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Halide-free CO₂ cycloaddition onto styrene oxide catalysed by first row transition-metal derivatives of polyoxotungstates

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Abstract. Quaternary ammonium salts of metal derivatives of polyoxometalates [XW₁₁O₃₉M(H₂O)]ⁿ⁻ (X = P, Si; M = Cr, Mn, Co, Ni, Zn) were successfully tested instead of quaternary ammonium halides as catalysts in the cycloaddition of CO₂ to styrene oxide. Remarkably, they gave very satisfactory yields of styrene carbonate at moderate temperature (80°C).

Keywords: carbon dioxide, polyoxometalates, first row transition metal, cyclic carbonates.

Cyclic carbonates are key compounds with a large scope of applications, such as polymers, solvents in paints, batteries, degreasers, or for the synthesis of dimethylcarbonate.¹ However, industrial production of cyclic carbonates/polycarbonates still uses C(IV) sources such as phosgene which is extremely toxic and gives rise to HCl.² A promising strategy to improve sustainability is the “one-pot” synthesis of cyclic carbonates from alkenes using oxidants and CO₂, referred as oxidative carboxylation cascade reaction which requires the successive use of oxidation (OxCat) and CO₂ cycloaddition (CyCat) catalysts. Over the past two decades, deep progress was made in the development of CyCat systems, mainly based on quaternary ammonium (QAS) or imidazolium salts, especially iodide and bromide ones, coupled with Lewis acids.⁴ In particular, their utilization allowed the reaction of CO₂ with epoxides under mild conditions, a prerequisite for a one-pot oxidative carboxylation.⁵ Regarding epoxidation, efficient catalysts (OxCat) were reported for decades, including polyoxometalates (POMs) or their transition-metal substituted derivatives (M-POMs)⁶ which are a widely studied class of molecular compounds allowing the activation of O₂⁷ or H₂O₂⁸ in mild conditions. However, to date, publications dealing with the global oxidative cycloaddition cascade remain scarce.⁹ This is all the more surprising regarding the quantity of available alkene substrates, the potential interest of cyclic carbonates as well as the good compatibility between CO₂ and oxidants. Several explanations can be put forward, such as the difficulty of tuning the experimental parameters of the two successive steps. Furthermore, in the case where the oxidation step

is carried out with hydrogen peroxide as the oxidant, other problems appear since H₂O₂ reacts with bromide and iodide. It is therefore better to set up procedures that avoid the use of these halides to enable the one-pot reaction. A few studies have mentioned that some M-POMs can be used as CyCat alone in the absence of halides.^{10,11} Among these, our attention has turned to the use of tetraalkylammonium salts of the monometallic substituted Keggin-type [XW₁₁O₃₉{M(H₂O)}]ⁿ⁻. Some of these compounds indeed showed their ability to catalyze the cycloaddition reaction of CO₂ on certain very reactive epoxides (such as propylene oxide or epichlorohydrin), however harsh experimental conditions (150°C, P_{CO2} = 30 bar) were used. The mechanism which was initially proposed in this case relied on the ability of certain M-POM derivatives to efficiently activate CO₂.¹² It is noteworthy that this property has recently been exploited in the electrocatalytic CO₂ reduction for the formation of CO and formaldehyde, using the tetraoctylammonium salt of [SiW₁₁O₃₉(Co^{II})]⁶⁻.¹³ There is therefore a real interest in studying the catalytic activity of these [XW₁₁O₃₉{M(H₂O)}]ⁿ⁻ metal derivatives. Indeed, these compounds are particularly flexible since several parameters can be played on:

- i) the nature of the inserted metal cation. Such a study was initiated by Sakakura and coworkers who showed that at constant heteroelement X it was possible to classify the inserted cations by order of increasing reactivity towards the cyclization (Co²⁺ > Mn²⁺ > Ni²⁺ > Fe³⁺ > Cu²⁺).¹⁴
- ii) the nature of the heteroelement X. Indeed, depending on the nature and oxidation state of this heteroelement, the overall charge of the anion can be modulated, and thus the electronic density of the inserted metal.
- iii) the nature of the counter-ion associated to the POMs. In particular the length of the alkyl chains of supported quaternary ammonium cation has been recently reported in the literature as one parameter important for modulating the reactivity of QAS of halides.¹⁵

