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PAPER

Insights in the Aerobic Oxidation of Aldehydes[†]

Laurent Vanoye,^a Alain Favre-Réguillon,^{a,b*} Asma Aloui,^a Régis Philippe,^a and Claude de Bellefon^{a*}

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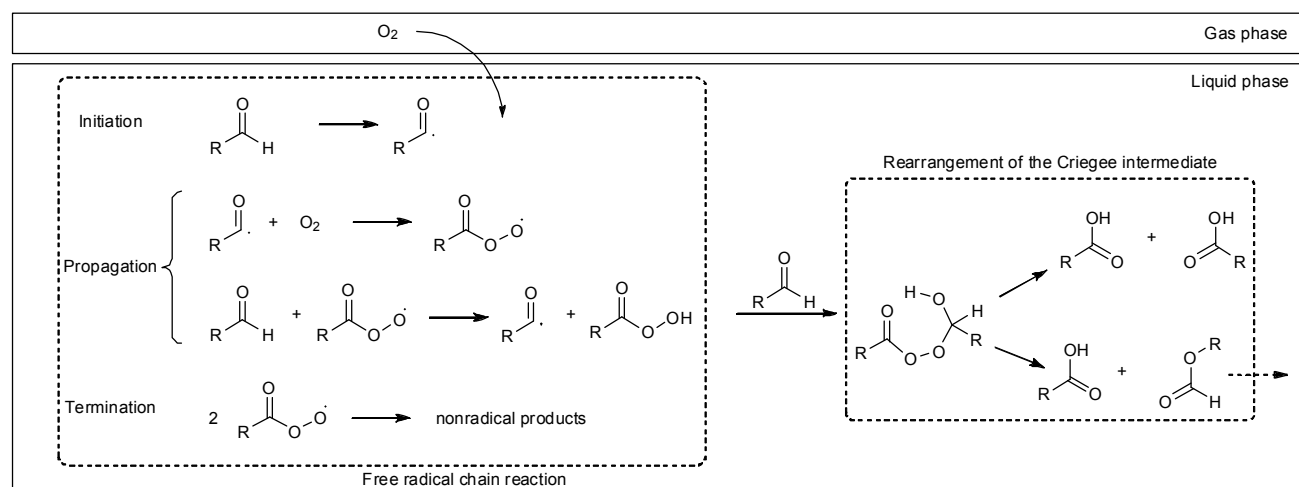
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5 The hydroformylation of olefins (oxo synthesis) is the most important process for the production of higher aldehydes (> C₄). The liquid phase oxidation of the latter to carboxylic acids by molecular oxygen or air has been known for more than 150 years and is an industrially important process. However, in the recent literature, several different oxidizing reagents and catalytic processes have been reported for this oxidation but most of them have limitations as they use environmentally unacceptable reagents or
10 unnecessarily sophisticated conditions. Herein, we re-evaluated the air oxidation of aldehydes. We show that under mild conditions (air or oxygen and non-optimized stirring), reactions are transfer limited and thus catalyst has no effect on reaction rate. Using efficient stirring (self-suction turbine), uncatalysed air oxidation of 0.8 M aldehyde is possible in 50 min. at room temperature whereas less than 10 min. was necessary with 10 ppm of Mn(II). Thus, recommendations for avoiding common pitfalls that may rise
15 during the evaluation of new catalysts are made.

1. Introduction

The principal method for the commercial production of C₄-C₁₃ carboxylic acids is the oxidation in air (autoxidation) of the corresponding aldehydes¹ obtained by hydroformylation of olefins (oxo synthesis).² This reaction is catalysed on an industrial scale by Co complexes.¹ The autoxidation of aldehydes in the liquid phase was shown by Bäckström^{3,4} to be a chain reaction yielding, as the initial product, a peracid (Scheme 1). A

subsequent condensation between the peracid and the aldehyde
25 produces the corresponding carboxylic acid via a tetrahedral adduct similar to the Criegee intermediate observed in the Bayer-Villiger reaction. The migration of the hydride from the aldehyde moiety to the nearest peroxide oxygen gives two carboxylic acids whereas the migration of the alkyl group from the aldehyde gives
30 an equimolar mixture of carboxylic acid and formate.^{5,6} The ratio of hydride to alkyl migration was found to depend critically on the structure of aldehydes, temperature, solvent, ...



