CATALYSED LIQUID PHASE OXIDATION OF ACETALS BY MOLECULAR OXYGEN

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Nine different acetals have been oxidized in the presence of $Co(OOCCH_3)_2.4 H_2O$ under isobaric conditions $(0.1—0.2 MPa\ O_2)$ while following the uptake of molecular oxygen. The reactivity of acetals was expressed by the rate constants of the autocatalytic model of oxidation. The main products of the oxidation are alcohols, esters and acids. The distribution of products and the total reactivity of acetals are controlled by the structure of both parts of acetal molecule. The dominant effect on the course of the reaction exerts the type of carbon atoms on which radicals are formed. The oxidation is accompanied by consecutive and co-oxidation reactions, by deactivation of the catalyst and by decarbonylation of intermediate products. The effect of oxygen pressure is reported and the more detailed radical mechanism of the oxidation is proposed.

Acetals of the type $R_aCH(OR_b)_2$ are commonly prepared by the acid catalysed reaction of aldehydes with alcohols

$$R_aCHO + 2 R_bOH \xrightarrow{\ H^+\ } R_aCH(OR_b)_2 + H_2O.$$
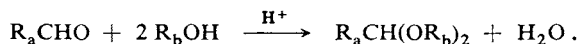
They are also undesired by-products of hydroformylation of olefins to aldehydes at high carbon monoxide pressures and high temperatures catalysed by cobalt carbonyls. Acetals are formed also during hydrogenation of the hydroformylation mixture to alcohols[1]. Under hydroformylation conditions and subsequent treatment, acetals undergo different decompositions to form other oxygen-containing by-products[2-4] which after distilling off the required products constitute a residue difficult to distillate.

It would be therefore desirable to convert acetals by oxidation to carboxylic acids, either by one step or two step (*via* esters) process. Several procedures are disclosed in patent literature. Thus, for example, acetals were oxidized by dioxygen to carboxylic acids in formic acid[5], by peroxoacetic acid to esters (particularly unsaturated acetals)[6], by hypochlorite[7] or trioxygen[8].

Oxidation of low molecular aliphatic linear and cyclic acetals was studied by Zlotskii and Rakhmankulov who reported some basic data on the mechanism of liquid phase oxidation of acetals in the presence of initiators of radical reactions[9-11]. Decomposition of linear acetals initiated by thermal decomposition of di(tert-butyl)peroxides[12], oxidation of cyclic acetals catalysed by Fe(III), Cr(III), and Co(III) compounds to give alkyl hydroperoxides[13] and the effect of radical inhibitors[14] have also been investigated.

The results of these works support the idea that the oxidation of acetals proceeds *via* radical chain mechanism, the C—H bond on the carbon atom substituted with two oxygens atoms being the most accessible to attack by peroxy radicals. Intermediate products of the reaction are alkyl

hydroperoxides which decompose under given conditions to stable products. The substitution of one hydrogen atom in $H_2C(OC_2H_5)_2$ for methyl, $CH_3CH(OC_2H_5)_2$, leads to an increase in oxidation ability given by $k_p/(2k_t)^{0.5}$ equaling up to three (for cyclic acetals to a factor of ten)[9,15]. The ability of acetals to undergo oxidation depends (but not distinctly) on the length of alkyl chain of the substituent of the alkoxy part of acetal (R_b)[16]. The rate of oxidation depends linearly on substrate concentration and on square route of initiator concentration[17]; in the reaction with cumyl peroxo radical the rate depends on substrate and radical concentrations[18]. The most active catalysts for oxidation of acetals are those based on cobalt salts[13,19].

Starting from the above data, in the present work we were concerned with the effect of structure of acetals on their reactivity. The liquid phase oxidation of acetals by dioxygen catalysed by cobalt(II) acetate in the absence of solvents and radical initiators has been chosen as a model reaction and the attention has been paid to product analysis and dependence of product distribution on oxidation conditions.

EXPERIMENTAL

Synthesis of acetals. Acetals *1—3, 5* and *6* were obtained by refluxing a mixture of the appropriate aldehyde (0·4 mol), the alcohol in excess (1·2 mol) and methylene chloride (400 ml) with addition of gaseous hydrogen chloride as a catalyst (1 g at the beginning and the same amount in the course of the reaction). The reaction was carried out in a flask equipped with azeotropic condenser and was stopped after nearly theoretical amount of the water was released. After removal of the solvent, the unreacted alcohol and HCl by distillation, crude acetals were distilled first *in vacuo* and then fractionated, using the distillation column packed with ceramic rings. The synthesis of mixed acetals of C_4 aldehydes with butanol and 2-methylpropanol (acetals *4* and *7*) by the same procedure gave a mixture of three acetals which could not be separated by rectification. The pure mixed acetals were obtained by preparative gas chromatography[20]. In the course of the synthesis of acetal *1*, the compound undergoes decomposition to yield the unsaturated ether, $(C_2H_6)_2C{=}CHOC_4H_9$, as a main product (around 70% yield) while the acetal is formed only in about 25% yield. Acetal *8* was obtained from butanol and 2-butanol by the method of simultaneous removal of water and catalysis with a molecular sieve[21]. The thoroughly dried butanal (0·3 mol), 2-butanol (1·2 mol), cyclohexane (400 ml) and *p*-toluenesulphonic acid (0·06 mol) were mixed at $0—5°C$ with A-4 molecular sieve which was dried *in vacuo* (60 g). The fractional distillation of the reaction mixture afforded a small amount of isomeric unsaturated ethers and the pure acetal in c. 50% yield. Ketal *9* was obtained by the reaction of $CH(OC_2H_5)_3$ with cyclohexanone in excess propanol[22]. The preparation and purification of acetals was carried out under nitrogen and the products were stored under nitrogen in a refrigerator in the dark (Table I).

All the acid esters used to identify the oxidation products and to make GLC calibrations were prepared by esterification of the acids by the alcohols (H_2SO_4 as a catalyst) and had expected physical properties.

