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INTERMEDIATES IN COBALT-CATALYSED METHANOL HOMOLOGATION: LABELLING STUDIES WITH DEUTERATED METHANOL AND METHYL IODIDE

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Summary

The cobalt-catalysed homologation of perdeuterated methanol with CO/H_2 gives C_2 products in which the CD_3 group remains intact. GC/MS measurements showed that no H/D exchange unless the methanol conversion exceeded 50%. These results indicate that methylene species are unlikely to be as catalytic intermediates, and favour methyl species for such intermediates.

In the presence of iodine promoters methyl iodide is a likely intermediate since it is much more readily consumed than methanol in carbonylation/hydrocarbonylation reactions. This was shown by treating a 5/1 mixture of CH_3OH and CD_3I with CO/H_2 in the presence of $Co_2(CO)_8$; at short reaction times only the carbonylation/hydrocarbonylation products of methyl iodide could be detected by GC/MS. Methyl iodide can be formed from a variety of iodine compounds under homologation conditions, as was confirmed by separate experiments.

Introduction

The homologation of methanol with synthesis gas in a cobalt-catalysed reaction to give acetaldehyde (eq. 1) or ethanol (eq. 2) has been of much interest in recent years because it would give oxygenated C_2 products in a two-step process from CO/H_2 derived from coal. Recent reports show that essentially two types of catalysts have been developed [1–3]: cobalt/iodine systems, which catalyze the formation of

$$CH_3OH + CO + H_2 \longrightarrow CH_3CHO + H_2O \qquad (1)$$

$$CH_3OH + CO + 2\ H_2 \longrightarrow CH_3CH_2OH + H_2O \qquad (2)$$

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acetaldehyde according to eq. 1, and cobalt/ruthenium/iodine systems which are more suitable for the synthesis of ethanol according to eq. 2. The selectivity and stability of each catalyst systems can be enhanced by addition of suitable ligands, such as phosphines [4,5]. However the selectivity between acetaldehyde or ethanol remains limited, and a variety of side products are observed, such as acetals, esters, ethers and methane. Thus commercialization of the process depends on further improvements of product selectivity and for this a more detailed knowledge of the mechanism of the homologation reaction, for which conflicting proposals have been made, would be helpful. We recently described the properties of cobalt/iodine/ligand catalyst systems for methanol homologation which are selective towards formation of acetaldehyde [6]. We now describe model reactions with these catalyst systems using deuterium labelled substrates, which throw light on the nature of the C_1-intermediates and on the role of iodine promoters.

Experimental

Reagents were either commercially available, viz. MeOH, MeI, and Ph_3P or were prepared by standard methods, viz. $Co_2(CO)_8$ [7] and $CoI_2(Ph_3P)_2$ [8]. Deuterated reagents such as CD_3OD (99.5% D) and CD_3I (99% D) were obtained from EGA and used without further purification.

All experiments were carried out in a 150 ml stainless steel autoclave (No. 2.4610) equipped with a magnetic stirrer, a dropping funnel, and a syngas storage system with a pressure-regulation device to maintain a constant pressure. GC analysis was carried out on a 100 m Carbowax 1500 SCOT column (WGA, Düsseldorf) of 0.25 mm ID using toluene as internal standard. Methanol conversion was calculated from the unchanged methanol determined by GC. Molar selectivities are based on the amount methanol consumed, and allow for the number of methyl groups in the molecule. GC/MS measurements were carried out on a Varian MAT 112 S/SS 200 system and high resolution MS measurement of gaseous products with a Varian MAT 212 Dietz Mincal 621/8 instrument [9].

Homologation of CD_3OD

With 0.113 g (0.135 mmol) $CoI_2(Ph_3P)_2$ as the catalyst 9.73 g (270 mmol) of CD_3OD were allowed to react for 2 h at 200°C and 300 bar CO/H_2 (1/1). After

TABLE 1

MASS SPECTROMETRIC ANALYSIS OF THE REACTION PRODUCTS FROM THE HOMOLOGATION OF CD_3OD WITH CO/H_2 (methanol conversion 48%) [a]