Scheme 1 Autoxidation of aldehydes to the corresponding acids

35 On the lab-scale, the autoxidation of aldehydes has been catalysed by different metallic ions in the form of salts or organic complexes of Mn, Co, Fe, Cu, Ni, Cr or Au.^{4,6-13} However, the wide variety of reaction conditions, catalyst characteristics and methods for rate calculations make comparing the literature

40 results difficult. Moreover, the pronounced effect of small amounts of inhibitors and initiators upon the rate has made quantitative measurement and comparison of rates obtained by different investigators very difficult.^{4,8,14} The comparison is further complicated because some reactions are carried out in a

mass transfer limited regime where the rate limiting step is the rate of oxygen transfer from gas bubbles into the liquid.^{4,7,8,11,14}

Recently, the growing awareness of the environment has created a demand for efficient oxidation process with environmentally friendly oxidants under mild conditions and has led to rich developments during recent decades.¹⁵ Highly efficient, selective and metal-free oxidations of aldehydes have been reported with hydrogen peroxide and oxone.¹⁶ However, di-oxygen and in particular di-oxygen from air is the ultimate

“green” oxidant and several procedures have been reported for the aerobic oxidation of aliphatic aldehydes to the corresponding carboxylic acids using such green oxidant. In order to compare the different systems described in the literature, air or oxygen oxidation of aliphatic aldehydes at room temperature only will be considered. The productivity of these reactions calculated as mM of aldehyde converted by volume of liquid phase by hour and for 0.2 bar of O₂ (*i.e.* air) are listed in Table 1.

Table 1 Comparison of aldehyde oxidation by molecular oxygen at room temperature described in the literature.^a

Entry	Oxidant	Catalyst	Substrate	Solvent	Time (h)	Conversion (%)	Productivity (mM/L/h) ^b	Ref.
1	O ₂ bubbling	–	2-ethylhexanal	CH ₃ CN	2.0	82-93	98-112	^{5,6}
2	air bubbling	–	<i>n</i> -heptanal	CH ₃ CN	3.5	12	41	12
3	air	–	2-ethylhexanal	water ^c	12	86	23	17
4	O ₂ ballon	–	2-ethylhexanal	water ^c	2.3	88	28	17
5	air bubbling	Au/CeO ₂	<i>n</i> -heptanal	CH ₃ CN	3.5	78	263	12
6	O ₂ ballon	Ni (II) ^d	<i>n</i> -octanal	dichloroethane	3.0	97	65	9
7	O ₂	Fe (III) ^d	2-ethylhexanal	dichloroethane	3.0	100	83	10
8	O ₂ bubbling	H ₂ TTP ^e	<i>n</i> -octanal	CH ₃ CN	48.0	96	0.27	18
9	air sat. solv.	Sb(II) ^d	<i>n</i> -decanal	water/ CH ₃ CN	80.0	69	60	19

^a Oxidation performed at room temperature and at atmospheric pressure in classical glassware using magnetic stirring. ^b Productivity was calculated as mM of aldehyde converted by volume of liquid phase by hour and for 0.2 bar of O₂. ^c Aldehyde was insoluble in water; “on water” effect was discussed *vide infra*. ^d soluble catalyst. ^e H₂TTP : non metallated porphyrins and irradiation ($\lambda > 350$ nm) was used.