Oxidation of acetals (1—5 ml) was carried out in a temperature-controlled reactor equipped with a magnetic stirrer (c. 600 r.p.m.) and cooled tube which connected the reactor to the gas burette in which a constant oxygen pressure was maintained by an automatic change of liquid level. The apparatus[23] was complemented by the outlet for withdrawing samples of the gas phase. The reaction temperature was 90°C, $Co(OOCCH_3)_2.4 H_2O$ concn. − 0·3 to 3 mol.%, oxygen pressure = 0·1 to 0·2 MPa. In the course of the reaction, the uptake of oxygen was recorded and

TABLE I
Physical properties of model acetals

Acetal	Density g cm^{-3}	B.p. °C/kPa	Acetal	Density g cm^{-3}
$(CH_3)_2CHCH(OCH_2CH(CH_3)_2)_2$	0·826	74—76/1·7	$(CH_3)_2CHCH(O(CH_2)_3CH_3)_2$	0·836
$CH_3CH_2CH_2CH(OCH\big\langle{}^{CH_3}_{C_2H_5}\big\rangle)_2$	0·833	108·5—109·5/5·1	$CH_3(CH_2)_2CH(OCH_2CH_2CH(CH_3)_2)_2$	0·832
$(C_2H_5)_2CHCH(O(CH_2)_3CH_3)_2$	0·842	123/3·5	$CH_3(CH_2)_3CH(O(CH_2)_3CH_3)_2$	0·857
$\overline{(CH_2)_5}\!\!-\!\!C(OCH_2CH_2CH_3)_2$	0·899	111—113/2·9	$(CH_3)_2CHCH\big\langle{}^{O(CH_2)_3CH_3}_{OCH_2CH(CH_3)_2}$	0·825[a]
			$CH_3(CH_2)_3CH\big\langle{}^{O(CH_2)_3CH}_{OCH_2CH(CH_3)_2}$	0·827[b]

[a] n_D^{20} 1·4124, [b] n_D^{20} 1·4176.

at fixed time intervals, samples of the liquid phase were withdrawn and analysed by GLC. After completion of the reaction, the sample of the gas phase was withdrawn and analysed.

Analysis of the liquid phase. The samples (0·03—0·05 ml) were charged with microsyringe to an excess of the silylating agent, trimethylsilylimidazol, containing the known amount of *p*-diethylbenzene as an internal standard. Samples were analysed gas chromatographically on Chrom 5 instrument equipped with a flame-ionization detector and CI 100 integrator (3·6 m — glass column of 3 mm i.d., hydrogen as a carrier gas, OV 17 (10%) silicone on Chromaton Super, programmed temperature in the range 70 to 150°C with an increase of 3°C/min). Gas phase was analysed also gas chromatographically (a thermal conductivity detector) using the column packed with an active carbon. Carbon dioxide and carbon monoxide were analyzed at 48°C and 56°C respectively. The calibration of the injected amount of the gas with the response of the detector was linear.

NMR spectra were measured for 20—50% solutions of the compounds in deuteriochloroform (Institute of Nuclear Research, Poland), using 1% TMS as an internal reference. ^{13}C NMR spectra were recorded using broad-band proton decoupling (Tesla BS 497 spectrometer equipped with BP 4970 adapter). $^{1}J_{CH}$ coupling constants were determined by the method of key decoupling with the use of positive Overhauser effect to strengthen ^{13}C NMR signal (Table II).

RESULTS

Reactivity of acetals. Time dependence of the uptake of dioxygen was used to evaluate the reactivity of a given acetal in the initial stage of the reaction (to 5 000 s) in which consecutive oxidations and decompositions play only a minor role. We have used the model of autocatalytic reaction:

$$A + (C + C') + O_2 \rightarrow P' + C \rightarrow P + (C + C')$$
$$-dA/dt = k \cdot P_{ox}^d A^p(C_0 \cdot (f + A_0 - A))^r, \tag{1}$$
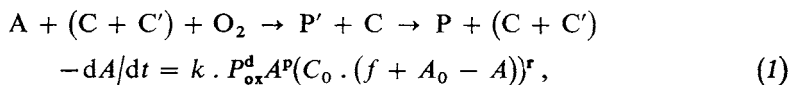
where A is the acetal, C is the added catalyst, C' is a catalytically active species formed during the oxidation, P' is the intermediate alkyl hydroperoxide, P are products, d, p, r are reaction orders, and f is the autocatalytic factor which expresses the activity of the added catalyst in the initial phase of the reaction (values 0–1). As the order d in dioxygen does not have to be necessarily constant for the whole series of acetals examined, their reactivity was compared by using the modified rate constant $k_P = kP_{ox}^d$. The Eq. (2) was solved by the method of nonlinear regression with optimation of p and r orders for the values of factor f equaling to 0 or to 1.

$$-dA/dt = k_P A^p(C_0(f + A_0 - A))^r \tag{2}$$

We have minimized the weighed objective function which

$$\bar{Q}_i = \left(\sum_{i=1}^{i=n} Q_i\right)/n \tag{3}$$

$$Q_i = \left(A_{calc} - A_{exp}\right)^2 A_{exp}(1 + A_0 - A_{exp}), \tag{4}$$

TABLE II
^{13}C NMR spectral parameters

No	Compound^a	Chemical shift ppm	Coupling constants $^1J_{C-H}$, Hz
1	$(CH_3CH_2)_2CHCH(OCH_2CH_2CH_2CH_3)_2$ d c b a e f g h	a 105·7 b 43·9 c 21·1 d 11·2 e 66·5 f 32·1 g 19·4 h 13·8	$^1J_a = 156·5$; $^1J_e = 139·8$
8	$CH_3CH_2CH_2CH(O{-}CH{\langle}^{CH_3}_{CH_2CH_3})_2$^{b} d c b a e h f g	a (t) 100·6 b (t) 37·7 c (s) 18·0 d (s) 13·8 e (t) 72·7 g(d) 9·5 f (d)? 30·0 h (d)? 19·8 $\Delta a = 0·6{-}0·7$ $\Delta b = 0·1{-}0·2^c$ $\Delta e = 0·2{-}0·4$ $\Delta g = 0·4$ $\Delta f? = 0·9$ $\Delta h? = 0·6$	$^1J_a = 156$; $^1J_b = 126·8$ $^1J_e = 138·9$
9	$CH_2{\langle}^{CH_2CH_2}_{CH_2CH_2}{\rangle}\underset{b}{C}{\langle}^{c}_{c}$ ... $\underset{b}{C}(OCH_2CH_2CH_3)_2$ d a e f g	a 99·6 b 33·8 c 23·4 d 23·0 e 61·1 f 25·8 g 10·8	$^1J_e = 139·9$
2	$(CH_3)_2CHCH(OCH_2CH_2CH_2CH_3)_2$^{d} c b a d f g h	a 108·0 b 31·4 c 17·8 e 66·2 f 32·1 g 19·5 h 13·9	$^1J_a = 159·6$; $^1J_b = 124·9$ $^1J_e = 139·7$
5	$CH_3CH_2CH_2CH(OCH_2CH(CH_3)_2)_2$^{d} d c b a e f g	a 103·3 b 35·7 c 18·2 d 14·0 e 72·3 f 28·8 g 19·6	$^1J_a = 157·8$; $^1J_b = 126·5$ $^1J_e = 137·1$
6	$(CH_3)_2CHCH(OCH_2CH(CH_3)_2)_2$^{d} c b a e f g	a 108·1 b 31·4 c 17·8 e 73·2 f 28·8 g 19·6	$^1J_a = 158$; $^1J_b = 125·6$ $^1J_e = 139·5$
	$(CH_3CH_2)_2C{=}CHOCH_2CH_2CH_2CH_3$ d c b a e f g h	a 140·0 b 122·0 e 71·5 f 32·0 c, g 19·2–24·5 d, h 12·7–13·8	

