

Factors Affecting the Selectivity of Air Oxidation Of 2-Ethylhexanal, an α -Branched Aliphatic Aldehyde

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Abstract:

Various solvents and metal catalysts were tested in air oxidation of 2-ethylhexanal to elucidate the effects of different variables on the reaction path of the substrate. The primary goal was to determine the optimal conditions for maximising the yield of carboxylic acid and minimising the formation of other products. Solvents and catalysts both had a significant impact on the product distribution. The best selectivity of 2-ethylhexanal to 2-ethylhexanoic acid, 84%, was obtained with octanoic acid as solvent and manganese(II) acetate as catalyst. Addition of an aromatic aldehyde, benzaldehyde, or *p*-methoxybenzaldehyde retarded the oxidation rate of both 2-ethylhexanal and aromatic aldehyde dramatically.

Introduction

Many carboxylic acids are produced from the corresponding aldehyde by dioxygen oxidation, both industrially and on laboratory scale. The reaction mechanism and kinetics of the oxidation of various aldehydes with dioxygen have been widely studied, but few comparisons have been made of the effects of different catalysts^{1,2} or solvents³ on the oxidation path of aldehyde.

Larkin et al.¹ have studied oxidation of 2-methylpropanal presence of Cu(II), Co(II), and Mn(II)acetates and have got some promising results with a mixture of these catalysts. In addition, oxidation of 2-ethylhexanal has been researched both in the presence² and absence⁴ of metal soaps. The highest selectivity to carboxylic acid in the absence of catalyst was 71.4%, and the maximum selectivity, 80.8%, was reached in the presence of Mn(II) ethylhexanoate. There is a report by Yamada et al.³ on the effects of the presence of solvents on nickel(II)complex in air oxidation of octanal, but no comparative studies of different catalysts in various solvents or solvent studies without catalyst present on the oxidation of aliphatic aldehydes have been reported.

In the present study we have looked at the effects of catalysts and solvents in different combinations on the product formation in the oxidation of 2-ethylhexanal. We chose 2-ethylhexanal as an example of an aliphatic aldehyde as it is a starting material for 2-ethylhexanoic acid, which is widely used in the dye and varnish industries. Oxidation of

α -branched aliphatic aldehydes which are prone to side reactions⁵ can be expected to yield more information on possible reaction paths of aldehydes.

Our special interest was in understanding how to diminish the formation of by-products—3-heptanone, 3-heptanol, 3-heptyl formate, and low boiling hydrocarbons—and to maximise the yield of 2-ethylhexanoic acid. Besides the influence of solvent and catalyst, study was made of the effects of temperature, oxygen concentration, amount of water, and added NaOH on the oxidation of 2-ethylhexanal. Also investigated was the effect on the oxidation of the aliphatic aldehyde of adding an aromatic aldehyde, benzaldehyde, or *p*-methoxybenzaldehyde.

Results and Discussion

Conversion of aldehyde to carboxylic acid takes place in two stages: in a typical reaction the aldehyde is first converted to peracid (Scheme 1, (II)) in a free radical chain reaction, and then the peracid reacts with another aldehyde molecule⁶ and forms an intermediate (III) as shown in Scheme 1. In principle, the intermediate can decompose by migration either an α -carbonyl group or hydrogen, leading either to 1 mol of acid and 1 mol of formate (path a) or to two mol of acid (path b). Normally path b dominates. 2-Ethylhexanoic acid was the main product in all oxidation reactions of 2-ethylhexanal.