The productivity calculated for uncatalysed oxidation (Table 1, entries 1-4) can vary by a factor of 4. These differences can be explained by the different aldehyde reactivity (Table 1, entries 1 and 2) or by solvent effects (Table 1, entries 1 and 4). It should be mentioned that using the correction of the partial pressure of O₂, the same productivity for the same reaction performed with air or with pure O₂ was obtained (Table 1, entries 3-4). More surprising are the similar or lower productivities observed with the catalysed reactions compared to the uncatalysed reaction, except for entry 5, Table 1. Indeed, the liquid-phase oxidation of organic compounds with air or oxygen as the oxidant involves a complex interplay of intrinsic parameters (aldehyde reactivity, solvent, ...) and extrinsic parameters (concentration, oxygen partial pressure, catalyst, initiators/inhibitors, ...) as well as physical phenomenon such as gas to liquid mass transfer. When oxygen transfer becomes the rate limiting step, the rate of the overall process is no longer controlled by the chemical mechanisms but rather by physical transport phenomena (diffusion, convection). Under these conditions, the chemical performances (productivity, selectivity) can be severely falsified by oxygen starvation in the liquid.^{4,7,8,11,14} Thus, one could suspect that the differences in productivity observed in Table 1 could be explained by oxygen mass transfer resistance. This prompted us to re-investigate the lab-scale oxidation of aldehyde with air at room temperature.

2. Experimental section

2.1 Safety

It is worth mentioning that in the case of oxidation reactions, fuel, oxidant and energy are present at the same time in the reactor. Thus, the safety of the process should receive explicit attention. While oxidation reactions are run routinely and safely on large scale following safety regulations and procedures, the possibility of forming explosive vapour space on lab-scale is greatly reduced when pure oxygen is replaced by air and the temperature is

limited to room temperature to decreased vapour pressure of organic compounds.²⁰

2.2 General

2-ethylhexanal (96%), *n*-octanal (99%), cyclohexanecarboxaldehyde (97%) benzaldehyde (>99.5%), analytical grade solvents (>99%) (Aldrich) were used as obtained from the supplier and stored at 4 °C under N₂ with protection from light. Mn(II) 2-ethylhexanoate (40% in mineral spirit) was used as obtained from Strem. Reconstituted air (O₂ 21%wt and N₂ 79%wt) was supplied from Air Liquide.

2.3 Procedure of the oxidation of aldehydes

The reactions were performed in a 135 mL thermo-regulated stainless steel autoclave (120 mL of useful capacity) operating in batch mode. Four baffles were mounted to the reactor walls. The reaction medium was stirred by a Rushton turbine or a self-suction turbine. A total volume of 40 mL of the desired mixture of 2-ethylhexanal and solvent were placed in the reactor. The temperature was set to 25 °C and the reactor was then pressurized with lab bench compressed air (8 bar) in about 10 s. When the pressure reading has stabilized (typically after about 10 s), the aldehyde oxidation experiment was started by switching on the agitator. The time-course of the gas pressure decrease was measured with a pressure transducer and recorded on-line using Labview®. The reaction mixture was analysed at the end of each experiment using a Shimadzu 2010 GC-MS system equipped with a DB-5 column. In all cases, the conversion calculated from oxygen consumption and determined by GC-MS was within the experimental error (5%). For higher pressure (24 to 40 bar), the same procedure was used with reconstituted air (O₂ 21%wt and N₂ 79%wt). For catalytic reaction, catalyst was added to the organic phase at room temperature before pressurization.

3. Results and Discussion

3.1 Uncatalysed autoxidation of 2-ethylhexanal

Initial attempts to optimize the reaction conditions for the autoxidation of aldehydes to the corresponding carboxylic acids were done using 2-ethylhexanal, an industrially important aldehyde produced worldwide on a large scale.^{1,21} For safety reasons, the autoxidation of diluted aldehyde with air was studied. A blank experiment was first performed in a thermo-regulated stainless steel autoclave operating in batch mode with 0.8 M of 2-ethylhexanal in heptane. The reactor was pressurized with lab bench compressed air (8 bar) at 25 °C. The reaction medium was stirred at 1000 rpm by a Rushton turbine (RT) and the time-course of the pressure decrease in the reactor was recorded on-line (Fig. 1). Note that, under these conditions and considering the volume of solution (40 mL) and the volume of the reactor (120 mL), the molar ratio between the aldehyde and the oxygen is 2.9 and oxygen is the conversion limiting reagent.

