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Hydroformylation of 1-octene in the presence of cobalt alkylidynecarbonyl clusters

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The hydroformylation of 1-octene in the presence of $Co_3(CO)_9(\mu-CR)$ (R = H, Me, Ph, CO_2Me , CO_2Et , CO_2Pr^i , CO_2Bu^t , Cl, Br, OMe) alkylidynecarbonyl clusters, as well as triphenylphosphine derivatives of these complexes and heteronuclear Co_2Ni compounds have been studied. The nature of the catalytically active species in hydroformylation, as well as the processes of their formation and transformation during the reaction, have been established by means of IR spectroscopy. The effects of the reaction conditions, the nature of the substituent at the apical carbon atom, the electron donating phosphine substituent, and the substituent in the metal cluster framework have been discussed.

Key words: 1-octene, hydroformylation; cobalt carbonyls.

The elucidation of the nature of the catalytically active species is of great importance in homogeneous catalysis with clusters. Only a few reactions are known in which the cluster itself is such a species.¹⁻⁵ Cobalt alkylidynecarbonyl clusters can serve as a model for the precursor of hydroformylation catalysts. The possibility of using $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ as a catalyst for hydroformylation of 1-pentene was shown previously.⁵ It was established that this form is the catalytically active species, despite the fact that, according to UV, IR, and ¹H NMR spectroscopy data,⁶ the $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ and $\text{Co}_3(\text{CO})_9(\mu\text{-CMe})$ clusters partially decompose in the course of hydroformylation to form $\text{Co}_2(\text{CO})_8$.

According to the data of ref. 7, the reaction occurs with an induction period. After the completion of hydroformylation the original cluster is regenerated in 60 % yield. The efficiency of $\text{Co}_2(\text{CO})_8$, taken in the amount corresponding to that which would be formed by the decomposition of 35 % of the $\text{Co}_3(\text{CO})_9(\mu-\text{CPh})$, is close to the efficiency of the non-decomposing cobalt alkylidynecarbonyl complex, *i.e.*, the declusterization products may possess many times greater reactivity than the original cluster and may be responsible for the catalysis even at very small concentrations. The present work reports on the results of a study of homogeneous hydroformylation of 1-octene in the liquid phase using cobalt carbonyl clusters as catalysts.

Experimental

The synthesis of the $Co_3(CO)_9(\mu$ -CR) clusters, where R = H, Me, Ph, Cl, Br, OMe, CO_2Me , CO_2Et , CO_2Pr^i , CO_2Bu^t , was carried out using the reported procedure,^{8,9} and that of $Co_2(CO)_6NiCp(\mu$ -CR), where R = Ph, CO_2Pr^i (Cp is cyclopentadiene), as described in ref. 10.

The clusters $\text{Co}_3(\text{CO})_8(\text{PPh}_3)(\mu\text{-CR})$, where R = Ph and CO_2Pr^i , and $\text{Co}_3(\text{CO})_7(\text{PPh}_3)_2(\mu\text{-CCO}_2\text{Pr}^i)$ were obtained by means of the interaction of the respective carbonyl clusters with nickel (η^2 -ethylene)bis(triphenylphosphine). Depending on the nature of the substituent at the apical carbon atom (C_{apic}), the ligand environment of the nickel complexes, and the ratio of the reaction components, the mono-, bis-, and triphenylphosphine derivatives and heterometallic complexes were formed.

