O_{40}] \times 32H_2O$ (**HPA-2**) and $H_6[PMo_9V_3O_{40}] \times 34H_2O$ (**HPA-3**), have been achieved. Methane forms acetic acid in ca. 20% yield, ethane leads to propionic (main product) and acetic (minor product) acids with a total yield of ca. 77%, whereas propane is transformed into a mixture of *iso*- and *n*-butyric acids in ca. 65% overall yield, under typical reaction conditions. The catalyst amount has a pronounced effect and very high catalyst TONs up to 12.4×10^3, 11.3×10^3 and 3.0×10^3 are obtained for ethane, propane and methane transformations, respectively, by using a sufficiently low HPA amount. In addition, the product distribution is also dependent on the catalyst amount and, in the cases of ethane and propane, low amounts of HPA favour the formation of acetic acid relatively to the other acids. Acetic acid may then even become the major detected product. Hence, in order to improve the selectivity towards propionic (from ethane) and butyric (from propane) acids, as well as the yields of these acids, one should not use a too high substrate-to-catalyst molar ratio.

The studied HPA catalysts, under typical reaction conditions, exhibit comparable activities towards each of the alkanes in the carboxylation reaction, which follow the order ethane > propane > methane. Hence, the catalytic activity is then not markedly dependent on the number of V atoms per molecule, but for the lowest catalyst amounts the activity increases with the vanadium content. In any case, the presence of vanadium in the HPA catalyst is essential for the occurrence of carboxylation, showing the relevant catalytic role played by this metal.

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