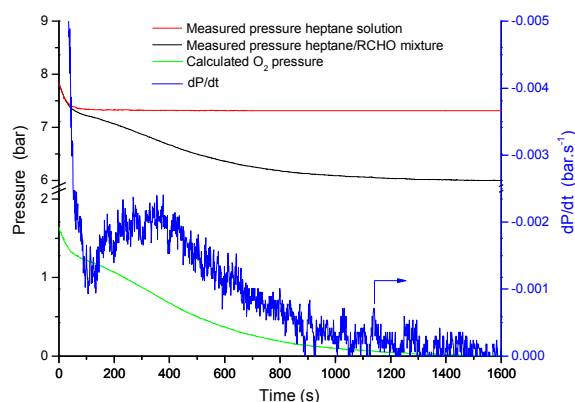


Fig. 1 Reactor pressure, calculated oxygen partial pressure and oxygen consumption rate as the function of time and composition of the liquid phase. Liquid phase 40 mL, 80 mL of air at 8 bar, 25 °C, RT at 1000 rpm.

After stabilization at the desired pressure (8 bar) at room temperature, the experiment was started by switching on the agitator. A rapid and complex evolution of the reactor pressure with time, in the absence of catalyst, could be noticed. After 1400 seconds, a constant pressure was obtained. GC-MS analysis of the reaction mixture shows an aldehyde conversion of 35% and a selectivity of 80% towards the carboxylic acid comparable to previously published catalysed autoxidation.^{5,6} The by-products were identified, *i.e.* 3-heptylformate, 3-heptanol and are compatible with a Criegee intermediate.

For given solvent and pressure conditions, the measured reactor pressure includes the partial pressure of O₂, N₂, solvent and solutes. For a given reaction, the partial pressures of N₂ and solvent are constant and the variation of the partial pressures of solute could be neglected. Thus, from the reactor pressure, the oxygen partial pressure (P_{O₂}) can be calculated quite directly and plotted as the function of time as shown in Fig. 1. Under those conditions, we could estimate that the oxygen present in the reactor was quantitatively reacted in less than 1400 s. This is in agreement with the aldehyde conversion and the stoichiometry of the reaction. Thus, the derivatives of the total pressure (dP/dt)

could be considered as a fairly reliable approximation of the oxygen consumption rate (dnO₂/dt). From the P=f(t) plot, the dnO₂=f(t) plot is constructed as shown in Fig. 1.

From the oxygen consumption rate (Fig. 1), three reaction steps were distinguished: i) the first 100 s correspond to the dissolution of gas in the liquid phase. No further pressure decrease could be observed with pure heptane. ii) A concomitant rapid increase of O₂ consumption was observed which could be related to aldehyde autoxidation through free radical chain mechanism. The overall reaction rate increases to a maximum after 400 s in this experiment. iii) Afterwards, the reaction rate slows down to zero due to the decrease of the ratio of chain propagation over termination. This ratio drops because of the decrease of reagents concentrations (aldehyde, O₂...) in the liquid phase. After 1400 s, the conversion of O₂ was quantitative and corresponds to the measured conversion of 2-ethylhexanal, *i.e.* 35%.

Under these conditions, a productivity of 140 mM/L/h for 0.2 bar of O₂ (*i.e.* air) could be calculated. This value is comparable to the best value obtained with pure oxygen (Table 1, entry 1) or with catalysed reaction with air as oxidant (Table 1, entry 5) but far exceeds the productivity for catalysed reactions listed in Table 1. The results could be explained by oxygen mass transfer resistance obtained using classical glassware used in the literature with poor agitation and without baffles. To emphasize such a limitation, we studied the effect of the stirring rate and the turbine type on the latter solution, *i.e.* 0.8 M.

3.2 Effect of stirring rate

Even under lab-scale conditions (diluted solution, 25 °C), an improvement of the oxidation rate was observed with increasing the stirring rate (ESI). For these specific conditions, the reaction controlled regime was only obtained using a self-suction turbine (SST) for stirring rates above 1000 rpm (Fig. 2). Under these conditions, the oxygen conversion was total in less than 600 s. It should be emphasized that, as expected, the selectivity was not influenced by the improvement of the oxidation rate.