Product (% selectivity)	Molecular ion, *m/e* (% rel. intensity)	Fragment ions, *m/e* (% rel. intensity)
CD_3CHO	47 (73)	CDO^+, 30 (100)
(0.3)		CHO^+, 29 (86)
$CD_3CH(OCD_3)_2$	98 ($M^{+\cdot}-1$, 1.4)	$CH(OCD_3)_2{}^+$, 81 (33)
(64.5)		$CD_3CH(OCD_3)^+$, 65 (100)
$CD_3CO_2CD_3$	80 (12)	$CD_3CO_2{}^+$, 62 (4)
(33.7)		CD_3CO^+, 46 (100)
CD_3CH_2OH	49 (20)	$CD_3CH_2O^+$, 48 (42)
(1.0)		CH_2OH^+, 31 (100)

[a] Resolution 800, electron energy 80 eV, electron current 0.7 mA, temperature of ion source 280°C.

TABLE 2

HIGH RESOLUTION MS ANALYSIS OF DEUTERATED METHANES IN THE GASEOUS PHASE FROM THE HOMOLOGATION OF CD_3OD WITH CO/H_2 (methanol conversion > 70%) [a]

Ion	Rel. intensity (%)	m/e Found (calcd.)
$CD_4^{+\cdot}$	38	20.0565 (20.0564)
$CD_3H^{+\cdot}$	100	19.0499 (19.0501)
CD_3^+	55	18.0427 (18.0423)
CD_2H^+	39	17.0360 (17.0360)

[a] Resolution, 15000 electron energy 70 eV, electron current 1.0 mA, temperature of ion source 200°C. Intensity data without isotopic correction.

cooling, depressurizing and addition of the standard, the mixture was analysed by GC and GC/MS. The results are given in Table 1. The high resolution MS data for the gaseous products are given in Table 2.

Reaction of iodine compounds in methanol with CO/H_2

In the absence of a cobalt compound, 3.20 g (0.1 mol) of methanol and 0.01 mol of "I" in the form of various iodine compounds were autoclaved for 30 min at 190°C and 300 bar CO/H_2 (1/1). After work up the mixture was analysed by GC and its approximate pH was determined using an indicator (Macherey-Nagel, Duotest). The results are given in Table 4.

Reaction of CD_3OD/CH_3I (5/1) with CO/H_2

A mixture of 5.0 g (0.139 mol) of CD_3OD, 3.94 g (0.028 mol) of CH_3I and 11.5 mg (0.035 mmol) of $Co_2(CO)_8$ was kept for 15 min under 300 bar CO/H_2(1/1) at 190°C. The autoclave used allowed rapid heating and cooling. The product mixture was analyzed by GC/MS, and the results are given in Table 5.

In a control experiment a mixture of 1.94 g (0.054 mol) of CD_3OD, 1.42 g (0.01 mol) of CH_3I and 4.6 mg (0.014 mmol) of $Co_2(CO)_8$ was heated for 15 min at 190°C at a pressure of 300 bar (N_2/H_2 (1/1). After cooling the product mixture was analyzed by GC/MS. The mixture contained mainly unchanged CD_3OD and CH_3I, and traces of dimethyl ether. No trace of CD_3I was observed, indicating that exchange of methyl groups between CH_3I and CD_3OD can be excluded under these conditions.

Reaction of CH_3OH/CD_3I (5/1) with CO/H_2

A mixture of 4.43 g (0.139 mol) of CH_3OH, 4.05 g (0.029 mol) of CD_3I and 11.5 mg (0.035 mmol) $Co_2(CO)_8$ was kept for 15 min under 300 bar CO/H_2 (1/1) at 190°C. After cooling the mixture was analyzed by GC/MS and the results are given in Table 6.

Results and discussion

The activation of methanol in homologation processes can involve either methyl intermediates, as proposed by Wender [10] and other authors [1], or methylene intermediates, as was postulated by Ziesecke [11]. Stoichiometric formation of

$$CD_3OD + HCoL_n \longrightarrow CD_3CoL_n + HOD \qquad (3)$$

$$CD_3OD \longrightarrow \text{"}CD_2\text{"} + D_2O \qquad (4)$$

$$\text{"}CD_2\text{"} + HCoL_n \longrightarrow HCD_2CoL_n \qquad (5)$$

oxygenated C_2 products such as alkyl acetates from methylene bridged complexes has also been reported recently [12,13].