Table 1. Spectroscopic characteristics of the $Co_3(CO)_9(\mu$ -CR) clusters

Cluster	IR ¹³ C NMR		R	Cluster	IR	¹³ C NMR		
	$\nu CO/cm^{-1}$	Solven	;	δ		vCO/cm ⁻¹	Solven	tδ
Co ₃ (CO) ₉ (μ-CH) (1)	2107m, 2057v.s, 2041v.s, 2024m	CDCl ₃	263.0 200.2	(C _{apic}); (CO _{term})	Co ₃ (CO) ₉ (μ-CPh) (9)	2102s, 2054v.s, 2040v.s, 2021m	CDCl ₃	286.0 (C _{apic}); 200.9 (CO _{term}); 167.4,133.8, 130.1, 129.1 (C ₂ H ₂)
(2)	2069v.s, 2047v.s, 2035m	CDCl ₃	268.0 198.2 198.0 52.0 ($(C_{apic});$ $(CO_{term});$ (CO); $CH_3)$	Co ₃ (CO) ₉ (μ-CMe) (10)	2112w, 2060v.s, 2048v.s, 2030m	C ₆ D ₆	296.8 (C _{apic}); 200.1 (CO _{term}); 44.6 (CH ₃)
Co ₃ (CO) ₉ (µ-CCO ₂ Et) (3)	2111m, 2068v.s, 2049v.s, 2035m	_	-		$Co_{3}(CO)_{8}(PPh_{3})(\mu - CCO_{2}Pr - i)$ (11)	2073v.s, 2020v.s, 2000v.s,	C ₆ D ₆	258.4 (C _{apic}); 202.1 (CO _{term}); 179.2 (CO);
Co ₃ (CO) ₉ (μ-CCO ₂ Pr ⁱ) (4)	2109m, 2063v.s, 2045v.s,	C ₆ D ₆	259.3 198.9 177.1	(C _{apic}); (CO _{term}); (CO);		1973v.s, 1933m, 1907m*		68.5 (CH); 21.7 (CH ₃)
	2033m		69.3 (21.5 (СН); СН ₃)	$Co_3(CO)_7(PPh_3)_2(\mu - CCO_2Pr-i)$	2053v.s, 2000v.s,	C ₆ D ₆	252.1 (C _{apic}); 205.8 (CO _{term});
Co ₃ (CO) ₉ (μ-CCO ₂ Bu ^t) (5)	2109m, 2064v.s, 2047v.s,	_			(12)	1960s, 1927m*		181.4 (CO); 68.1 (CH); 22.1 (CH ₃)
	2033m	CDCI	260.0	$(\mathbf{C}_{\mathbf{i}})$	$Co_3(CO)_8(PPh_3)(\mu-CPh)$	2080v.s, 2030v.s.		
(6)	2061v.s, 2045v.s.	CDCI3	209.0 199.0	$(C_{apic}),$ (CO_{term})	(13)	2006v.s, 1960s*		
	2021s, 1986m				$Co_2(CO)_6NiCp(\mu-CCO_2Pr-i)$	2095s, 2060v.s,	C ₆ D ₆	257.8 (C _{apic}); 198.4 (CO _{term});
Co ₃ (CO) ₉ (µ-CCl) (7)	2110m, 2063v.s, 2047v.s, 2031s	CDCl ₃	276.0 198.5	(C _{apic}); (CO _{term})	(14)	2038v.s		177.5 (CO); 68.5 (CH); 21.7 (CH ₃)
Co ₃ (CO) ₉ (μ-COMe) (8)	2102m, 2070v.s, 2036v.s, 2013c	C ₆ D ₆	301.2 200.5 68.6 ((C _{apic}); (CO _{term}); (CH ₃)				

* Pellets with KBr; in the rest of the cases - solution in n-heptane.

The IR spectra of the reaction solutions were registered over a range of $1500-2500 \text{ cm}^{-1}$ at p = 5 MPa with the use of a high-pressure cuvette-reactor of 15 mL capacity (the thickness of a layer is 300 µm, CaF₂ glass) equipped with a stirrer and a means for heating (2.5 °C/min) in the range 25-110 °C. The course of hydroformylation was monitored by the decrease in the synthesis-gas pressure in the reaction volume, as well as the decrease in the optical density of the absorption band (AB) of the C=C bond stretching vibration (1650 cm⁻¹) and the increase in the density of the AB of the aldehyde carbonyl group (1745 cm⁻¹).

The clusters were identified by spectroscopic methods (Table 1) and on the basis of elemental analysis data. The IR spectra were recorded on UR-20 and Specord IR-75 spectrometers. The ¹H and ¹³C NMR spectra were registered on a Jeol FX-90Q spectrometer (operating frequency 89.6 MHz). The GLC analysis was performed on a Tsvet-100 chromatograph in thermoprogramming mode (50–175 °C, 4 °C/min) with a glass column (1.6 m×2 mm) filled with 10 % PEG-20M using argon as the carrier gas and butanol-1 as the internal standard, respectively.