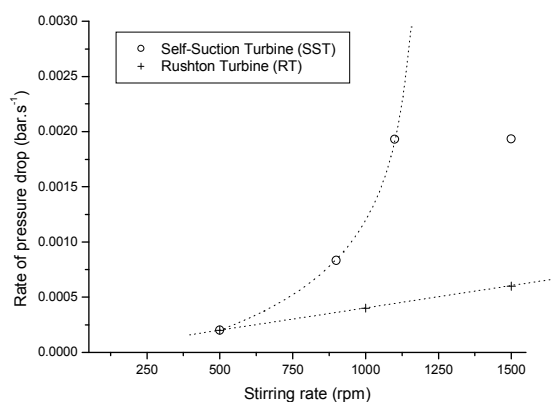


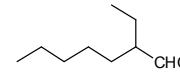
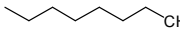
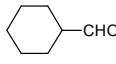
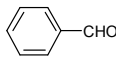
Fig. 2 Rate of pressure loss determined at P(O₂)=0.1 bar as the function of stirring rate and turbine type. 2-ethylhexanal 0.8 M in heptane 40 mL, 80 mL of air at 8 bar, 25 °C.

3.3 Substrate scope

Under the same conditions, autoxidation of different aldehydes was studied and the results are shown in Table 2. As expected from literature data, a strong influence of aldehyde structure both on selectivity and on productivity could be noticed. The highest

selectivity was observed with the linear aliphatic aldehyde (Table 2, entry 2), while the lowest selectivity was obtained with 2-ethylheptanal (Table 2, entry 1).⁶ Aromatic aldehydes show the lowest productivity due to higher termination rate constant.²²

Table 2 Influence of aldehyde on selectivity, productivity and maximum oxygen consumption. Aldehyde 0.8 M in heptane 40 mL, 80 mL of air at 8 bar, 25 °C, SST 1500 rpm

Entry	Aldehyde	Conversion (%)		Time ^c (s)	Selectivity ^d (%)	Productivity ^e (mM/L/h)
		RCHO ^a	O ₂ ^b			
1		35 ^[b]	100	300	85	672
2		35 ^[b]	100	2000	99	101
3		35 ^[b]	100	120	95	1680
4		35 ^[b]	100	3000	99	67

^a GC/MS analysis. ^b an aldehyde / oxygen ratio of 2.9 is used. ^c time required to obtain a constant reactor pressure. ^d Selectivity towards the corresponding carboxylic acid, determined by GC/MS analysis of the crude. ^e Productivity calculated as mM of aldehyde converted by volume of liquid phase by hour and for 0.2 bar of O₂.

3.4 Effect of aldehyde concentration

The influence of the aldehyde concentrations in heptane from 0.16 M to 6.4 M (100% w/w) was studied using 2-ethylhexanal. Results are reported in Fig. 3.

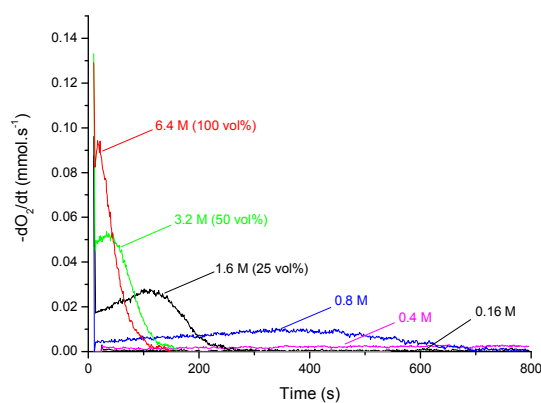


Fig. 3 Oxygen consumption rate as the function of time and concentration of 2-ethylhexanal in heptane. 40 mL of solution, 80 mL of air at 8 bar, 25 °C, SST at 1500 rpm.

Under these conditions, total conversion of oxygen was observed (except for 0.16 M where O₂ was in large excess but the reaction was stopped before completion) and the selectivity determined by GC-MS was comparable within experimental errors. As expected from free radical chain reaction mechanism, the oxygen consumption rate was strongly dependent on the aldehyde concentration as it is an important factor for radical chain reaction. For concentrations above 0.8 M (*i.e.* 12.5 vol%) maximum overall reaction rate was observed in less than 100 s. After, the reaction rates are limited by oxygen concentrations in the reactor. For lower aldehyde concentration, *i.e.* 0.16 and 0.4 M, the aldehyde autoxidation proceeds slowly and very little

variation of the oxygen consumption rate as the function of time are noticed (Fig. 3). For a concentration of 0.8 M, maximum overall reaction rate was obtained after 400 s until a decrease of the ratio of chain propagation over termination was noticed.