^{a} Chemical shifts and coupling constants reproducible within ±0·2 ppm and ±0·5 Hz, respectively; ^{b} multiplicity due to diastereoisomers on carbon atoms e; ^{c} differences in chemical shifts due to diastereoisomerism; ^{d} chemical shifts taken from ref.[4].

expresses deviation of the calculated curve from experimental data. This function is most sensitive in the region of approximate half-time of the reaction. This way enabled us to obtain the common scale of rate constants as the measure of the reactivity of all the acetals studied (Table III).

To describe also the final stages of the oxidation of acetals, the Eq. (2) was modified by introducing into it the time dependence of decrease in the catalyst concentration:

$$-dC/dt = k_1 C(A_0 - A)^m,$$ (5)

where at optimum p, r, and f values, also m values (0–2) and k_1 (Table IV, Figs 1 and 2) were optimized.

TABLE III

Average rate constants $\overline{k}_P$ for the initial stage of the reaction, $t < 5\,000$ s (temp. 90°C, Co(OOCCH$_3$)$_2$.4 H$_2$O concn. $= 1$ mol.%, reaction orders $p = 3$, $r = 0.5$, error in $\overline{k}_P = 8$ rel.%)

No	Acetal	$\overline{k}_P \cdot 10^5$ (1^3 mol^{-3} s^{-1}) for P_{ox}		
		0·1 MPa, $f = 0^a$	0·1 MPa, $f = 1^b$	0·2 MPa, $f = 0^c$
1	(C$_2$H$_5$)$_2$CHCH(OCH$_2$CH$_2$CH$_2$CH$_3$)$_2$	7·9	3·2	8·4
2	(CH$_3$)$_2$CHCH(OCH$_2$CH$_2$CH$_2$CH$_3$)$_2$	4·9	2·0	7·7
3	CH$_3$(CH$_2$)$_2$CH(OCH$_2$CH$_2$CH$_2$CH$_3$)$_2$	4·0	1·7	6·4
4	(CH$_3$)$_2$CHCH⟨ OCH$_2$CH$_2$CH$_2$CH$_3$ / OCH$_2$CH(CH$_3$)$_2$	3·8	1·7	3·6
5	CH$_3$(CH$_2$)$_2$CH(OCH$_2$CH(CH$_3$)$_2$)$_2$	3·5^d	1·3	5·3
6	(CH$_3$)$_2$CHCH(OCH$_2$CH(CH$_3$)$_2$)$_2$	3·4^d	1·2	4·1
7	CH$_3$(CH$_2$)$_2$CH⟨ O(CH$_2$)$_3$CH$_3$ / OCH$_2$CH(CH$_3$)$_2$	2·6	0·9	2·6
8	CH$_3$(CH$_2$)$_2$CH(OCH⟨ CH$_3$ / C$_2$H$_5$)$_2$	1·4	0·3	1·7
9	⌐(CH$_2$)$_5$—C(OCH$_2$CH$_2$CH$_3$)$_2$	0·8	0·15	0·9

^{a} Optimum values, $\overline{Q}_i = 0.007$ (for the whole series); ^{b} $\overline{Q}_i = 0.05$; ^{c} $\overline{Q}_i = 0.09$ (l^{-4} mol^4); ^{d} values not optimal, the optimum value is $f = 1$.
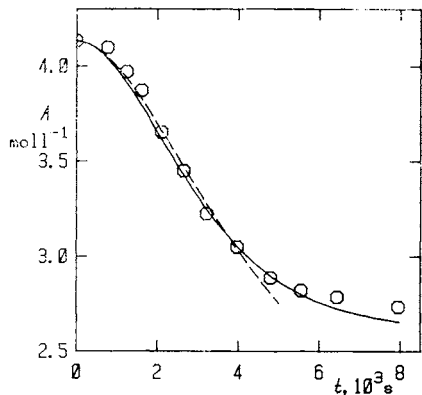
Fig. 1

Oxidation of $(CH_3)_2CHCH(OCH_2CH_2CH_2.$ $.CH_3)_2$ at $90°C$ in the presence of 1 mol.% of $Co(OOCCH_3)_2.4\ H_2O$, $P_{ox} = 0.1$ MPa; solid line denotes theoretical change in acetal concn. including catalyst deactivation, $p = 3$, $r = 0.5$, $m = 2$, $k_P = 5.38\ .\ 10^{-5}\ l^3\ mol^{-3}$. $k_1 = 5\ .\ 10^{-4}\ l^2\ mol^{-2}\ s^{-1}$, $f = 0$; $Q_i = = 2.2\ .\ 10^{-2}\ mol^4\ l^{-4}$, dashed line denotes changes in acetal concn. without regarding catalyst deactivation, $p = 3$, $r = 0.5$, $f = 0$, $k_P = 5.05\ .\ 10^{-5}\ l^3\ mol^{-3}\ s^{-1}$, $Q_i = 1.5\ .$ $.\ 10^{-2}\ mol^4\ l^{-4}$.
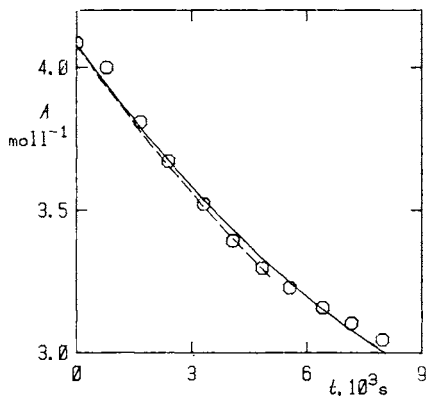
Fig. 2

Oxidation of $(CH_3)_2CHCH(OCH_2CH.$ $.(CH_3)_2)_2$ at $90°C$ in the presence of 1 mol.% of $Co(OOCCH_3)_2.4\ H_2O$, $P_{ox} = 0.1$ MPa; solid line denotes theoretical change in the acetal concn. including catalyst deactivation, $p = 3$, $r = 0.5$, $m = 2$, $f = 1$, $k_P = 1.32\ .$ $.\ 10^{-5}\ l^3\ mol^{-3}\ s^{-1}$, $k_1 = 1\ .\ 10^{-4}\ l^2\ .$ $.\ mol^{-2}\ s^{-1}$, $Q_i = 5.7\ .\ 10^{-3}\ mol^4\ l^{-4}$; dashed line is for the change without regarding catalyst deactivation, $p = 3$, $r = 0.5$, $f = 1$, $k_P = 1.38\ .\ 10^{-5}\ l^3\ mol^{-3}\ s^{-1}$, $Q_i = = 2.9\ .\ 10^{-3}\ mol^4\ l^{-4}$.