In the present work, our aim was to explore the key parameters that are truly influencing the conversion of styrene oxide (SO), taken here as the benchmark molecule, into styrene carbonate (SC) in the presence of CO₂. The experimental conditions were chosen in accordance with our previous studies using salophen complexes as CyCats,^{16,17} in terms of temperature (between 80 and 120°C), CO₂ pressure (P_{ini} = 11 bar at RT) and SO: CyCat mol/mol ratio (= 120:1, corresponding to 0.82 mol% of catalysts) (figure 1). With the

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autoclave used, the initial CO₂:SO mol/mol ratio was 4.5. Furthermore, although the idea of working without any solvents was particularly attractive, the solubility of CyCat M-POMs in the SO substrate proved insufficient. The catalytic tests were therefore carried out in a mixture of SO with the minimum amount of benzonitrile (2:1 v/v ratio, *i.e.* 1.4 mL of SO and 0.7 mL of benzonitrile).

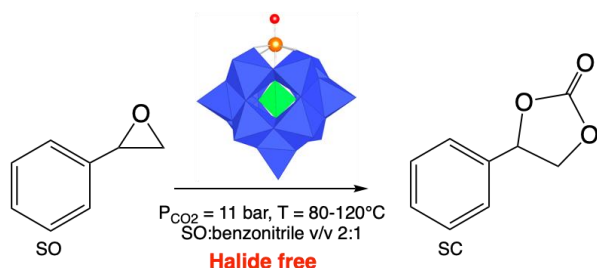


Figure 1. Experimental conditions for CO₂ cycloaddition onto styrene oxide catalyzed by (NR₄)_xK_y[XW₁₁O₃₉M(H₂O)]

Table 1 shows the results of the reaction between CO₂ and SO in the presence of the different (NBu₄)₃K_n[PW₁₁O₃₉M(H₂O)].3H₂O (M = Co(II), Mn(II), Ni(II), Zn(II), n = 2 and Cr(III), n = 1) used as CyCat. While the SO conversion was negligible after 5h at 80°C in the presence of the parent oxotungstate (NBu₄)₃[PW₁₂O₄₀] (table 1, entry 0), the conversion was found significant for all metallic cations (see table 1, entries 1, 4, 7, 11 and 14).¹⁸ In details, SO conversion was in between 15 to 26% at 80°C after 5h, except for the chromium complex for which it reached 56% (table 1 entry 1). However, in this last case, the yield of SC was low (12%), since we observed the formation of large amounts of oligomeric materials (44%). The composition of these oligomeric samples was determined by mass spectroscopy (MALDI-TOF, figure S4), which showed that the majority of these oligomeric species in the mixture were relatively small molecules, formed from the combination of the various individual constituents expected: SO, SC and benzonitrile (highest mass detected: m/z = 696.49). As expected, increasing the temperature led to a net increase in both SO conversion and SC yield with all M-POMs. For sake of illustration, (NBu₄)₃K₂[PW₁₁O₃₉Co(H₂O)].3H₂O (table 1, entries 7-9) showed almost complete conversion in 5 hours at 120°C. However, this was at the expense of the selectivity into cyclic carbonate, the target species, since the amounts of oligomeric species increased from 2% at 80°C to 53% at 120°C. This trend was comparable with all the metals (Table 1, entries 3, 6, 9, 13 and 16), with the exception once again of the Cr³⁺ derivative. Indeed, whatever the temperature, the predominant formation of polymeric compounds was observed, with the yield of cyclic carbonate being between 8 and 12% (table 1, entries 1-3). In a more general way, the most satisfying results (*i.e.* good SO conversion and SC selectivity at once) were obtained with the Ni²⁺-substituted derivative (table 1, entries 11-13).

Furthermore, In order to confirm that the cycloaddition reaction is actually metal-centred, we prepared the (NBu₄)₃K₂[PW₁₁O₃₉Co(imidazole)].3H₂O derivative (see supplementary information for the synthesis), in which the Co(II) centre was linked to an imidazole ligand in the terminal position. Using the same experimental conditions (80°C, 5h, table 1, entry 10), the catalyst appeared less efficient. A SO conversion of around

6% was observed, combined with an SC yield of 3%, the quantity of oligomeric species remaining more or less constant (3%). For sake of comparison, we checked that the N,N'-Bis(salicylidene-ethylenediimino)-Cobalt (II) ([Co(salen)]) complex (see SI for details), which also contains Co(II), had little or no catalytic activity under the same experimental conditions. This family of compounds is indeed known to behave as excellent co-catalysts (Co-CyCat) in the presence of halides. Under the conditions of this study, *i.e.* in the absence of halides, the SO conversion observed at 80°C after 5 hours was very low 7%, with an SC yield of 3% again (Table 1, entry 17).