Thus it seemed of interest, to design experiments which allowed these various routes to be distinguished. The homologation of perdeuterated methanol would involve eq. 3 as the alkylating step in the case of Wender's mechanism and eqs. 4 and 5 in the case of Ziesecke's mechanism. The hydrogen of the metal hydride must originate in both cases from synthesis gas (CO/H_2), and homologation products formed via methylene as in eq. 5 would therefore contain CHD_2-methyl groups.

The homologation of CD_3OD proceeds clearly according to eq. 6 to give oxygenated C_2 products in which the CD_3 groups have remained intact. This was

$$CD_3OD + CO/H_2 \xrightarrow[200^\circ C,\ 300\ \text{bar},\ 2\ \text{h}]{CoI_2(Ph_3P)_2} \begin{array}{l} CD_3CHO + CD_3CH_2OH + \\ CD_3CH(OCD_3)_2 + CD_3CO_2CD_3 \end{array} \qquad (6)$$

shown unequivocally by GC/MS, as can be seen from Table 1. Only when methanol conversion was allowed to exceed 50%, resulting in the presence of large amounts of free acetaldehyde, was H/D exchange of unspecified amount observed. This is obviously the consequence of the keto-enol equilibrium for free acetaldehyde, and in agreement with this no such H/D exchange was observed with methyl acetate. Under more drastic conditions Novotny et al. found deuterium to be randomly distributed between the methyl and methylene carbons of the ethanol obtained by reaction between CH_3OH, CO and D_2O [14].

The isotope content of the methane fraction of the gaseous products from the homologation of CD_3OD was determined by high resolution mass spectrometry. As shown in Table 2, only CD_4 and CHD_3 were present, in a ratio of roughly 1/3. Their formation can be rationalized by eqs. 7 and 8, which involve reductive elimination of a CD_3 ligand from a cobalt hydride or deuteride species. The detection of CD_4 and CD_3H can also be taken as a further proof that the methane side product in homologation comes from methanol and not from CO hydrogenation. Our results for the homologation of deuterated methanol summarized in Tables 1 and 2 clearly

$$CD_3CoHL_n \longrightarrow CD_3H + CoL_n \qquad (7)$$

$$CD_3CoDL_n \longrightarrow CD_4 + CoL_n \qquad (8)$$

TABLE 3

EFFECT OF IODINE PROMOTERS ON SYNGAS UPTAKE, METHANOL CONVERSION AND PRODUCT SELECTIVITY IN METHANOL HOMOLOGATION (Conditions: 2 mol MeOH, 1 mmol $Co(OAc)_2 \cdot 4H_2O$, 2 mmol Ph_3P, 2 mmol "I", 300 bar CO/H_2 (1/1), 190°C, 2 h)

Iodine compound	Syngas uptake (l)	Methanol conversion (%)	Selectivity (mol %)			
			CH_3CHO	C_2H_5OH	Acetals	Acetates
CH_3I	43.6	71.1	23.1	5.8	45.7	15.8
HI	47.1	76.3	20.1	3.7	37.9	16.8
I_2	48.1	72.3	22.0	5.0	34.0	20.1
CoI_2 [a]	45.2	77.6	18.3	3.7	38.9	16.8
EtI	35.8	71.7	22.0	4.7	45.6	15.5
PhI	20.2	49.9	7.2	2.4	75.2	5.4
NaI	< 0.5	9.7	tr.	tr.	18.6	2.1
Et_4NI	< 0.5	11.7	tr.	tr.	15.4	1.7

[a] No $Co(OAc) \cdot 4H_2O$ added.

indicate that it is highly improbable that methylene species are intermediates in this process.

The role of iodine promoters in methanol homologation has been discussed ever since their discovery in 1956 by Berty et al. [15]. Virtually all types of iodine compounds have been claimed to be active as promoters for cobalt catalysts. However, in the presence of ligands such as triphenylphosphine three groups of iodides can be distinguished in respect of their efficiency as promoters, as is shown in Table 3. Taking account of the syngas uptake, methanol conversion and selectivity towards formation of free acetaldehyde, HI, I_2, CoI_2, MeI and EtI were found to be most active; for PhI a lower conversion and syngas uptake was observed as well as a pronounced induction period. Ionic iodides such as NaI and Et_4NI were almost inactive, although ionic iodides are excellent promoters in the absence of phosphine ligands.