Oxidation of 2-Ethylhexanal in the Absence of Catalyst. *Oxidation without Additional Solvent.* The results of noncatalysed oxidation of 2-ethylhexanal without solvent are presented in Table 1. In noncatalysed reactions with no added solvent the best yield of carboxylic acid was obtained at room temperature with air bubbled through the reaction mixture. Eighty percent of aldehyde was converted to carboxylic acid and 12% to formate over 2 h. The amounts of 3-heptanone and 3-heptanol were 2.4 and 2.1%, respectively, and only 1% of unidentified products were formed (entry 5). Gradual addition of aldehyde to the reaction did not change the product composition (entry 1). The main reaction path leading to ketones and alcohols as by-products are presented in Scheme 2.^{1,7}

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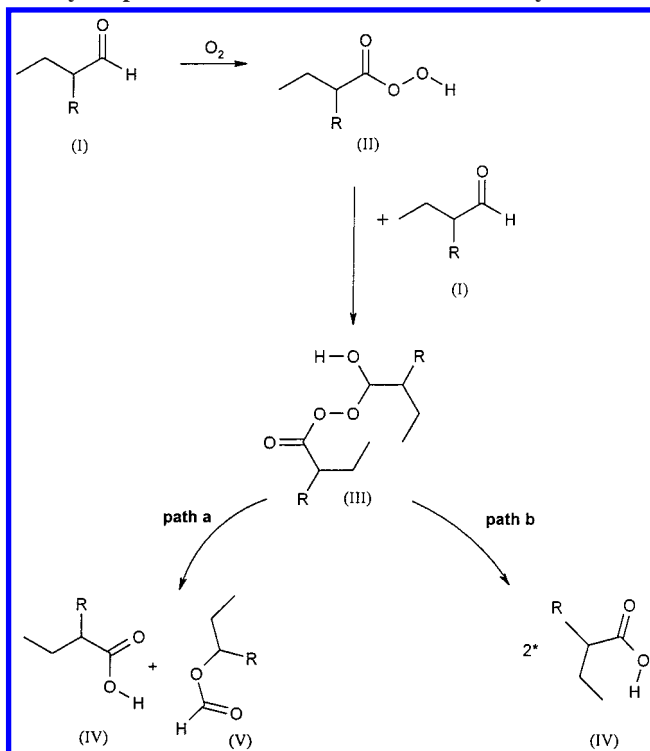
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Scheme 1. Two possible routes of decomposition of aldehyde-peracid adduct in air oxidation of 2-ethylhexanal



The reaction without added solvent was influenced by oxygen concentration in the reaction. Only 9.5% of 2-ethylhexanal reacted when the liquid was stirred under air (entry 2), whereas with continuous air bubbling only 3.5% of aldehyde remained after 2 h (entry 5). The use of pure oxygen as oxidant increased the amount of by-products (entry 3). Likewise, raising the temperature to 60 °C increased the amount of by-products and also slightly retarded the reaction rate (entry 4). Presumably, the reason for the slower reaction rate and increased amount of by-products at 60 °C is that oxygen solubility in the reaction mixture at higher temperature is lower, causing oxygen starvation in the reaction.

Oxidation Using Additional Solvent. The influence of various solvents on the oxidation path of 2-ethylhexanal was tested both in pure oxygen atmosphere and under continuous air bubbling with and without catalyst. The results of noncatalysed oxidation in solvent are presented in Table 2.

In chloroform 59% of reacted aldehyde converted to acid and 23.6% to formate (entry 12) and, correspondingly, in dichloroethane, 63% to acid and 26.7% to formate (entry 14). The best conversions of 2-ethylhexanal to 2-ethylhexanoic acid were afforded in octanoic acid (79%, entry 11), acetonitrile (82%, entry 17), and especially methanol (100%, entry 16), even though in the last case reaction was very slow. These solvents are known for their ability to form hydrogen bonds.

2-Ethylhexanal did not dissolve in the perfluorous solvents perfluoro-2-butyltetrahydrofuran (FC-75) and perfluorodecalin either at room temperature or at 60 °C (FC-75), and the reaction mixture was a two-phase system. The trends of aldehyde oxidation in perfluorous solvents were similar to those in the more polar solvents, acetonitrile and octanoic acid. Contrary to the results in nonsolvent conditions, the

reaction rate of aldehyde was not retarded at 60 °C in FC-75, which is well-known for its ability to dissolve oxygen.

The effects of adding water or alkali to the reaction mixture are presented in Table 1.