3.5 Solvent effect

Solvent effect for air autoxidation of 2-ethyl-hexanal was then studied with an aldehyde concentration of 0.8 M (Fig. 4). With all the solvents tested (except for DBE and *i*PrOH where the reaction was stopped before completion), total conversion of oxygen was found (*i.e.* an aldehyde conversion of 35% was determined by GC/MS) and the determined selectivity for the corresponding carboxylic acids was only influenced by the solvent to a small extent.⁶ For comparison purposes, one experiment was performed under “on water condition” (Table 1, entries 3-4).¹⁷ Using water, 30/1 volume ratio, reaction rate comparable to those obtained with organic solvents using an autoclave stirred with a self-suction turbine. Thus, the “on water effect” observed with hydrophobic aldehyde may be tentatively interpreted by a concentration effect (Fig. 4) and by aldehyde spreading on the air bubble surface obtained by magnetic stirring.²³ Such spreading increases the oxygen transfer usually obtained in classical glassware as used by A. Vigalok *et al.* and thus increase the reaction rate.¹⁷

An influence of the solvent on the reaction rate of aldehydes autoxidation has been noticed.^{6,24} In particular, under our conditions, low reaction rates were obtained using *i*PrOH and dibutylether (DBE) (Fig. 4). The latter, and especially DBE, can form peroxide via an autoxidation process that could compete with the free radical chain reaction and thus inhibit aldehyde autoxidation. Surprisingly, the reaction rate observed with hexanoic acid, acetonitrile and heptane was inversely proportional to the calculated oxygen solubility in the solvent (ESI). The highest O₂ consumption was obtained in heptane after 400 s (Fig. 4), whereas the lower were obtained for acetonitrile

and particularly for hexanoic acid (decreased by a factor of 7). Furthermore, the maximum O₂ consumption rate is shifted in time, 800 and 1300 s for acetonitrile and hexanoic acid respectively.

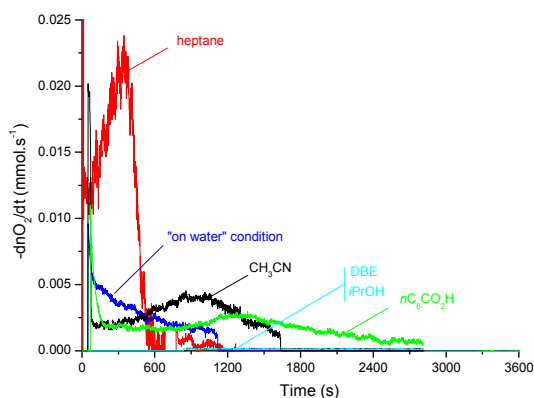


Fig. 4. Oxygen consumption rate as the function of time and solvent. 2-ethylhexanal 0.8 M 40 mL, 80 mL of air 8 bar, 25 °C, SST at 1500 rpm.

Table 3 Viscosity, O₂ solubility and Maximum oxygen consumption rate as the function of solvent

Entry	Solvent	Viscosity ^[a] (mPa.s ⁻¹)	O ₂ solubility ^[b] (mmol.L ⁻¹ .PO ₂ (bar) ⁻¹)	Maximum oxygen consumption rate ^[c] (mmol.s ⁻¹)
1	pentane	0.225	12.29	0.033
2	heptane	0.393	7.15	0.023
3	nonane	0.648	5.41	0.012
4	decane	0.92	4.56	0.008
5	Tetradecane	2	3.57	0.003

^a ref. ²⁷, ^b ref. ²³, ^c determined with 2-ethylhexanal 0.8 M 40 mL, 80 mL of air at 8 bar, 25 °C, SST at 1500 rpm.