Results and Discussion

The results of the study of the hydroformylation of 1-octene in the presence of cobalt cluster complexes are presented in Table 2. The data on hydroformylation with the use of $Co_2(CO)_8$ as the catalyst are given for a comparison. Although the catalysts examined are different in efficiency, when the temperature is increased from 65 °C to 140 °C, the selectivity and induction period (τ_{ind}) of the reaction are decreased in all cases, but the dynamics of this alteration are specific for each complex.

The decrease in the yield of aldehydes on $Co_2(CO)_8$ at 140 °C is related to the thermal instability of this complex.¹¹ Apparently, the corresponding effects for $Co_3(CO)_9(\mu$ -CR), where R = H, CO_2Me , CO_2Et , CO_2Bu^t , Me, Ph, are explained analogously. The rest of the catalysts reveal relative stability under the conditions studied.

The introduction of PPh_3 into the cluster molecule facilitates a decrease in the induction period. The yield of products increases when complex **4** is used and decreases in the case of cluster **9** with a phenyl substituent at the apical carbon atom.

The differences in behavior of heterometallic Co₂Nicomplexes and their Co₃-analogs depend on the substituent at the apical C atom: when a Co(CO)₃ fragment in Co₃(CO)₉(μ -CPh) is replaced with NiCp, a decrease in the yield of aldehydes and a 2-fold decrease in selectivity are observed, whereas this replacement virtually does not affect the activity of the Co₃(CO)₉(μ -CCO₂Prⁱ) complex.

The differences in catalytic activities of the $Co_3(CO)_9(\mu$ -CPh) cluster precursor and of $Co_2(CO)_8$

occur also when the total pressure of the synthesis gas is increased (Table 3): changes in the induction period, yield of aldehyde, and selectivity are observed in both cases; for the cluster, however, extreme dependence of the aldehyde yield is characteristic.

Thus, the data presented testify to essential differences in the catalysis with the use of Co_3 and Co_2Ni type cluster systems as compared with the employment of $Co_2(CO)_8$.

Table 2. Hydroformylation of 1-octene in the presence of $Co_3(CO)_9(\mu$ -CR) complexes ([Co] = 4.13 mM, [Olefin]₀ = 516 mM, p = 5 MPa, CO:H₂ = 1:3 (vol.), $\tau = 5$ h)

Catalyst	<i>T/</i> °C	τ _{ind} /min	Yield of alde- hyde (%)	Ratio of n-: iso-
$Co_2(CO)_8$	80	136	28	8.0
	95	50	64	4.1
	110	16	46	2.7
	140	2	40	2.2
1	80	74	49	8.7
	95 110	24	64 76	4.2
	140	2	10	2.4
2	80	200	10	57
2	95	60	75	2.0
	110	20	84	1.6
	140	0	10	1.0
3	95	140	29	4.8
	110	22	83	1.6
	140	3	34	2.2
4	95	92	80	2.1
	110	22	75	1.8
	140	3	96	1.2
5	80	180	3	7.4
	95	96	98	2.7
	110	18	97	1.6
	140	0	8	1.0
6	110	138	71	2.5
	140	2	94	1.2
7	140	50	98	1.5
8	140	36	90	2.1
9	110	120	84	4.0
	140	6	25	1.5
10	95	132	43	2.4
	110	44	84	1.7
	140	3	10	1.0
11	110	5	88	1.6
12	110	10	80	1.8
13	110	110	64	1.9
14	110	24	76	1.6
Co ₂ (CO) ₆ NiCp(μ-CPh) (15)	110	60	74	1.7

Table 3. The effect of pressure on hydroformylation of 1-octene ([Cat] = 4 mM, 110 °C, $CO:H_2 = 1:3$ (vol.), solvent – toluene, $\tau = 5$ h)

<i>p</i> /MPa	[⊤] ind ∕min		Yield (%)		Ratio of n-: iso-	
	Co ₂ (CO) ₈ 9	Co ₂ (CO) ₈	9	Co ₂ (CO) ₈	9
1	18	116	27	24	1	1
5	16	120	56	56	3	4
8	30	140	65	50	3	3
10	20	40	64	68	3	3
12	20	110	70	53	5	3
15	20	120	68	52	2	2

Important information about the nature of the active species formed during hydroformylation in the presence of the $\text{Co}_2(\text{CO})_8$ and $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ complexes can be obtained from the IR spectra of the reaction solutions, using for this purpose a high-pressure cuvette-reactor.