Fig. 3

Oxidation of $(C_2H_5)_2CHCH(OCH_2CH_2.$ $.CH_2CH_3)_2$ (for conditions see Fig. 1). Lines denote formation of n-butanol (◑), 2-ethylbutyric acid (◓), $(C_2H_5)_2CHC(O)O.$ $.(CH_2)_3CH_3$ (○), and butyric acid (●). Reaction orders and constants of Eq. (6) are given in Table VI.
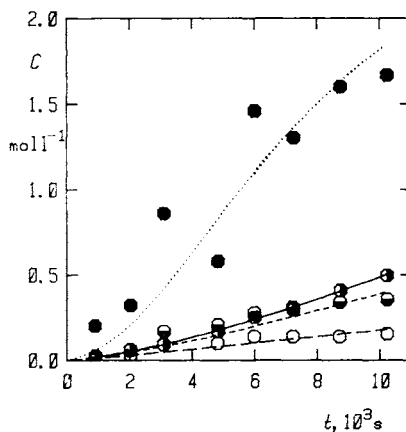
Product distribution. Distribution of the oxidation products determined by GLC is presented in Table V. GLC analysis was also used to describe kinetics of formation of individual products. For that reason, the composition of samples of the reaction mixture was followed in the course of the reaction. Also in these cases the autocatalytic course of the reaction has been observed. We have used the following kinetic equation:

$$dP_i/dt = k_{iP}A^x(C_0 + P_i)^y ,\qquad(6)$$

where P_i is a given product, k_{iP} is the rate constant including term for dependence on dioxygen pressure, A is acetal concentration, and x, y are reaction orders (Fig. 3).

DISCUSSION

By optimation, we have selected pairs of p and r orders for a given value of the autocatalytic factor $f = 0$ or 1, which fulfill the criterion of minimum value of the Q function. The best pair for the whole set at $P_{ox} = 0.1$ MPa is $p = 3$ and $r = 0.5$. The third order of the reaction with respect to the starting acetal speaks for the complex reaction. Higher reaction orders are usually observed for degenerative branching of the radical chain[24]. The order of the overal reaction in the catalyst which was found for several acetals by experiments with varying initial catalyst concentrations corresponds to the initiation reaction, the rate of which is proportional to the substrate concentration[25]. In several cases we have determined separately the order d in dioxygen pressure by experiments at different P_{ox}. For acetals of butanal with n-butanol and 2-methylpropanol and the acetal of 2-methylpropanal with n-butanol the order d was 2 and for the acetal of 2-methylpropanal with 2-methylpropanol, the order d equaled to 0.5.

The optimum value of the autocatalytic factor f for most acetals under study was $f = 0$. This indicates a slow increase in the rate of oxidation of acetals in the initial stage of the reaction. The integral kinetic curve of this type speaks for the conversion of the added catalyst to a catalytically active complex during initial stage of the oxidation. However, the rate of oxidation of the acetals containing $R_b = 2$-methylpropyl group increases from the very beginning of the reaction. This indicates that here, the description based on $f = 1$ is the more appropriate. In this case, the active form of the catalyst is thus formed faster than with the other acetals. It seems likely that some of the oxidation products or intermediate products become the part of the catalytic complex. This resembles formation of the cobalt complexes with alkyl hydroperoxides[26] or aldehydes[27]. In the absence of the catalyst, the oxidation of acetals does not proceed under given reaction conditions for 3 h and any oxidation or co-oxidation of the esters has not been observed even in the presence of the catalyst.

TABLE IV
Optimum parameters for kinetic Eq. (2) including catalyst deactivation (5) ($p = 3$, $r = 0.5$)

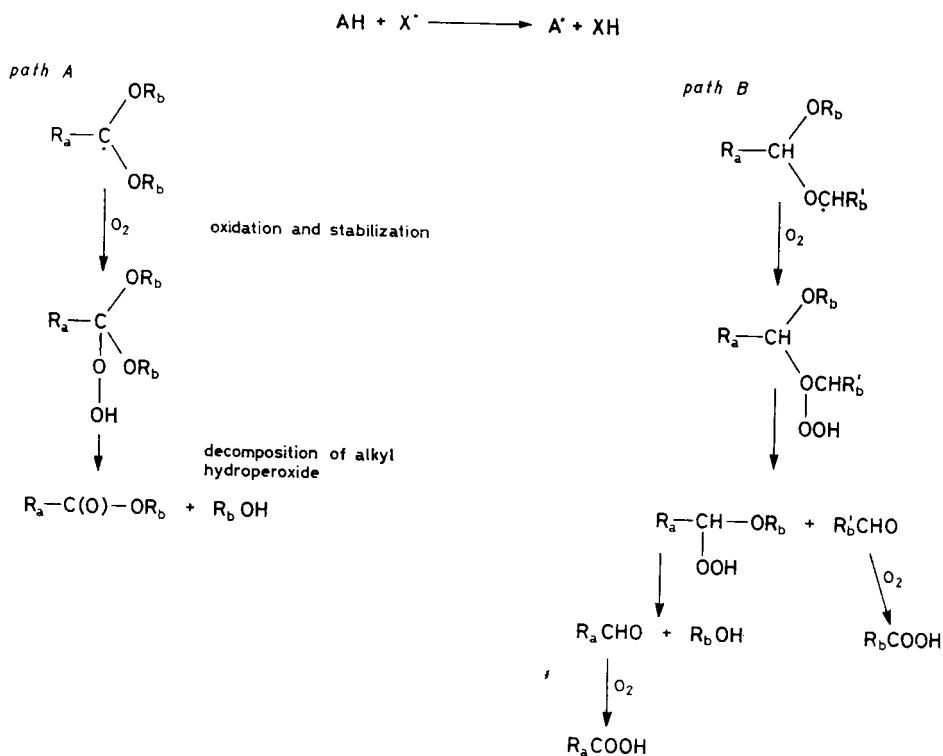| No	Acetal	f mol l^{-1}	$k_P \cdot 10^5$ mol^{-3} l^3 s^{-1}	$k_1 \cdot 10^5$ according to m	m	$\bar{Q}_i \cdot 10^3$ l^4 mol^{-4}
1	$(C_2H_5)_2CHCH(OCH_2CH_2CH_2CH_3)_2$	0	8·0	7·5	2	43
2	$(CH_3)_2CHCH(OCH_2CH_2CH_2CH_3)_2$	0	5·2	75	2	14
3	$CH_3(CH_2)_2CH(OCH_2CH_2CH_2CH_3)_2$	0	5·1	100	1	2
5	$CH_3(CH_2)_2CH(OCH_2CH(CH_3)_2)_2$	1	1·4	10	0·5	12
6	$(CH_3)_2CHCH(OCH_2CH(CH_3)_2)_2$	1	1·3	10	2	6
9	$(CH_2)_5{-}C(OCH_2CH_2CH_3)_2$	0	0·71	25	2	12