Adding 1.5 g of water (entry 7) or NaOH mixed with 2-ethylhexanoic acid (entry 9) did not have a marked effect on the product distribution, even though in the patent literature alkali metal salts are claimed to improve the yields of carboxylic acid in air oxidation of aldehydes.⁸ When NaOH was added to the system as an aqueous solution (entry 8), the selectivity of oxidation of aldehyde to acid was slightly decreased. In addition to the usual by-products some new unidentified products were formed.

Effect of Metal Complexes in the Oxidation of 2-Ethylhexanal. *Reactions without Additional Solvent.* Metal(II) acetates of copper, manganese, cobalt, and nickel were tested as catalysts in the oxidation of 2-ethylhexanal. Manganese and cobalt in particular⁵ are often used as catalysts in aldehyde oxidation. In most tests oxygen provided the oxygen source. The results of the metal-catalysed oxidations of 2-ethylhexanal are presented in Table 3.

Two reaction temperatures, room temperature and 60 °C, were tested in the oxidation of 2-ethylhexanal with Cu(II) acetate as catalyst. The higher reaction temperature (60 °C, entry 23) decreased the formation of carboxylic acid and also retarded the overall reaction rate. The effect is the result of oxygen starvation in liquid phase and was observed also in oxidations of 2-ethylhexanal without metal complex present.

The reaction of 2-ethylhexanal was often slower in the presence than in the absence of metal complex. Ni(II)- and Mn(II)acetate, in particular, retarded the oxidation 34.5%, and 36% of aldehyde was still present after 4 h (entries 29 and 26). The retarding effect of some nickel catalysts in the oxidation reaction of aldehyde has been reported by Nam et al.⁹

Another difference besides the slower rate of reaction in the presence of metal acetate was the lower conversion of aldehyde to formate. The suggested reason for this is the ability of metal catalyst to decompose the peracid formed in the oxidation reaction faster than the Baeyer–Villiger reaction takes place.¹⁰ The effect was most notable with Mn(II) acetate where only traces of formate were detected. The yield of formate was also low in the cobalt- and nickel-catalysed reactions. The conversion of aldehyde to formate was least affected by Cu(II)acetate.

Even though less 3-heptyl formate was formed in the presence of catalyst, the quantity of other by-products was greater. Usually, a few percent of 3-heptanol and a few percent of 3-heptanone were formed. When Co(II) acetate was used as catalyst, 3-heptanol represented almost 8% of the products (entry 28). Heptanol is formed either in the termination reaction of peroxyradical, formed in the reaction of 2-ethylhexyl acyl radical decarbonylation product and dioxygen,¹ or in a decomposition reaction of 3-heptyl

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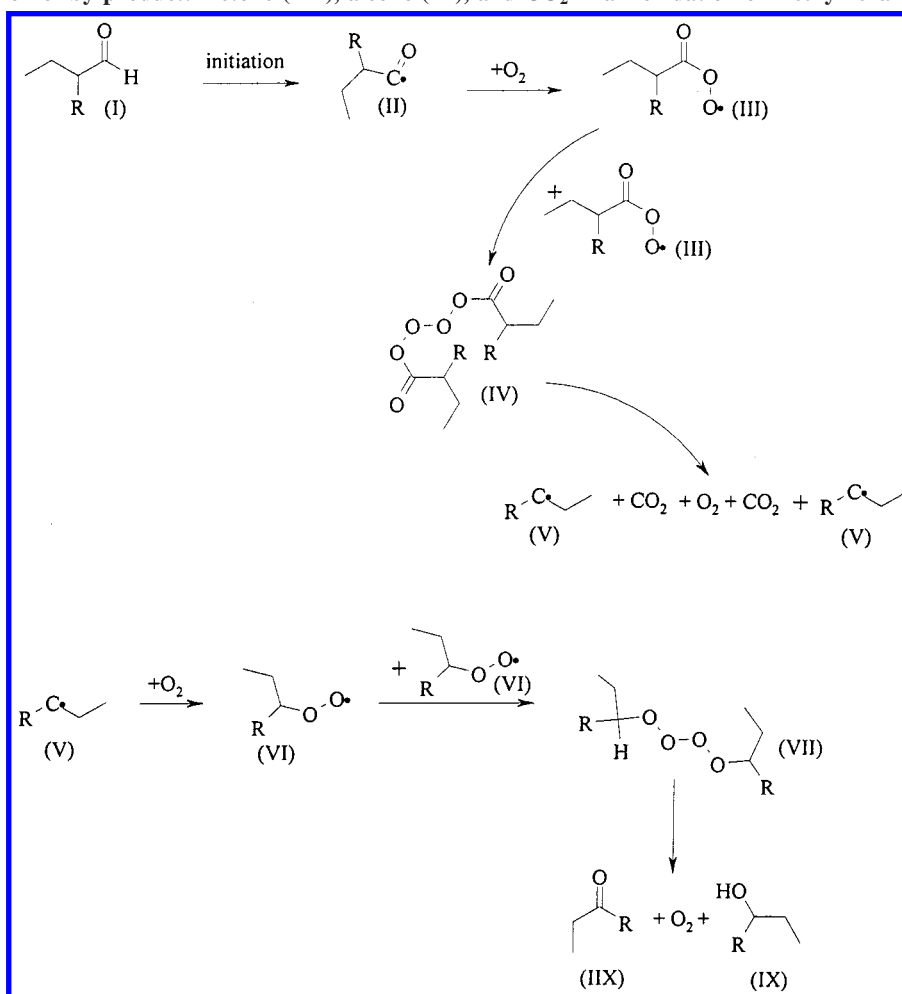
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Table 1. Effects of different reaction parameters on the product distribution in O₂ oxidation of 2-ethylhexanal (%) in the absence of solvent^a