In addition, control experiments were done in the presence of NBu₄Br for several catalysts (see Table S2 in supplementary information for details). As expected, we observed a significant increase of both the SO conversion and SC yield in all cases, which is the sign of a different mechanism in the presence of bromide. It is noteworthy that the yields in styrene carbonate obtained with the M-POM catalysts in the presence of NBu₄Br are significantly higher than those obtained in our previous studies with [M(salophen)] co-catalysts (M = Ni²⁺, Co²⁺, {Cr(Cl)}²⁺, {Mn(Cl)}²⁺) as well as with NBu₄Br alone (Table 1, entry 18) in the same conditions.¹⁷

Table 1. Catalytic activity of (NBu₄)₃K_n[PW₁₁O₃₉M(H₂O)].3H₂O (*cf.*

S.I.)

entry	M ⁿ⁺ inserted	T (°C)	SO conv. (%)	SC Yield (%)	Others (%)
0	PW ₁₂ ^a	80	-	traces	0
1	Cr ³⁺	80	56	12	44
2	Cr ³⁺	100	95	12	83
3	Cr ³⁺	120	100	8	92
4	Mn ²⁺	80	15	12	4
5	Mn ²⁺	100	30	22	8
6	Mn ²⁺	120	63	17	52
7	Co ²⁺	80	17	15	2
8	Co ²⁺	100	80	67	13
9	Co ²⁺	120	98	45	53
10	Co ²⁺ /imidazole	80	6	3	3
11	Ni ²⁺	80	26	22	4
12	Ni ²⁺	100	44	34	10
13	Ni ²⁺	120	75	70	5
14	Zn ²⁺	80	18	14	4
15	Zn ²⁺	100	41	32	9
16	Zn ²⁺	120	83	57	26
17	[Co(salen)]	80	7	3	4
18	(NBu ₄)Br	80	53	50	3

Reaction time: 5h, SO (12.2 mmol, 1.4 mL, CyCat (0.1 mmol), initial P_{CO2} = 11 bar, benzonitrile (0.7 mL) is used as solvent for the complete dissolution of CyCat and as internal reference. ^a(NBu₄)₃[PW₁₂O₄₀] was used as reference here to check the effect of an all oxotungstate core.

As mentioned in the introduction, a majority of studies dealing with the CO₂ cycloaddition used QAS halides as CyCat catalysts. In this regard, it was observed that the length of the alkyl chains in the tetraalkylammonium cations may play an important role.¹⁵ The hypothesis generally retained is that the increase of the lipophilicity of the nitrogen substituents resulted in the formation of loose anion/cation pairs.¹⁹ It follows that when the pair was more dissociated, the nucleophilicity of the halide toward the epoxide was increased. In the present study, the situation could be *a priori* different since the kinetically determining steps proposed in the literature corresponds either to the fixation of CO₂ or of the

epoxide on the transition metal incorporated into the M-POM.⁹ However, the results obtained in our case, *i.e.* in the absence of halides (see Table 2), showed that there is also a dramatic effect of chain length. While very little activity was observed for the shortest substituents (ethyl/propyl, table 2, entries 1 and 2), this activity increased significantly with the longest chains tested (NPen₄⁺, NHex₄⁺ and NOct₄⁺ cation with SO conversions in the range 45 to 54 %, and SC yield in the range 40 to 47%, table 2, entries 4-6). This was not a linear variation, but it does seem that the use of longer organic chains had a significant effect on the reactivity of CyCat. However, above a certain size (NPen₄⁺), the catalytic performances could not be improved anymore. One possible explanation is that beyond a certain chain length, the lipophilicity of QAS no longer changes. Electrostatic interactions of ammonium with M-POMs are then probably little different.