In order to find an explanation for this behaviour, the iodine promoters used in Table 3 were submitted to the homologation conditions in the absence of cobalt. In the case of CoI_2 the syngas was replaced by a 1/1 mixture of N_2/H_2. After the

TABLE 4

REACTIONS OF IODINE COMPOUNDS IN METHANOL WITH CO/H_2 [a]

Iodine compound	Methyl iodide (% yield)	pH value
CH_3I	> 50	< 3
HI	> 50	< 3
I_2	> 50	< 5
CoI_2 [b]	< 10	< 5
EtI	< 10	< 6
PhI	< 10	< 6
NaI	–	~ 7
Et_4NI	–	~ 7

[a] Conditions: 0.1 mol MeOH, 0.01 mol "I", 300 bar CO/H_2 (1/1), 190°C, 30 min. [b] 300 bar N_2/H_2 (1/1).

TABLE 5

MASS SPECTROMETRIC ANALYSIS OF THE PRODUCTS FROM THE REACTION OF CH_3I/CD_3OD (1/5) WITH CO/H_2 IN THE PRESENCE OF $Co_2(CO)_8$ (methanol conversion ~ 10%) [a]

Product (% selectivity)	Molecular ion, m/e (% rel. intensity)	Fragments ions, m/e (% rel. intensity)
$CH_3CH(OCD_3)_2$	95 ($M^{+\cdot}-1$, 2.1)	$CH(OCD_3)_2^+$, 81 (37)
(~ 60)		$CH_3CH(OCD_3)^+$, 62 (100)
$CH_3CO_2CD_3$	77 (16)	$CO_2CD_3^+$, 62 (7)
(~ 30)		CH_3CO^+, 43 (100)

[a] MS conditions see Table 1.

reaction the yield of methyl iodide, based on the amount of iodide compound fed, and the pH value were determined. As is shown in Table 4, the ability of the iodides to form methyl iodide and to lower the pH value of the solution can be related to their promoting efficiency. Only in the case of the inactive compounds NaI and Et_4NI was no trace of methyl iodide detected, and the solution remained neutral.

From these results it can be assumed, that in the case of active iodine promoters the species CH_3I, I_2 and HI are present under the conditions of methanol homologation and are inter-related by the equilibria 9–11. The lack of activity of NaI and Et_4NI in the presence of phosphines can be explained by the enhanced electron density of the metal in the ligand-substituted cobalt carbonyls, which would make the nucleophilic attack of I^- more difficult.

$$HI + CH_3OH \rightleftharpoons CH_3I + H_2O \qquad (9)$$

$$I_2 + H_2 \rightleftharpoons 2\ HI \qquad (10)$$

$$CoI_2 + H_2 \rightleftharpoons 2\ HI + Co^0 \qquad (11)$$

Having demonstrated the ready formation of methyl iodide under homologation

TABLE 6

MASS SPECTROMETRIC ANALYSIS OF THE PRODUCTS FROM THE REACTION OF CD_3I/CH_3OH (1/5) WITH CO/H_2 IN THE PRESENCE OF $Co_2(CO)_8$ (methanol conversion ~ 10%) [a]

Product (% selectivity)	Molecular ion, m/e (% rel. intensity)	Fragments ions, m/e (% rel. intensity)
$CD_3CH(OCH_3)_2$	92 ($M^{+\cdot}-1$, 1.5)	$CH(OCH_3)_2^+$, 75 (32)
(~ 60)		$CD_3CH(OCH_3)^+$, 62 (100)
$CD_3CO_2CH_3$	77 (16)	$CO_2CH_3^+$, 59 (4)
(~ 30)		CD_3CO^+, 46 (100)

[a] MS conditions see Table 1.

conditions, it seemed of interest to determine whether this compound acts as an alkylating agent for cobalt. As an alternative, oxidative addition of methanol to a coordinatively unsaturated cobalt iodine species has been proposed recently by Bahrmann et al. [2].