entry	conditions	3-heptanone	3-heptanol	3-heptyl formate	other ^e products	sum of by-products	2-ethyl hexanal	2-ethyl hexanoic acid	aldehyde converted to acid(%)
1	<i>b</i>	trace	trace	12.9	2.6	15.5	9.1	75.4	83
2	<i>c</i>	-	-	trace	2.0	2.0	90.5	7.5	79
3	<i>d</i>	3.0	3.2	12.7	8.0	26.9	1.6	71.5	73
4	<i>d</i> , 60 °C	4.7	7.2	5.7	31.0	47.7	14.3	38.0	44
5		2.4	2.1	12.0	-	16.5	3.5	80.0	83
6	25.7 mg H ₂ O	2.6	2.0	12.5	5.9	23.0	2.5	74.5	76
7	1.52 g H ₂ O	-	-	11.2	6.4	17.6	11.3	71.1	80
8	90 mg NaOH/ 1.52 g H ₂ O	-	-	12.4	16.0	28.4	9.3	62.3	69
9	90 mg NaOH/ 0.32 g acid b,d	1.3	0.6	12.7	3.4	18.0	4.0	78.0	81

^a Reaction time 2 h and reactions performed in room temperature under continuous air bubbling 34 mL/min if not otherwise mentioned. ^b Continuous addition of aldehyde. ^c Air atmosphere, no bubbling. ^d O₂ atmosphere. ^e NaOH was mixed into 2-ethylhexanoic acid and added to reaction.

Scheme 2. Formation of by-product: ketone (IIX), alcohol(IX), and CO₂ in air oxidation of 2-ethylhexanal



formate.² No significant differences between the metal complexes were detected in the conversion of aldehyde to 3-heptanone. In general after 6 or 7 h reaction the amount of unidentified products was 30–35%.

The amount of catalyst had little effect on the product distribution, but it affected the reaction rate. Reducing the amount of catalyst to 10% of normal (entries 22 and 27) lowered the rate of aldehyde oxidation by 30% with the

manganese catalyst and by about 10% with the copper catalyst.