However, even for alkanes, the viscosity and the solubility of oxygen are coupled. The viscosity of the solvent increase while chain length of the alkanes is increasing²⁷ but the solubility of oxygen decreases with increasing chain length of the alkanes.²³ Therefore, determination of kinetic parameters, especially reaction orders, is required for further discussion.

In all previous reactions, aldehyde was present in large molar excess (aldehyde / oxygen ratio of 2.9). In order to determine the apparent reaction order, the reaction had to be performed using excess of oxygen. Thus, pressurized reconstituted air (O₂ 21 wt% and N₂ 79 wt%) was used. Under our conditions, with a reactor pressure of 24 bar, oxygen is in stoichiometric amount and with 30 and 40 bar of reconstituted air, an excess of oxygen is obtained. The reactor was pressurized with reconstituted air at 25 °C to the desired pressure (24 to 40 bar). When the pressure reading has become constant, the experiment was started by switching on the agitator.

Aldehydes autoxidation involves different types of radicals and among them the acylperoxy radical “RCO₃•” (Scheme 1). Radical-radical recombination reactions require so little activation energy that they are usually diffusion controlled in solvents of normal viscosity.²⁵ Thus, depending of the viscosity of the solvent, the diffusion of the radical species out of the solvent cage²⁶ could be decrease and favour the recombination (termination step). The latter decrease the reaction rate. To further probe such a “cage effect”, air oxidation of 2-ethylhexanal was studied under the same conditions with alkanes of various viscosity, *i.e.* pentane (*n*-C5), heptane (*n*-C7), nonane (*n*-C9), decane (*n*-C10) and tetradecane (*n*-C14) (Table 3).

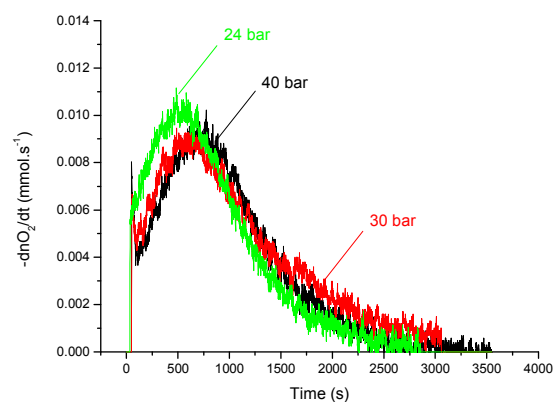


Fig. 5 Oxygen consumption rate as the function of time and pressure. 2-ethylhexanal 0.8 M in heptane 40 mL, 80 mL of O₂/N₂ (21/79 wt%), 25 °C, SST at 1500 rpm.

The reaction profiles were almost identical as a function of the initial reactor pressure. After 2000s, a stable pressure was obtained (ESI). For all pressures, GC/MS analysis of the crude reaction mixture shows a complete conversion of the 2-ethylhexanal with a selectivity of 85% towards the corresponding carboxylic acid product. The oxygen consumption rate profiles (Fig. 5) are identical for the three pressures within experimental errors clearly indicate that the apparent reaction order in oxygen, under those conditions, is zero. Thus, the variation of the

maximum reaction rate observed for alkanes (Table 3) could not be explained by the oxygen solubility in the solvent but by the viscosity of the solvent (Fig. 6). Aldehyde autoxidation shows a complex solvent effect and among others, viscosity of the solvent was clearly an important factor.

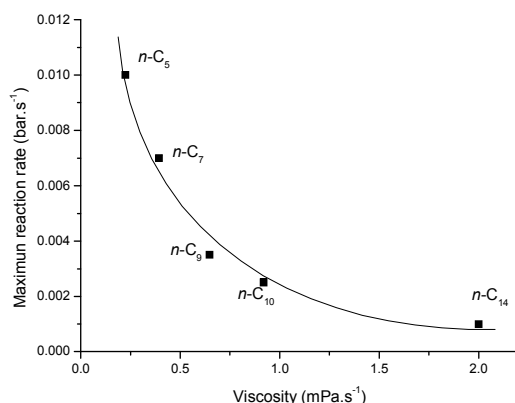


Fig. 6 Maximum reaction rate as the function of viscosity of the solvent (see ²⁷). 2-ethylhexanal 0.8 M 40 mL, 80 mL of air at 8 bar, 25 °C, SST at 1500 rpm.