Hydroformylation in the presence of Co₂(CO)₈. The IR spectrum of Co₂(CO)₈ recorded in the course of treating the complex with the synthesis gas under a pressure of 5 MPa in the presence of olefin in an *n*-heptane solution at 25 °C is characterized by absorption bands (AB) at 1864 and 1872 cm^{-1} (the bridge CO groups), as well as by more intense AB at 2028, 2038, 2050, 2065, and 2075 cm^{-1} assigned to the terminal CO groups (CO_{term}). The spectrum obtained coincides with data published previously¹¹ and does not change for 16 h under the conditions indicated. At temperatures >90 °C aldehvde formation is observed, and the hydroformylation reaction proceeds intensely, and is accompanied by the appearance of a system of new AB in the region of carbonyl vibrations at 1640, 1995, 2008, 2110 cm⁻¹ and by strengthening of the band at 2038 cm^{-1} . The intensity of these bands increases as the reaction proceeds. With decreasing concentration of olefin, the AB at 1640. 1995, 2008, 2038, 2068, and 2110 cm^{-1} weaken.

According to data of ref. 12, the bands at 1640, 1995, and 2110 cm⁻¹ can be assigned to the carbonyl group vibrations of the cobalt acylcarbonyl complex, and the first of them characterizes the stretching vibrations of CO in the R(CO)Co acyl group. The AB at 2008 and 2038 cm⁻¹ correspond to the stretching vibrations in the cobalt hydrocarbonyl molecule.

Thus, in hydroformylation with $Co_2(CO)_8$ a catalytic system of the following composition is realized: $Co_2(CO)_8$:HCo(CO)_{4(or 3)}:R(CO)Co(CO)_{4(or 3)} = 1:0.28:0.17. The ratio of the components has been evaluated on the basis of the optical densities of the AB at 2075 cm⁻¹ [Co₂(CO)₈], 2008 cm⁻¹ [HCo(CO)₄] and 2108 cm⁻¹ (acyl complex) in the spectrum, which characterize intense hydroformylation. The data obtained are in agreement with results described¹³ for hydroformylation under similar conditions (9.5 MPa, 80 °C), according to which the same forms of cobalt carbonyls



Fig. 1. The plot of optical density (D) of the bands at 2106 cm⁻¹ (I) of the Co₃(CO)₉(μ -CPh) cluster and 1650 cm⁻¹ (2) of the olefin versus the hydroformylation time ([Olefin]₀ = 516.0 mM; [Co] = 4.13 mM; T = 110 °C; p = 5 MPa; CO:H₂ = 1:1 (vol.); solvent – n-heptane).

are present in the reaction mixture, but with a higher content of acyl cobalt carbonyl $[Co_2(CO)_8:HCo(CO)_4: R(CO)Co(CO)_4 = 1:0.29:0.61].$

Thus, hydroformylation of 1-octene in the presence of $\text{Co}_2(\text{CO})_8$ is accomplished by stabilizing the acyl cobalt carbonyl derivative, which is in equilibrium with $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$. Mononuclear forms of cobalt carbonyl in the absence of the synthesis gas are transformed at room temperature to $\text{Co}_2(\text{CO})_8$. The formation of polynuclear complexes under the hydroformylation conditions indicated has not been observed.

Hydroformylation in the presence of $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ cluster. The IR spectra of a $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ solution both in the absence and in the presence of the synthesis gas (5 MPa) at 25 °C exhibit AB characteristic of the stretching vibrations of the terminal CO groups in the starting compound (see Table 1). Holding a solution of this complex (25 °C, 16 h) under the synthesis gas in the presence of 1-octene does not lead to changes in the form of the spectrum of the cluster.

At temperatures >85 °C hydroformylation of 1-octene is observed. The process is completed within 110 min. However, both in the initial period of the reaction and when it proceeds intensely, the IR spectrum does not change from the spectrum of the original cluster (Fig. 1). Hence, the hydroformylation reaction is catalyzed by the cobalt carbonyl cluster.