TABLE V

Distribution of products for oxidation of acetals (in mol. per cent, $P_{ox} = 0.1$ MPa, data in parentheses for $P_{ox} = 0.2$ MPa)

No	$R_aCH(OR_b)_2$	R_b-OH	R_a-COOR$_b$	R_a-COOH	R_b'-COOH	Side products	Acetal
1	$(C_2H_5)_2CHCH(OCH_2CH_2CH_2CH_3)_2$	46 (44)	6 (7)	2 (5)	10 (26)	11[a] (7)[b]	25 (11)
2	$(CH_3)_2CHCH(OCH_2CH_2CH_2CH_3)_2$	19 (41)	9 (13)	2 (9)	4 (11)	—	66 (26)
3	$CH_3(CH_2)_1CH(OCH_2CH_2CH_2CH_3)_2$	14 (43)	8 (17)	2 (5)	—[c]	—	76 (36)
5	$CH_3(CH_2)_2CH(OCH_2CH(CH_3)_2)_2$	14 (59)	8 (13)	0 (0)	<0.1(0.4)	—	78 (29)
6	$(CH_3)_2CHCH(OCH_2CH(CH_3)_2)_2$	11 (19)	5 (11)	15 (28)	—[c]	—	70 (42)
8	$CH_3(CH_2)_2CH(OCH(CH_3)(C_2H_5))_2$	33 (19)	9 (5)	22 (59)	—	12[d] (12)[e]	24 (1.5)
9	$\lfloor(CH_2)_5{-}C(OCH_2CH_2CH_3)_2$	33 (51)	—	—	—	26[f] (30)	41 (19)
4	$(CH_3)_2CHCH{<}^{OCH_2CH_2CH_2CH_3}_{OCH_2CH(CH_3)_2}$	iso-12 (8.6) / n-14 (9.8)	iso-6 (5.1) / n-6 (5.1)	iso-26 (33) / n-33 (37)	—[c]	—	4 (1.2)
7	$CH_3(CH_2)_2CH{<}^{OCH_2CH_2CH_2CH_3}_{OCH_2CH(CH_3)_2}$	iso-5.5 (5.4) / n-7 (6.4)	iso-3.5 (3.5) / n-3 (3.4)	iso-5 (5.4) / n-73.5 (68.4)	—[c]	2[g] (2.4)	0.5 (4.9)

[a] Propanol + pentanols (1 : 7); [b] (1 : 5); [c] $R_aCOOH = R_b'COOH$; [d] methyl ethyl ketone; [e] and 4% of a mixture of acetic and propionic acid (1 : 1); [f] cyclohexanone; [g] propanol + propionic acid (1 : 2).

Mechanism of Oxidation of Acetals

Based on data reported by other authors (see introduction) and on our analyses of the reaction mixtures after oxidation of acetals, a radical chain course can be accepted for the catalysed oxidation studied (Scheme 1).

$$AH + X^{\cdot} \longrightarrow A^{\cdot} + XH$$

path A

$$R_a{-}\underset{\underset{OR_b}{|}}{\overset{\overset{OR_b}{|}}{C}}$$

$\downarrow O_2$ oxidation and stabilization

$$R_a{-}\underset{\underset{OH}{\underset{|}{O}}}{\overset{\overset{OR_b}{|}}{C}}{\diagdown}OR_b$$

↓   decomposition of alkyl hydroperoxide

$$R_a{-}C(O){-}OR_b \;+\; R_bOH$$

path B

$$R_a{-}CH{\overset{OR_b}{\diagdown}}_{OCHR_b'}$$

$\downarrow O_2$

$$R_a{-}CH{\overset{OR_b}{\diagdown}}_{\underset{OOH}{OCHR_b'}}$$

↓

$$R_a{-}\underset{\underset{OOH}{|}}{CH}{-}OR_b \;+\; R_b'CHO$$

$\downarrow$ $\diagdown O_2$

$$R_aCHO \;+\; R_bOH \qquad\qquad R_bCOOH$$

$\downarrow O_2$

$$R_aCOOH$$

SCHEME 1

The oxidation is initiated by catalysed homolysis of the C—H bond

$$A{-}H + M^{(n+1)} \longrightarrow A^{\cdot} + M^{n+} + H^{+},$$
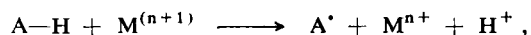
the catalyst being re-oxidized during catalytic decomposition of intermediate products, *i.e.* alkyl hydroperoxides

$$ROOH + M^{n+} \longrightarrow RO^{\cdot} + M^{(n+1)+} + OH^{-}.$$

The source of the radicals in the reaction system can be also thermal decomposition of alkyl hydroperoxides (particularly if it is induced catalytically by coordination of the hydroperoxide to the metal)

$$ROOH \longrightarrow RO^\bullet + HO^\bullet ,$$
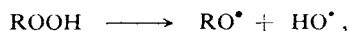
which in oxidation reactions is frequently the reason for the autocatalytic course of the reaction[24]. The radical site in acetal molecule is then formed by chain transfer reactions
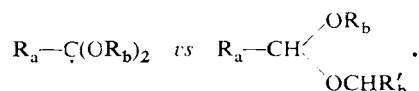
$$AH + RO^\bullet \longrightarrow A^\bullet + ROH$$

$$AH + HO^\bullet \longrightarrow A^\bullet + H_2O .$$
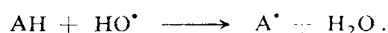
Nevertheless, even bimolecular initiation cannot be excluded,

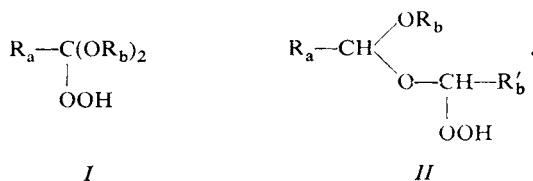$$AH + O_2 \longrightarrow AO_2^\bullet + H^\bullet .$$
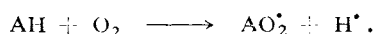
This initiation will be the more likely for acetals compared to *e.g.* alkenes and one can thus relate it to the observed dependence of the oxidation rate on dioxygen pressure. However, under the conditions used and in the absence of the catalyst, the acetals do not undergo oxidation to a measurable degree.