Metal-Catalysed Reactions in Dichloroethane and Octanoic Acid. Octanoic acid and dichloroethane were tested as solvents in reactions catalysed with manganese and copper. The amount of aldehyde oxidised was ~25% of that in the nonsolvent system. The oxidation was slow in air atmosphere (C₂H₄Cl₂, Cu(OAc)₂), and some aldehyde was still present

Table 2. Product distribution in O₂ oxidation of 2-ethylhexanal (%) in various solvents^a

entry	solvent	3-heptanone	3-heptanol	3-heptyl formate	other ^b products	sum of by-products	2-ethyl hexanal	2-ethyl hexanoic acid	aldehyde converted to acid %	dielectric constant $\epsilon^{20,25}$ of solvent
10	octane	1.0	0.8	13.4	6.6	21.8	2.3	75.9	78	1.9
11	octanoic acid			16.0	3.5	19.5	8.5	72.0	79	2.5
12	chloroform			15.3	11.1	26.4	35.8	37.8	59	4.8
13	ethyl acetate	2.9		8.7	9.7	21.3	5.9	72.8	78	6.0
14	C ₂ H ₄ Cl ₂	1.0		13.0	4.5	18.5	51.0	30.5	63	10.4
15	acetone	2.0	1.0	3.5	14.0	20.5	2.0	77.5	79	21
16	methanol					-	92.0	8.0	100	32.6
17	acetonitrile	1.6	1.7	12.7		16.0	6.5	77.5	82	38.8

^a By method b, reaction 2 h, room temperature, oxidant source O₂ balloon. ^b Amount of aldehyde reacted to other products than mentioned in the table.

Table 3. Product distribution in O₂ oxidation of 2-ethylhexanal (%) with various catalysts

entry	metal acetate reaction conditions	reaction time (h)	3-heptanone	3-heptanol	3-heptyl formate	other ^f products	sum of by-products	2-ethyl hexanal	2-ethyl hexanoic acid	aldehyde converted to acid (%)
18	Cu ^{b,e}	6	1.5	1.5	3.9	20.7	27.6	54.0	18.4	40
	C ₂ H ₄ Cl ₂ , air atmosphere	23	3.2	2.3	5.7	33.8	45.0	12.2	42.8	50
19	Cu ^b	1	1.1	0.5	21.0	7.3	29.9	11.5	58.6	66
	C ₂ H ₄ Cl ₂ , octanoic acid	2	trace	trace	18.0	2.3	20.3	3.0	76.7	79
21	Cu ^c	2	1.8	1.0	7.8	13.5	24.1	28.6	47.3	66
22	Cu 1/10 ^d	2	1.8	1.8	6.1	17.4	27.1	32.4	40.5	60
	no solvent									
23	Cu ^c	2	2.7	1.8	6.0	16.6	27.1	34.9	38.0	58
	60 °C									
24	Mn ^b	2	11.0	5.0	0.7	19.3	36.0	5.0	59.0	62
	C ₂ H ₄ Cl ₂ , octanoic acid	2	6.9	2.7	-	6.0	15.6	1.5	82.9	84
26	Mn ^c	2	2.9	3.5	0.4	19.2	26.0	36.0	38.0	59
27	Mn 1/10 ^d	2	2.1	4.0	1.0	15.9	23.0	53.8	23.2	50
28	Co ^c	6	3.9	7.7	1.1	30.6	43.3	9.5	47.2	52
29	Ni ^c	4	2.2	5.2	3.3	15.8	26.5	34.5	39.0	60

^a Reactions performed under O₂ atmosphere without additional solvent present if not otherwise mentioned. ^b Amount of aldehyde 0.012 mol and catalyst 0.012 mmol. ^c Amount of aldehyde 0.035 mol and catalyst 0.035 mmol. ^d Amount of aldehyde 0.035 and catalyst 0.0035 mmol. ^e Air atmosphere, no bubbling. ^f Amount of aldehyde reacted to products other than those mentioned in the table.

after 23 h (entry 18). The reaction under oxygen was slightly more selective and markedly faster (entry 19). The higher oxygen concentration in the system also considerably accelerated the Baeyer–Villiger reaction of 2-ethylhexanal. The most significant difference between Cu(II)- and Mn(II) acetate-catalysed reactions in solvents was the absence of 3-heptyl formate as the product when manganese was the metal.