Hydroformylation in the presence of $Co_3(CO)_9(\mu$ -CBr) cluster. The IR spectrum of a solution of this compound in the presence of olefin at 25 °C and 5 MPa does not



Fig. 2. The plot of optical density (*D*) of the bands at 2114 cm⁻¹ (*I*) of the $Co_3(CO)_9(\mu$ -CBr) cluster and 1650 cm⁻¹ (*2*) of the olefin *versus* the hydroformylation time. For the reaction conditions see Fig. 1.

differ from that of the starting compound (see Table 1).

When the sample is heated the intensities of the AB of the carbonyl groups in the IR spectrum of the cluster decrease sharply.

Figure 2 demonstrates the dynamics of the decrease in the high-frequency (2114 cm⁻¹) optical vibration band of the carbonyl group of the $Co_3(CO)_9(\mu$ -CBr) cluster in the course of hydroformylation, as well as that of the olefin band at 1650 cm⁻¹. The dramatic deceleration of hydroformylation within 30 min after the onset of the reaction is noteworthy: the concentration of olefin does not change during the subsequent 50 min. The formation of aldehyde begins at 84 °C, when the degree of cluster decomposition is 30 % (Table 4).

At 28 % conversion of the hydroformylation reaction ($\tau = 55$ min) bands at 2043 and 2105 cm⁻¹ characteristic of the acyl cobalt carbonyl complex appear in the IR spectrum, and AB typical of systems based on Co₂(CO)₈ are observed later on: 1868, 1873, 2010, and 2073 cm⁻¹.

Thus, the differences in the hydroformylation of 1-octene in the presence of $Co_2(CO)_8$ and $Co_3(CO)_9(\mu$ -CBr) are expressed as a change in the selectivity of the process and a decrease in the minimum temperature of aldehyde formation when the cluster is used (see Table 4), as well as a change in the dynamics of olefin consumption and cluster decomposition (see Fig. 2). Based on this, one may assume that the catalytically active system is formed from $Co_3(CO)_0(\mu$ -CBr), which includes clusters of the original structure undergoing decomposition along with mononuclear species. In the case of $Co_3(CO)_9(\mu$ -CBr) the latter species are, apparently, more active than those formed from $Co_2(CO)_8$. Thus, the value of τ_{ind} for the process at 110 °C in the presence of the former complex is 8.6 times greater than that in the case of $Co_2(CO)_8$ (see Table 2), and the aldehyde yield in 5 h is 71 % and 46 %, respectively.

The examples considered of the behavior of Co_3 -clusters under the hydroformylation conditions substantiate the possibility of cluster catalysis.

The stability of a cluster under the hydroformylation conditions studied depends primarily on the nature of the substituent at C_{apic} . The study of the $Co_3(CO)_9(\mu$ -CCl), $Co_3(CO)_9(\mu$ -COMe), and $Co_3(CO)_9(\mu$ -CMe) complexes (5 MPa, 110 °C) by means of IR spectroscopy testifies to the stability of these compounds in the course of the reaction: their spectra do not change during the entire time of olefin transformation to aldehyde; the transformation rate, however, depends on the nature of the

Table 4. The properties of the Co cluster complexes in hydroformylation of 1-octene ($[Olefin]_0 = 516 \text{ mM}$, [Co] = 4.13 mM, T = 110 °C, p = 5 MPa, solvent — *n*-heptane)