Depending on the structure of $A^\bullet$, two different paths can be proposed for the oxidation studied. The path *A*, which is more probable one, involves formation of the radical centre on the carbon atom substituted with two oxygen atoms $R_a\!-\!\overset{\bullet}{C}(OR_b)_2$. Path *B* involves the C—H bond cleavage in the alkoxy part of the acetal,

$$R_a\!-\!\overset{\bullet}{C}(OR_b)_2 \quad vs \quad R_a\!-\!CH\!\!\begin{array}{c} \nearrow OR_b \\ \searrow O\overset{\bullet}{C}HR_b' \end{array} .$$

The subsequent fast radical chain propagation by the oxidation of the alkyl radical $A^\bullet$ to alkylperoxo radical $AOO^\bullet$ $(E_A \approx 0 \text{ kJ/mol})$ followed by chain transfer $(E_A \approx 40-50 \text{ kJ/mol})$[28] gives intermediate alkyl hydroperoxides *I* and *II*:

$$\begin{array}{cc}
R_a\!-\!C(OR_b)_2 & R_a\!-\!CH\!\!\begin{array}{c} \nearrow OR_b \\ \searrow O\!-\!CH\!-\!R_b' \end{array} \\
\;\;\;| & \;\;\;\;\;\;\;\;\;\;\;\;\;| \\
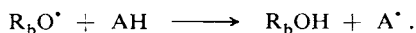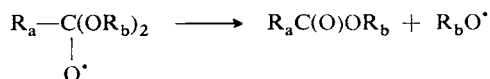\;\;OOH & \;\;\;\;\;\;\;\;\;\;\;OOH \\
\\
I & II
\end{array}$$

The content of peroxo compounds attains maximum during the oxidation at around 0·08 mol/l.

Decomposition of I gives the alkoxy radical:
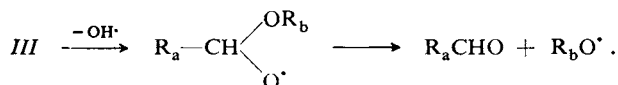
$$I \longrightarrow R_a\text{--}\underset{\underset{O^\bullet}{|}}{C}(OR_b)_2 + HO^\bullet,$$
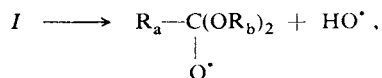
which decomposes to give ester and alcohol:

$$R_a\text{--}\underset{\underset{O^\bullet}{|}}{C}(OR_b)_2 \longrightarrow R_aC(O)OR_b + R_bO^\bullet$$

$$R_bO^\bullet + AH \longrightarrow R_bOH + A^\bullet.$$

The alkyl hydroperoxide II gives via its decomposition another alkyl hydroperoxide III and aldehyde

$$II \longrightarrow R_a\text{--}CH{\overset{OR_b}{\underset{OOH}{<}}} + R'_bCHO.$$

$$III$$
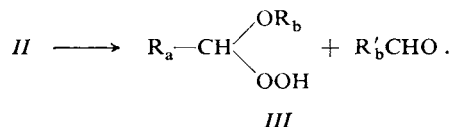
Decomposition of the hydroperoxide III results in formation of another aldehyde

$$III \xrightarrow{-OH^\bullet} R_a\text{--}CH{\overset{OR_b}{\underset{O^\bullet}{<}}} \longrightarrow R_aCHO + R_bO^\bullet.$$

Both aldehydes undergo radical oxidation to carboxylic acids R_aCOOH and R'_bCOOH. This oxidation proceeds via acyl radicals $R_aCO^\bullet$ and $R'_bCO^\bullet$ which can decarbonylate to carbon monoxide and the alcohols by one carbon atom shorter, providing that the acyl radical is branched in the position α to the C=O group[29]. The carboxylic acids can then decarboxylate to evolve carbon dioxide. All these main and side reaction products were found in the reaction mixture after oxidation of the acetals.

Of other side reactions, the co-oxidation of alcohols deserves mentioning. This reaction decreases the content of alcohols and increases the amount of R'_bCOOH acids. The branched alcohols are less co-oxidized than linear ones. As found experimentally, under the reaction conditions used, the esters are not co-oxidized. The content of the esters in the reaction mixture could be also increased by esterification of the acids by alcohols. However, the high ratio of the alcohols to the esters (Table VI) and the absence of the ester in greater amounts while the concentration of the acids is high indicates that the esterification does not takes place.

TABLE VI

Average rate constants k_i ((l mol^{-1} s^{-1}, Eq. (6)) for formation of alcohols and esters in the oxidation of acetals (P_{ox} = 0·1 MPa, data in parentheses for P_{ox} = 0·2 MPa, y = 1)

No	Acetal	Alcohol		Ester		
		x	$k_i . 10^5$ ^{a}	x	$k_i . 10^5$ ^{a}	Alc./est.
1	$(C_2H_5)_2CHCH(O(CH_2)_3CH_3)_2$	1	13 (17)	1	10 (10)	1·3 (1·6)^b
2	$(CH_3)_2CHCH(O(CH_2)_3CH_3)_2$	1 (2)	9·3 (4·8)	1 (2)	9·5 (3·5)	0·98 (1·4)^c
3	$CH_3(CH_2)_2CH(O(CH_2)_3CH_3)_2$	2	2·0 (4·1)	1 (2)	7·0 (3·2)	(1·3)
4	$(CH_3)_2CHCH{<}^{O(CH_2)_3CH_3}_{OCH_2CH(CH_3)_2}$	1 n	6·9 (5·0)	1 n	5·0 (4·0)	1·4 (1·3)
		1 iso	6·5 (4·8)	1 iso	5·0 (4·0)	1·3 (1·2)^d
5	$CH_3(CH_2)_2CH(OCH_2CH(CH_3)_2)_2$	1 (2)	7·7 (5·0)	1 (2)	6·6 (3·4)	1·2 (1·5)
6	$(CH_3)_2CHCH(OCH_2CH(CH_3)_2)_2$	1	7·9 (8·4)	1	6·1 (7·1)	1·3 (1·2)^e
7	$CH_3(CH_2)_2CH{<}^{O(CH_2)_3CH_3}_{OCH_2CH(CH_3)_2}$	1 n	7·4 (6·5)	1 n	5·6 (5·3)	1·3 (1·2)
		1 iso	7·0 (6·3)	1 iso	5·8 (5·3)	1·2 (1·2)^f
8	$CH_3(CH_2)_2CH(OCH{<}^{CH_3}_{C_2H_5})_2$	1	6·8 (8·1)	1	4·9 (6·0)	1·4 (1·3)^g
9	$(CH_2)_5{-}C(OCH_2CH_2CH_3)_2$	1 (2)	4·4 (1·4)	1	4·0 (4·1)	1·1