The best selectivity of aldehyde to carboxylic acid (84%) was achieved in octanoic acid in the presence of Mn(II) acetate (entry 25). An explanation for the small amount of by-products and high conversion to acid could be the ability of octanoic acid to reduce the acyl radical formation from 2-ethylhexanal, while at the same time Mn(II)acetate improves the efficiency of conversion of 2-ethyl perhexanoic acid to carboxylic acid.¹⁰

Simultaneous Oxidation of Two Aldehydes. On the oxidation of 2-ethylhexanal the effect of adding another aldehyde was studied to find out if Baeyer–Villiger reaction

products were formed. Benzaldehyde is a frequently used coreactant in Baeyer–Villiger reactions carried out in aerial conditions.¹¹

Addition of benzaldehyde did not significantly affect the reaction of 2-ethylhexanal, but the 2-ethylhexanal unexpectedly retarded the oxidation of benzaldehyde. Only 15% (total 9 mL) of benzaldehyde had converted to acid after 4 h, whereas benzaldehyde alone (6 mL) was fully oxidised in 2 h.

When benzaldehyde was replaced with *p*-methoxybenzaldehyde, which is known to react through Baeyer–Villiger reaction in the presence of *i*-butyryl aldehyde,¹² the oxidation of 2-ethylhexanal was hindered almost completely; only about 7% acid and 0.5% of 3-heptyl formate were formed

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Table 4. Product distribution in simultaneous oxidation of *p*-methoxybenzaldehyde and 2-ethylhexanal by method b

code	oxidant source	reaction time	products of <i>p</i> -methoxybenzaldehyde				products of 2-ethylhexanal				
			metal acetate	aldehyde	acid	formate	other ^a	aldehyde	acid	formate	other ^a
31	air	19	Co	4	90	4	1	-	73	6	21
32	air	24	Cu	67	13	20	-	24	56	20	-
33	O ₂	24	Cu	46	16	34	4	9	60	28	3
34	O ₂	20	-	100	-	-	-	95	5	-	-
35	O ₂ ^b	19	Cu	-	60	38	2	-	-	-	-
36	O ₂ ^b	20	-	100	-	-	-	-	-	-	-

^a Aldehyde reacted to products other than those identified in the table. ^b No 2-ethylhexanal present.

in 6 h. *p*-Methoxybenzaldehyde did not react at all. Results of the simultaneous oxidation of 2-ethylhexanal and *p*-methoxybenzaldehyde in dichloroethane are presented in Table 4.

The oxidation of *p*-methoxybenzaldehyde did not proceed in dichloroethane alone (entry 34) (the amount of aldehydes was only 5% of that reported above). However, the addition of Co(II) acetate as catalyst significantly accelerated the oxidation of both aldehydes (entry 31). All 2-ethylhexanal had reacted in 4 h, 73% of it converted to acid, and besides this also some by-products were formed. Oxidation of *p*-methoxybenzaldehyde was slower: about one-third had converted in 4 h, mostly to corresponding acid (90%), but also some formate (4%) was detected.

Relative to the noncatalysed reaction, also Cu(II) acetate slightly promoted the oxidation of both aldehydes (entry 32). The impact of higher oxygen concentration in the liquid was tested in the presence of copper catalyst (entry 33). The faster conversion rate was mostly due to the acceleration of the formate production of both aldehydes. The presence of 2-ethylhexanal accelerated the formate route of *p*-methoxybenzaldehyde, but the aromatic aldehyde had no particular influence on the oxidation path of the aliphatic aldehyde. As in the noncatalysed reaction, the single aldehyde was oxidised much faster than when aliphatic and aromatic aldehydes were oxidised simultaneously. To our knowledge this phenomenon has not been observed earlier. No mechanistic explanation for this effect can be offered at this time.

Conclusions

2-Ethylhexanoic acid was the main product in all oxidation reactions of 2-ethylhexanal. The best yield in noncatalysed reactions was 80%, while the yield of 3-heptyl formate was 12%. Higher temperature and oxygen concentration increased the amount of other by-products.