Original cluster	v ^a	τ ^b	T ^c	N ^d	v _{rel} e	¹³ C NMR, δ		
	/mol min ⁻¹	/min	/°C	(%)	/rel. unit.	δC_{apic}	δCO _{term}	Δ
$\overline{\text{Co}_3(\text{CO})_0(\mu\text{-CCl})}$	0.5	2400	110	0	0	276.0	198.5	77.5
$Co_3(CO)_9(\mu$ -CPh)	4.3	180	85	0	0	286.0	200.9	85.1
$Co_{1}(CO)_{9}(\mu - CMe)$	4.3	2400	45	0	0	296.8	200.1	96.7
$Co_2(CO)_0(\mu$ -COMe)	0.5	1020	104	0	0	300.3	200.5	99.8
$Co_2(CO)_0(\mu - CCO_2Pr^i)$	2.4	35	79	30	0.4	259.3	198.9	60.4
$Co_1(CO)_0(\mu-CH)$	2.0	15	61	12	1.0	263.0	200.2	62.8
$Co_2(CO)_0(\mu - CBr)$	1.5	5	84	30	1.6	269.0	199.0	70.0
$Co_2(CO)_0(\mu - CCO_2Et)$	2.3	20	85	30	1.2			
$Co_2(CO)_2(PPh_2)(u-CCO_2Pr^i)$	0.7	5	80	80	7.0	258.4	202.1	56.3
$Co_{2}(CO)_{7}(PPh_{3})_{2}(\mu-CCO_{2}Pr^{i})$	0.3		—	80	_	252.1	205.8	46.3
$Co_2(CO)_{e}(PPh_2)(u-CPh)$	0.6	15	55	80	10.6			
$Co_{2}(CO)_{4}NiCp(\mu-CCO_{2}Pr^{i})$	0.9	5	50	18	4.8	257.8	198.4	59.4

^a Initial rate of hydroformylation; $H_2:CO = 3:1$ (vol.). ^b The cluster life-time; $H_2:CO = 1:1$ (vol.). ^c Heating from 25 °C to 110 °C (2.5 °C/min), the temperature of aldehyde appearance; $H_2:CO = 1:1$ (vol.). ^d The degree of cluster decomposition at the instant the aldehyde appears. ^e Relative rate of cluster decomposition.

substituent at C_{apic} (see Table 4). The $Co_3(CO)_9(\mu$ -CCO₂Et), $Co_3(CO)_9(\mu$ -CCO₂Prⁱ), $Co_3(CO)_9(\mu$ -CCO₂Bu^t), and $Co_3(CO)_9(\mu$ -CH) clusters decompose in the course of hydroformylation, and the catalysis is performed with the participation of cluster species as well as mononuclear species.

The decomposition rate also depends on the nature of the substituent at C_{apic} (Table 4). Thus, $Co_3(CO)_9(\mu$ -CH) is the least stable compound: its decomposition occurs at the maximum rate, which is constant throughout the process. The $Co_3(CO)_9(\mu$ -CBr) complex has the lowest decomposition rate.

The stability of the carbonyl cluster depends on the reaction conditions (the temperature and time) as well. This is substantiated by the destruction of the cluster framework of the $Co_3(CO)_9(\mu$ -CPh), $Co_3(CO)_9(\mu$ -CCl), and $Co_3(CO)_9(\mu$ -COMe) complexes when their time of treatment with the synthesis gas increases. The onset of decomposition of $Co_3(CO)_9(\mu$ -CPh) is observed within 2–3 h, $Co_3(CO)_9(\mu$ -CCl) — within 48 h, and $Co_3(CO)_9(\mu$ -COMe) — after 16 h.

The degree of destruction of the complexes under the action of the synthesis gas is determined by the stability of the C_{apic} —Co bond to attack by CO and H_2 molecules, which follows from the experimental data:

 the stability of a cluster depends on the nature of the substituent at the apical carbon atom (see Table 4);
the process of cluster decomposition is irreversible;

— the treatment of $Co_3(CO)_9(\mu$ -CPh) with hydrogen leads, according to IR spectroscopy data, to pronounced acceleration of cluster decomposition with no change in the spectroscopic characteristics of the system from those observed during treatment with (CO+H₂) or (CO+H₂+olefin) mixtures. One may assume that the decomposition is preceded by H₂ activation followed by hydride transfer via the C_{apic}—Co bond:⁴



- the stability of a cluster depends on the presence of a heterometallic substituent in the cluster framework (see Table 4);

— the catalytic activity of clusters destroyed during hydroformylation occurs at significantly lower temperatures than that of $Co_2(CO)_8$ (see Table 4), which may be caused by the easier formation of $HCo(CO)_4$ from them

$$\operatorname{Co}_{3}(\operatorname{CO})_{9}(\mu\operatorname{-CR}) \xrightarrow{H_{2}^{2} \operatorname{CO}} \operatorname{HCo}(\operatorname{CO})_{4} \xrightarrow{+H_{2}^{2}} \operatorname{Co}_{2}(\operatorname{CO})_{8};$$