Table 2. Catalytic activity of (NR₄)_xK_y[PW₁₁O₃₉Co(H₂O)]·xH₂O or (NR₄)_nK_{5-n}[PW₁₁O₃₉Co(H₂O)]·xH₂O

Entry	NR ₄ ⁺	SO conv. (%)	SC Yield (%)	Others (%)
1	NEt ₄ ⁺	1	1	0
2	NPr ₄ ⁺	5	1	4
3	NBu ₄ ⁺	17	5	2
4	NPen ₄ ⁺	51	47	4
5	NHex ₄ ⁺	54	40	14
6	NOct ₄ ⁺	45	43	2

T = 80°C, Reaction time: 5h, SO (12.2 mmol, 1.4 mL), CyCat (0.1 mmol), initial P_{CO2} = 11 bar, benzonitrile (0.7 mL) is used as solvent for the complete dissolution of CyCat and as internal reference.

Furthermore, we were also interested in modulating the electron density at the metal centre introduced in the M-POMs by varying the charge of the oxotungstic core. We thus compared the reactivity of the phosphotungstic derivatives with the corresponding silicotungstic [SiW₁₁O₃₉{M(H₂O)}]⁶⁻ anions (see table 3). In this regard, several parameters were examined such as the nature of the transition metal cation (Co, Ni, Zn, table 3 all entries), the length of the alkyl chains of the QA (table 3, entries 1-4), the temperature (table 3, entries 7-8), We observed a weak but systematic decrease of the catalytic performance by replacing the phosphotungstate {PW₁₁O₃₉}⁷⁻ anion by the silico analogue {SiW₁₁O₃₉}⁸⁻. Hence the SO conversion was 54% with (NHex₄)₄K[PW₁₁O₃₉Co(H₂O)] while it was 43% for (NHex₄)₄K₂[SiW₁₁O₃₉Co(H₂O)] (table 3, entries 3 and 4). This behaviour seems to be consistent with the fact that the rate determining step proposed for this reaction involves the establishment of a metal-oxygen bond between the CO₂ or the epoxide and the metal.¹⁰ In view of the experimental results, we can therefore assume that it is the acceptor character of the metal that comes into play here: the greater the charge of the POM anionic ligand (*i.e.* the stronger the donor character of the POM ligand), the weaker the acceptor character of the metal. DFT calculations are currently underway to establish with certainty the reaction mechanism involving both the metal ion and the QAS counter ion.

Table 3. Comparative catalytic activity of the tetraalkylammonium salt of [XW₁₁O₃₉M(H₂O)]ⁿ⁻ (X = P, Si, M = Co, Ni, Zn).

entr	Complex	SO conv.	SC Yield	Others
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y	(%)	(%)	(%)	
1	(NOct ₄) ₅ [PW ₁₁ O ₃₉ Co(H ₂ O)]	45	43	2
2	(NOct ₄) ₆ [SiW ₁₁ O ₃₉ Co(H ₂ O)]	44	38	6
3	(NHex ₄) ₄ K[PW ₁₁ O ₃₉ Co(H ₂ O)]	54	40	14
4	(NHex ₄) ₄ K ₂ [SiW ₁₁ O ₃₉ Co(H ₂ O)]	43	37	6
5	(NBu ₄) ₃ K ₂ [PW ₁₁ O ₃₉ Ni(H ₂ O)]	26	22	4
6	(NBu ₄) ₃ K ₃ [SiW ₁₁ O ₃₉ Ni(H ₂ O)]	20	16	4
7	(NBu ₄) ₃ K ₂ [PW ₁₁ O ₃₉ Zn(H ₂ O)]*	41	32	9
8	(NBu ₄) ₃ K ₃ [SiW ₁₁ O ₃₉ Zn(H ₂ O)]*	34	26	8

T = 80°C, Reaction time: 5h, SO (12.2 mmol, 1.4 mL), CyCat (0.1 mmol), initial P_{CO2} = 11 bar, benzonitrile (0.7 mL) is used as solvent for the complete CyCat dissolution and as internal reference. * Temperature fixed at 100°C for these two samples.

In the continuity of this study, the catalytic performances of (NOct₄)₆[SiW₁₁O₃₉Co(H₂O)] were checked as a function of time at the lowest temperature studied (80°C). The SO conversion observed at 15h (63%), 24h (81%) and 48h (94%) as well as the final selectivity in SC (SC yield = 87 %, corresponding to a selectivity of 93% at 48h) were rather satisfactory at this temperature. Taking all these factors into account (*i.e.*: nature of the TM or and heteroatom, alkyl chain length), the compound (NHex₄)₄K[PW₁₁O₃₉Ni(H₂O)] was expected to exhibit the best catalytic activity at the lowest temperature (80°C). Indeed, after 15 h of reaction under the same experimental conditions as above, the conversion of styrene oxide reached 63% along with a yield of styrene carbonate of 57 % (SC selectivity above 90%) with this catalyst. This is currently the best result obtained by us at this temperature.