3.6 Catalytic oxidation of 2-ethylhexanal

All the previous oxidation reactions were performed without added catalyst. The promoting effect of stainless steel originated from autoclave walls has already been demonstrated for oxidation reaction and cannot be neglected a priori.²⁸ Aldehyde autoxidation in metal free reactor will be discussed in a forthcoming publication. However, manganese(II) 2-ethylhexanoate was evaluated as catalyst¹¹ for the air oxidation of 2-ethylhexanal and a comparison with uncatalysed reaction is presented in Fig. 7.

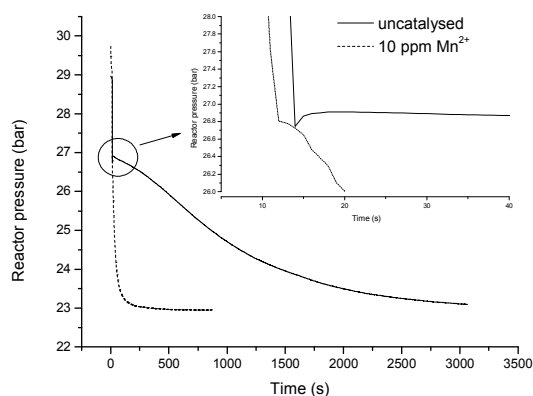


Fig. 7 Evolution of the pressure as the function of time and catalyst. 2-ethylhexanal 0.8 M in heptane 40 mL, 80 mL of O₂/N₂ at 30 bar, 25 °C, SST at 1500 rpm, Mn(II): 0 ppm or 10 ppm.

With an excess of oxygen (*i.e.* 30 bar of air), after 3000 s, the uncatalysed conversion of 2-ethylhexanal was complete whereas only 500 s were necessary with 10 ppm of Mn(II). The 20 fold improvement of oxidation rate in the presence of catalyst had no effect on the product selectivity. The strong improvement of the

oxygen consumption rate using catalytic amount of Mn(II) is obtained by significantly decreasing the initiation time (Fig. 7 insert). The maximum oxygen consumption rate reaction rate is achieved in 10 and 500 s for catalysed and uncatalysed reactions respectively.

Conclusions

The liquid phase autoxidation of aldehyde by air has been known for a long time^{4,8} and the reaction mechanism and kinetics of the oxidation have been widely studied. Recently, several new catalysts have been reported for this oxidation. However, in most case, we can suspect that the reactions are carried out in a mass transfer limited regime, *i.e.* the reaction rate is limited by the oxygen mass transfer. Such phenomenon could lead to much confusion in the interpretation of the results.

We have shown that uncatalysed oxidation of aldehydes using oxygen from air at room temperature is an effective method and a safe process to produce carboxylic acids. A strong influence of stirring rate, solvent type, solvents viscosity on the chemical rate was fully demonstrated. These classical effects have been neglected in most recent papers on liquid phase autoxidation of aldehyde by air and may have a strong impact on catalyst screening interpretations.

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Notes and references

^a Laboratoire de Génie des Procédés Catalytiques (LGPC), UMR 5285 CNRS/CPE Lyon, Université de Lyon, 43 boulevard du 11 novembre 1918, 69616 Villeurbanne cedex, France. E-mail: cdb@lgpc.cpe.fr

^b Conservatoire National des Arts et Métiers, Ecole SITI, Département CASER, Equipe CGP, 2 rue Conté, 75003 Paris, France. E-mail : favrereg@cnam.fr

[†] Electronic Supplementary Information (ESI) available: Figures of the evolution of the reactor pressure as the function of the parameters studied, rate of pressure loss against oxygen residual pressure determined as the function of the parameters studied, oxygen consumption rate as a function of the parameters studied, Calculated solubility of O₂ in solvent. See DOI: 10.1039/b000000x/

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TOC

For catalysed or uncatalysed air oxidation of aldehyde, efficient mixing is critical because the reaction rate is limited by oxygen mass-transfer.