Solvents had considerable effect on the product distribution of 2-ethylhexanal. Chloroform and dichloroethane enhanced the reaction route leading to formate. Certain solvents, octanoic acid, acetonitrile, and especially methanol, possibly because of the hydrogen bonding between solvent and substrate, preferred the conversion of 2-ethylhexanal to 2-ethylhexanoic acid. The best selectivity of 2-ethylhexanal to carboxylic acid, 84%, was obtained in octanoic acid in the presence of Mn(II)acetate. The reason for this might be that simultaneously when manganese catalyst accelerates the conversion of peracid to carboxylic acid the solvent reduces the acyl radical formation.

Oxidation of aliphatic and aromatic aldehydes simultaneously retarded the reaction rate of both aliphatic and especially that of the aromatic aldehydes. The catalysts tested and higher oxygen concentration both had a positive effect on the reaction rate of the aldehydes, mostly due to the acceleration of the formate production.

Experimental Section

General 2-Ethylhexanal, *p*-methoxybenzaldehyde, benzaldehyde (Aldrich), and all solvents were dried, distilled (except fluoruous solvents), and preserved under inert atmosphere until use. The metal complexes Co(NO₃)₂·6H₂O (Merck), Co(OAc)₂·4H₂O (J.T. Baker), Ni(OAc)₂·4H₂O (Fluka), Fe(OAc)₂ (Aldrich), and Mn(OAc)₂·2H₂O (Fluka) were used as obtained from the supplier.

Gas chromatographic analyses were performed on a HP 6890 instrument: Polar Innowax column 30 m; initial column temperature 40 °C; final column temperature 250 °C; progress rate 10 °C/min; constant flow 6.3 mL/min of carrier gas; initial pressure 0.93 bar. The main oxidation products of 2-ethylhexanal and *p*-methoxybenzaldehyde were identified and quantified by comparison with authentic samples. (for preparation, see below). Decane or tetradecane was used as internal standard to calculate the exact amount of substance present in the reaction mixture. The oxidation products were also identified by GC–MS and compared with library spectra.

Oxidation of Aldehyde. Method a. A flat-bottomed glass vessel equipped with a condenser and an oxygen balloon was charged with aldehyde (usually 0.035 mol) and decane and with catalyst (usually 0.35 mmol) where this was used. Magnetic stirring (1000–1250 rpm) was commenced, and the reaction mixture was evacuated and oxygenated three times at the chosen temperature. When reactions were done in air atmosphere, no evacuation was performed, and the oxygen balloon was replaced with a CaCl₂ tube. The same applies to air oxidations where air was bubbled to the reaction mixture. The airflow in synthesis was 34 mL/min if not otherwise mentioned.

Method b. Oxidation of aldehyde in solvent was done under air, air bubbling, and oxygen. Aldehyde (~0.012 mol), decane, catalyst (0.012 mmol), and 10–15 mL of solvent were added to a flat-bottomed reaction vessel. Start-up of the reaction was as in method a.

Oxidation of Two Aldehydes Simultaneously. Oxidations of 2-ethylhexanal in the presence of benzaldehyde or *p*-methoxyaldehyde were performed at normal pressure with

air bubbling at 70 mL/min at 40 °C. At the beginning of the reaction 1 mL of each of the two aldehydes was added to the vessel, and magnetic stirring of 1250 rpm was commenced. Continuous substrate addition of 2 mL/h was then begun. When the reaction was performed in solvent without continuous addition of substrates, the reaction procedure was similar to oxidation of a single aldehyde as in method b.

Preparation of Formates used as Model Compounds.

3-Heptyl formate was prepared from the corresponding alcohol (20 mmol) with dimethylformamide (20 mmol) and

benzoyl chloride (20 mmol) in 12 mL of dichloroethane according to the method of Barluenga et al.¹³ Besides formate a small amount of unreacted 3-heptanol was present in the crude product. The formate was purified with vacuum distillation, and the yield was 39%.

Methoxyphenyl formate was prepared from 4-methoxyphenol (0.1 mol) with formic acid/acetic anhydride (1:1) solution (0.1 mol) and pyridine (0.0015 mol) according to Van Es et al.¹⁴ The yield of formate was 80%. For GC analysis the formate was twice recrystallised from ethanol/hexane solution.

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