Finally, the reactivity of (NBu₄)₃K₂[PW₁₁O₃₉Co(H₂O)].3H₂O was tested towards several other substrates (see Table S2, supplementary information), again at 80°C. Depending on the substrate, the results were quite different. Indeed, no conversion was observed with limonene oxide, cyclohexene oxide and octene-1,2-oxide. On the other hand, modest and satisfactory conversions were respectively obtained for propylene oxide (10%) and epichlorohydrin (33%) after 5h of reaction. More interestingly, these conversions were associated with a 100% selectivity for the corresponding epoxide (no other products detected).

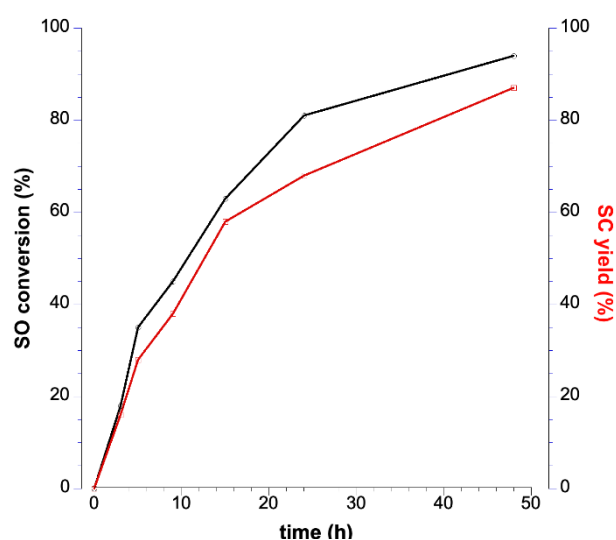


Figure 2. Evolution of the SO conversion (in black) and SC yield (in red) as a function of time using (NOct₄)₆[SiW₁₁O₃₉Co(H₂O)]. Exp. conditions: T = 80°C, SO (12.2 mmol, 1.4 mL), CyCat (0.1 mmol), initial P_{CO2} = 11 bar, benzonitrile (0.7 mL) is used as solvent for the complete dissolution of CyCat and as internal reference.

Conclusions

In this study, we showed that first-row transition metal derivatives of polyoxotungstates are promising homogeneous catalysts for the formation of cyclic styrene carbonate from styrene oxide (used here as a benchmark molecule) in the absence of Lewis bases such as halides, which are incompatible with oxidation processes involving H₂O₂. Even if this behaviour has been mentioned earlier in the literature, it has been noticed that reactions conditions were harsher. Here we showed that these catalysts were rather efficient at lower temperature and CO₂ pressure, leading to almost complete conversion after 48 hours in some cases. Although the nature of the metal cation introduced had a real influence on the conversion of the epoxide substrate, it also had a significant effect on the selectivity for cyclic carbonates. While the Cr(III)-based derivative was highly selective for the formation of polymeric species, most of the other metal ions tested showed promising yields of styrene carbonate.

Furthermore, the catalytic efficiency was also increased by using quaternary ammonium counter-ion with long chains. This point was particularly critical since the conversions rates may be multiplied by a factor of 3 simply by increasing the length of the chain by one carbon atom (from (NBu₄)⁺ to (NPen₄)⁺). These results need to be put into a broader context, since this particular reaction is also considered as the second step of the one-pot oxidative carboxylation of alkenes. One of the obstacles to implementing efficient processes for that complex reaction is the incompatibility of using halides and an oxidant such as H₂O₂ together. The preliminary results presented are therefore clearly a fundamental step towards one-pot catalytic systems for the oxidative CO₂ cycloaddition of alkenes.

Author Contributions

RV conceptualized and formulated the original ideas for this work. JR carried out the research and investigation process, specifically performing the experiments, and data/evidence collection. The experimental part was supervised and validated by FL and RV. JR collected and formatted the experimental data and bibliography necessary for the writing of the manuscript. The preparation of the first draft of the manuscript was done by RV. FL, AP and JR participated in the writing and correction of the manuscript.

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Conflicts of interest

There are no conflicts of interest to declare.

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