In an approach to this question we carried out competitive hydrocarbonylation experiments using unlabelled methyl iodide along with an 5/1 excess of deuterated methanol in the presence of $Co_2(CO)_8$ as catalyst. The reaction proceeded cleanly according to eq. 12 to give exclusively the hydrocarbonylation/carbonylation products of methyl iodide, whereas the deuterated methanol was involved only in acetalization or ester formation. This is evident from the GC/MS analysis, as shown in Table 5. A separate experiment using N_2/H_2 instead of synthesis gas showed there was no H/D scrambling or exchange of methyl groups between CH_3I and CD_3OH.

$$CH_3I + CD_3OD + CO/H_2 \xrightarrow[190^\circ C,\ 300\ bar,\ 15\ min]{Co_2(CO)_8} CH_3CH(OCD_3)_2 + CH_3CO_2CD_3 \tag{12}$$

$$CD_3I + CH_3OH + CO/H_2 \xrightarrow[190^\circ C,\ 300\ bar,\ 15\ min]{Co_2(CO)_8} CD_3CH(OCH_3)_2 + CD_3CO_2CH_3 \tag{13}$$

In order to exclude any isotope effects the experiment described above was repeated using CD_3I and an 5/1 excess of CH_3OH (eq. 13). Again only methyl iodide was hydrocarbonylated/carbonylated as is revealed by the GC/MS data in Table 6.

Our results show that methylene intermediates are unlikely in methanol homologation. Control experiments under homologation conditions indicate the presence of methyl iodide in all cases where active iodine promoters were chosen. Furthermore methyl iodide was shown to be much more reactive than methanol in cobalt-catalysed hydrocarbonylation and carbonylation reactions. On the basis of these results it is reasonable to conclude that methyl iodide is an important intermediate in methanol homologation. The results do not however permit a decision as to whether the alkylation of cobalt occurs in an S_N2 type process (eq. 14), as proposed by Pretzer et al. [4] or in an oxidative addition process (eq. 15), as proposed by Wender [10], Wilkinson and coworkers [16] and by us [3,6]. Kinetic investigations of methanol homologation revealed a second order dependence for methyl iodide and a negative activation entropy [17]. This indicates participation of methyl iodide in the rate determining step, which is probably an oxidative addition.

$$CH_3I + Co(CO)_4^- \rightleftharpoons CH_3Co(CO)_4 + I^- \tag{14}$$

$$CH_3I + CoL_n \rightleftharpoons CH_3\ CoL_n\ I \tag{15}$$

Iodine may also act as a ligand which labilizes the coordination sphere of cobalt [2]. In situ spectroscopic studies are in progress in order to elucidate the nature of the cobalt compounds which are involved in the catalytic cycle.

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References

1 D.W. Slocum in W. Jones (Ed.), Catalysis in Organic Synthesis, Academic Press, New York, 1980, p. 245.
2 H. Bahrmann and B. Cornils, Chem. Ztg., 104 (1980) 39.
3 K.-H. Keim, J. Korff, W. Keim and M. Röper, Erdöl Kohle, Erdgas, Petrochem. Brennst.-Chem., 35 (1982) 297.
4 W.R. Pretzer and T.P. Kobylinski, Ann. N.Y. Acad. Sci., 333 (1980) 58.
5 H. Bahrmann, W. Lipps and B. Cornils, Chem. Ztg., 106 (1982) 249.
6 M. Röper, H. Loevenich and J. Korff, J. Mol. Catal., 17 (1982) 315.
7 P. Szabó, L. Markó and G. Bor, Chem. Tech. (Leipzig), 13 (1961) 549.
8 F.A. Cotton, O.D. Faut, D.M.L. Goodgame and R.H. Holm, J. Am. Chem. Soc., 83 (1961) 1780.
9 E. Müller and U. Krienen, Fresenius Z. Anal. Chem. 294 (1979) 241.
10 I. Wender, Catal. Rev.-Sci. Eng., 14 (1976) 97.
11 K.H. Ziesecke, Brennst. Chem., 33 (1952) 385.
12 M. Röper, H. Strutz and W. Keim, J. Organomet. Chem., 219 (1981) C5.
13 C.E. Sumner Jr., J.A. Collier and R. Pettit, Organometallics, 1 (1982) 1350.
14 M. Novotny and I.L. Mador, in W.R. Moser (Ed.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1981, p. 249.
15 J. Berty, L. Markó and D. Kallo, Chem. Tech. (Leipzig), 8 (1956) 260.
16 J.R. Blackborow, R.J. Daroda and G. Wilkinson, Coord. Chem. Rev., 43 (1982) 17.
17 H. Loevenich and M. Röper, in preparation; H. Loevenich, Dissertation, Rheinisch-Westfälische Technische Hochschule Aachen, 1982.