^{a} For x = 2 dimension l^2 mol^{-2} s^{-1}; ^{b} for R'_bCOOH x = 1, k_i = 1·5 . 10^{-4}, R_aCOOH x = 1, k_i = 1·3 . 10^{-4}; ^{c} for R'_bCOOH x = 1, k_i = 4·8 . 10^{-5}, R_aCOOH x = 1, k_i = 3·5 . 10^{-5}; ^{d} butyric acid x = 1, k_i = 8·9 . 10^{-5} (k_i = 7·7 . 10^{-5}), isobutyric acid x = 1, k_i = 8·5 . 10^{-5} (7·4 . 10^{-5}); ^{e} for isobutyric acid x = 3, y = 0·5, k_i = 3·5 . 10^{-6} (1 . 10^{-6}); ^{f} for butyric acid x = 1, k_i = 1·6 . 10^{-4} (1·5 . 10^{-4}), for isobutyric acid x = 1, k_i = 7·2 . 10^{-5}; ^{g} for butyric acid x = 1, k_i = 8·3 . 10^{-5} (1·1 . 10^{-4}), for methyl ethyl ketone x = 1, k_i = 6·3 . 10^{-5} (7·9 . 10^{-5}).

The Dependence of the Reactivity of Acetals on their Structure

The ability of acetals to undergo oxidation depends first of all on whether the central carbon atom is substituted with hydrogen. If this is not the case (ketal *9*), path *A* in Scheme 1 can be disregarded. The fact that formation of the radical by path *A* requires hydrogen abstraction from tertiary carbon atom in difference to secondary carbon atom involved in path *B* makes formation of the radical *via* path *A* the more favourable route (by a factor of nearly ten)[30], not speaking about electronic effects due to the different number of neighbouring oxygen atoms. In our scale of the rate constants, the reactivity of ketal *9* is then ten times lower compared to *e.g.* acetal *1*.

The activating factor in the structure of acetal is branching on the α carbon of the R_a part. Product distributions presented in Table V indicate that path *A* is not the only one which leads to the observed products. From the content of the acid R_aCOOH and other side products it follows that path *B* plays — and in some cases important — role in formation of the reaction products. Thus, in the case of the oxidation of acetal *1*, relative proportion of the acids R_aCOOH and R'_bCOOH (1 : 5) and the alcohols (pentanols: propanol = 7 : 1) results from the cleavage of the alkyl hydroperoxide $R_aCH(OR_b)(OC^{\bullet}HR'_b)$ leading to aldehydes. These aldehydes are further oxidized and in the stage of acyl radicals they decarbonylate to yield alcohols which are by one carbon atom shorter (propanol from R_b and pentanols with predominant 3-pentanol from R_a) and carbon monoxide. The ratio of both alcohols corresponds to the ease of decarbonylation of the linear and branched acyl radical[2]. The amount of carbon monoxide found in gaseous products (c. 15% with respect to the starting acetal) equals nearly to the amount of the alcohols formed (11%). For other acetals, carbon monoxide formation did not take place. In all cases, the gas phase contained carbon dioxide $(2-10\%)$ formed by other decomposition oxidation reactions. Thus, for example, the oxidation of 2-ethylbutyric acid under the same conditions (catalyst, temperature, reaction time) gives 2·5% mol. CO_2 (calculated to the starting acid). The evolution of gaseous products during the oxidation makes the measurement of the oxygen uptake somewhat inaccurate, particularly at the end of the reaction.

The acetals nonbranched in R_b part are generally more capable of oxidation compared to the acetals with branched R_b part. Branching in the alkoxy part in the position α (acetal *8*) decreases the number of hydrogen atoms on the centres supposed to be involved in formation of radicals *via* path *B* and the overall reactivity thus decreases. On the other hand, the carbon α' becomes tertiary. The lower number of available α' C—H bonds is then compensated to a certain degree by the easier formation of the radical on the tertiary carbon atom, which is also the reason for formation of methyl ethyl ketone instead of RC'_bOOH.

Branching on the carbon β' affects the reactivity of acetals less than in the previous case. However, the type of integral conversion curve of the acetal in the initial stage

of the reaction is changed and the course of the oxidation is described better by using the autocatalytic factor $f = 1$.

Mixed acetals of butanal (acetal 7) and 2-methylpropanal (acetal 4) follow observed trend in the overall reactivity in that the acetal branched on the carbon α is the more reactive than the nonbranched one. The reactivity of the mixed acetal of 2-methyl-propanal falls between the reactivity of both acetals with the same R_b parts, which is not the case of the mixed acetal of butanal. The products contain the n-alcohol in excess compared to iso-alcohol, which is indicated also by the greater amount of the ester with iso-alcohol compared to that with n-alcohol. The relative proportion of the acids speaks for the easier formation of butyric acid than iso-butyric acid. This proportion is affected also by co-oxidation of alcohols with acetals. Comparative experiments with the alcohols added to the reaction mixture prior to the reaction have proved that under given reaction conditions, the rate of co-oxidation of n-butanol is approximately twice that of 2-methylpropanol.

The properties of C—H bonds on the sites of acetal molecule which would be attacked by radical are at least to some extent reflected in ^{13}C NMR shifts and especially in $^{1}J_{CH}$ coupling constants for the central and α' carbon atoms (carbon atoms a and e in Table II). Their values indicate that both positions are different, which is mainly caused by the different number of electronegative substituents. As $^{1}J_{CH}$ for carbon-a reflects also changes in the s-character of C—H bond[31], in the case of nearly the same substitution, one can expect that the reactivity of acetal would correlate with $^{1}J_{CH}$ constants for the central carbon atom. The situation is complicated by inaccuracy in determining these constants. Our results show that such a dependence seems likely, although it does not hold for all the acetals.