- the stability of a cluster depends on the presence of electron donating ligands at the cobalt atom. Thus, when PPh₃ is introduced into the $Co_3(CO)_9(\mu$ -CPh)

molecule, the interaction of $\text{Co}_3(\text{CO})_8(\text{PPh}_3)(\mu-\text{CR})$ with the synthesis gas under the hydroformylation conditions in the presence of an olefin results in considerable acceleration of cluster decomposition (as compared with $\text{Co}_3(\text{CO})_9(\mu-\text{CPh})$) and a decrease in the temperature of the onset of hydroformylation from 85 °C to 55 °C, when the degree of cluster decomposition is already 80 % (see Table 4).

The decomposition of the phosphine-substituted cluster dominates over the substitution of PPh₃ for CO, which proceeds under analogous conditions for Co₂(CO)₈ (*cf.* ref. 14). Such acceleration of decomposition is observed for Co₃(CO)₈(PPh₃)(μ -CCO₂Prⁱ) as well [compared with Co₃(CO)₉(μ -CCO₂Prⁱ)].

For the clusters that are stable under the hydroformylation conditions the values of the chemical shifts in the ¹³C NMR spectra are in a weaker field than those for the clusters inclined to decomposition (see Table 1). Relatively high values of Δ ($\delta C_{apic} - \delta CO_{term}$) are also characteristic for the former. This fact testifies that the strength of the C_{apic} -Co bond (and, hence, cluster stability) is greater, the smaller the electron density at C_{apic} , and the smaller the degree of delocalization of the electron density that characterizes the Co₃C fragment.

The destabilizing effect of the donor ligands (PPh_3) and/or of the NiCp moiety in the cluster (see Table 4) is also associated with an increase in the electron density on the Co atoms.

The data presented obtained by studying the hydroformylation reaction of olefins in the presence of Co₃-

Scheme 1



clusters with various substituents at C_{apic} , as well as the break-down process of the clusters under the action of the synthesis gas, allows one to suggest a scheme of action for such catalysts (Scheme 1).

According to the above scheme, cluster catalysis is realized if the reactivity of the C_{apic} —Co bond with respect to hydride transfer is comparatively small, *i.e.*, the rate $w_1 > w_2$ (where w_1 and w_2 are the rate of hydroformylation and the rate of decomposition, respectively). Otherwise, the catalyst is transformed into a mononuclear species, which is characteristic, for instance, of $Co_2(CO)_8$. Thermal stability of the latter system depends on the pressure of CO (see ref. 11) which in particular has an effect on the decrease in olefin conversion with increasing temperature (see Table 2). A similar influence of temperature on conversion is observed for clusters undergoing intense decomposition in the course of hydroformylation, for instance $Co_3(CO)_9(\mu$ -CH) (see Table 4).

Thus, on hydroformylating 1-octene in the presence of cobalt alkylidynecarbonyl clusters, both the starting cluster species and their decomposition products can be catalytically active. The formation of any particular form, and the stability of a cluster under the reaction conditions, depend on the nature of the substituent at C_{anic} and on the ligand environment of the Co atoms.

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Oxidation with the $H_2O_2-VO_3^-$ -pyrazine-2-carboxylic acid reagent 2.* Oxidation of alcohols and aromatic hydrocarbons

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Aromatic hydrocarbons are oxidized with hydrogen peroxide in the presence of catalytic amounts of VO_3^- and pyrazine-2-carboxylic acid into phenols (provided excess hydrocarbon is used) or into quinones (at high H_2O_2 concentrations). 2-Propanol, ethanol, cyclohexanol, and benzyl alcohol are transformed into the corresponding aldehydes and ketones under the same conditions (without a solvent or in MeCN).

Key words: oxidation, hydrogen peroxide, vanadium complexes; aromatic hydrocarbons; alcohols.

The oxidation of organic compounds with hydrogen peroxide is effectively catalyzed by different complexes

of transition metals.²⁻⁹ Peroxides are known to oxidize alcohols^{5,10} and aromatic hydrocarbons¹¹⁻¹⁷ in the presence of some vanadium complexes or peroxocomplexes. Previously, we have shown that the

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^{*}For part 1, see ref. 1.