Catalyst Deactivation

After certain period, the oxidation of acetals stops and proceeds further only after additional amount of the catalyst is introduced into the reaction mixture. The final conversion of acetals depends on oxidation conditions (especially on oxygen pressure) and on the type of acetal. The conversion of the most reactive acetal 1 is 75 mol.% at maximum. This situation has not been found for acetal 8 and for mixed acetals. With mixed acetals, specific conditions of their oxidation complicate situation (only 20% of the amount of the acetal was used in experiments as these acetals were obtained in limited amounts by preparative gas chromatography). However, their conversions were determined at the same time (Table V). In other cases in which the total conversion of acetals did not exceed 50%, we have observed formation of a pale pink precipitate which contained $31-32\%$ Co. This content corresponds to the compound in which one (28·47%) or two (35·72%) acetate ions are replaced by OH^- ions. The source of hydroxy ions in the reaction system could be decomposition of alkyl hydroperoxides according to Haber and Weiss[24]

$$ROOH + M^{n+} \longrightarrow RO^{\cdot} + M^{(n+1)+} + OH^{-},$$
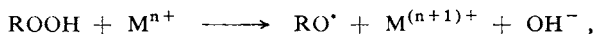
which re-oxidizes the metal to the higher valence state, forming thus conditions for initiation reaction. The oxidation of aldehydes is not accompanied by catalyst de-activation[29] since the products are peroxoacids. Also in all the cases in which de-activation has not been observed, the reaction mixture contained acids in greater amounts. In this respect, especially butyric acid was efficient. Comparative experiments in which 45 mol.% of butyric acid was added to the reaction mixture prior to oxidation increased both the overall reaction rate (for acetal 5, $k_P = 3 \cdot 5 \cdot 10^{-5}$ and $4 \cdot 1 \cdot 10^{-5}$ mol^{-3} l^3 s^{-1} without and with the acid respectively) and significantly also the conversion of the acetal to 89% compared to 22% conversion attained in the absence of the acid.

The course of the reaction can be described quantitatively by the kinetic model which includes catalyst deactivation by optimation of parameters in Eqs (2) and (3) (Table IV). For majority of the acetals studied, the rate of catalyst deactivation was proportional to the square power of product concentration; the acetals with $R_a = C_3H_7$ show the less distinct dependence given by $m = 1$ or $0 \cdot 5$. The k_1 values were determined with an accuracy of 25 rel. per cent. The sequence of their increase (acetals 1, 9, 2) reflects the opposite order of conversions, although the overall reactivity decreases in the order: acetals 1, 2, 9.

Product Distribution

In Table VI are presented the results of kinetic analysis of the formation of individual products according to the model kinetic equation (6). Formation of most products is best described by the dependence of the rate of their formation on the first power of acetal concentration and the first power of the sum of the catalyst and products concentration. Exceptional in this respect is the pressure oxidation of acetals 2, 3, 5 and 9, where the rate of formation of alcohol and ester is proportional to the square power of acetal concentration. Formation of isobutyric acid in the oxidation of acetal 6 arises from decomposition of initial products of the oxidation of the acetal *via* path *B* both from part R_a and part R_b of the acetal and also co-oxidatively from alcohol R_bOH and is described by kinetic equation of the third order in the acetal. The ratio of the rate constants for alcohol and ester formation documents the prevailance of the alcohol, which is further pronounced by carrying out the reaction under pressure.

It seems likely that the molar excess of the alcohols over the ester might result from formation of hemiacetal by the following reaction in the presence of acids

$$R_a{-}CH(OR_b)_2 \xrightarrow[H^+]{H_2O} R_a{-}CH{\Big\langle}{{OR_b} \atop {OH}} + R_bOH.$$
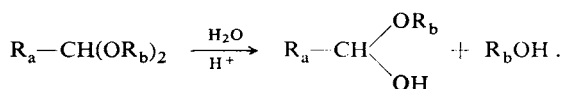
Its oxidation can yield another molecule of alcohol with synchronous formation of R_aCOOH

$$R_a\!-\!CH\!\!\begin{array}{c} OR_b \\ \\ OH \end{array} \xrightarrow[\text{2) decomp}]{\text{1) } O_2} R_aCOOH + R_bOH.$$
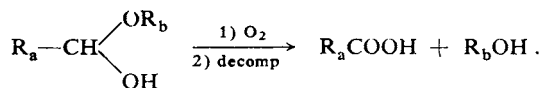
Oxidation of acetal 5 in the presence of catalytic amounts of sulphuric acid added in the initial stage of the reaction accelerates the oxidation and the final alcohol to ester mol. ratio is 3·7 compared to 1·75 in the absence of the acid. However, both the starting and final compounds are decomposed to the greater degree. In this connection we have also tested the product of thermal conversion of the starting dibutyl acetal of 2-ethylbutanal, *i.e.* 3-ethyl-5-oxo-3-nonene. Kinetics of its oxidation were however very different from the starting acetal and the reaction mixture contained a variety of decomposition products.

Effect of Dioxygen Pressure

The increase in the pressure of dioxygen during oxidation of acetals to about twice of the initial value (0·2 MPa) increases the overall reactivity of most acetals and the oxidation proceeds to the higher conversions of acetals (except for mixed acetals where high conversions were obtained already at low pressures). Also in this case, the reactivity of acetals was evaluated on the basis of the constants of the same kinetic model which was optimal for the low pressure oxidation, even though the pressure oxidation shifts optimum reaction orders $p = 3$ and $r = 0·5$ to $p = 2$ and $r = 1$.

Notwithstanding, the reactivity remains the same (except for acetal 4). The content of acetal in the final reaction mixture decreases to the one half of that found in the low pressure oxidation. As far as the conversion of acetals is less than 90 per cent, the content of alcohols is markedly increased while the amount of esters increases only slowly. If the conversion exceeds 90%, the content of $R_b'COOH$ increases by co-oxidation of alcohols with acetals. The increased dioxygen pressure makes path *B* more favourable, which results in the considerable increase in the content of R_aCOOH in the case of acetal 8. Furthermore, sec-butanol is oxidized to methyl ethyl ketone which is further oxidized. This is documented by the presence of propionic acid and acetic acid in the reaction mixture. As far as product distribution is concerned, the pressure of dioxygen does not affect significantly the course of the oxidation of mixed acetals 4 and 7.

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