Kurze Mitteilungen

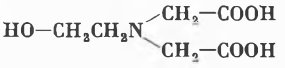
Bis zum 15. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht. Es werden auch Manuskripte aus dem Ausland angenommen, Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen).

Stability and Hydrolysis Constants of N-Hydroxyethyliminodiacetates of the Rare Earths*

Summary

The stability constants for the 1:1 and 1:2 complexes formed between the tetradentate ligand N-hydroxyethyliminodiacetate (HIMDA) and the rare earth ions have been determined at 20°C and at a metal concentration of 0.1 M. The hydrolysis of the 1:2 complexes has been investigated at 20°C in 0.15 M rare earth solutions; the protonation constants of the $M(HIMDA)_2OH^{2-}$ complexes have approximately the same values between La and Gd, but decrease strongly from Gd through Lu.

A large number of complexes of the tetradentate ligand N-hydroxy-ethyliminodiacetate (HIMDA) were investi-



HIMDA acid

gated and their formation constants reported[1,2]. With the rare earths M^{3+} stable complexes $[M(HIMDA)]^+$ and $[M(HIMDA)_2]^-$ are formed. Their formation constants at 25°C and at ionic strenth 0.1 (KNO_3) are known[3].
The hydrolysis of some 1:1 and 1:2 bivalent metal HIMDA complexes[1], of the 1:2 uranium(IV) complex[4], as well as the formation[5] of [La(HIMDA)OH] were studied by Martell and coworkers.
In connection with a series of papers dealing with NMR studies of rare earth polyaminocarboxylates[6], we have determined by *p*H titration, at high concentration, the formation constants of their 1:1 and 1:2 HIMDA complexes and the protonation constants of their ternary complexes $[M(HIMDA)_2OH]^{2-}$.

Experimental**

Syntheses. HIMDA acid was prepared by hydroxyethylation of the Na-imino-diacetate (Fluka) with ethylene oxide[8], and recrystallised twice from hot water.

Measurements. Potentiometric titration curves were obtained with a Compensator E 388, fitted with a combined glass-calomel Microelectrode EA 125 U; the sample solutions were placed in a 5 or 20 ml cell EA 876 equipped with a thermostatic jacket (20.00 ± 0,02 °C), and the titrant added with a Microburette E 457 under CO_2 free nitrogen (Metrohm equipment). The *p*H standardization was done by titration of HNO_3 with KOH (μ = 1, KNO_3; adopting a pK_t value of 13.94[9]). K_{ML} and K_{ML2} were established by titration of a $K[M(HIMDA)_2]$ solution with HNO_3 4M (metal concentration at 50% titration = 0.1M), and K^H_{ML2} by titration of a similar solution with carbonate free KOH 0.7M[10] (metal concentration at 50% titration = 0.15M). The $K[M(HIMDA)_2]$ solutions were prepared by adding KOH to the stoichiometric mixture of rare earth nitrate and KH(HIMDA). Each experiment was run at least twice.

Calculations. The simultaneous calculation of several stability constants from the titration curve was carried out according to the VARIAT programme with the approximate constants introduced as initial values. The subprogrammes NEWRAP[11] and APPROX[12] evaluate the theoretical quantities of base or acid required to obtain the *p*H values measured in the sample during titration.

APPROX is an adaptation of the programme described by Perrin and Sayce[13]. The metal and ligand concentrations are calculated with the recurrent equations (1) and (2) without accounting for the formation of complexes in the initial approximation.

$$[M_{a+1}] = [M_a] \sqrt{CM_{exp}/CM_{cal}} \quad (1)$$

$$[L_{a+1}] = [L_a] \sqrt{CL_{exp}/CL_{cal}} \quad (2)$$

CM, CL: total concentration of the metal (ligand),
$[M_a]$, $[L_a]$: approximate value for the free metal (ligand) concentration.

Table 1. Formation and protonation constants of N-hydroxyethyliminodiacetate (I.) rare earths complexes at 20°, and high concentration (log K^H_1 = 8.79, log K^H_2 = 2.44*)

M^{3+}	log K_{ML}** ± 0.2	log K_{ML2}***	log K_{ML2}**** ± 0.03
La	7.6	5.63 ± 0.03	10.56
Ce	7.9	6.22 ± 0.03	10.50
Pr	8.0	6.63 ± 0.03	10.52
Nd	8.1	6.94 ± 0.03	10.75
Sm	8.4	7.49 ± 0.03	10.62
Eu	8.3	7.72 ± 0.03	10.64
Gd	–	–	10.72
Tb	8.2	7.95 ± 0.05	10.48
Dy	8.2	7.96 ± 0.05	10.18
Ho	8.2	7.95 ± 0.05	10.08
Er	8.3	7.79 ± 0.05	9.73
Tm	8.5	7.79 ± 0.05	9.34
Yb	8.5	7.71 ± 0.05	9.12
Lu	8.6	7.83 ± 0.05	9.04
Y	8.1	7.70 ± 0.05	10.15

* $K^H_1 = [HL]/[H][L]$ and $K^H_2 = [H_2L]/[H][HL]$, with μ = 1 (KNO_3)
** $K_{ML} = [ML]/[M][L]$, with $[M]_{total}$ = 0.1 M
*** $K_{ML2} = [ML_2]/[ML][L]$, with $[M]_{total}$ = 0.1 M
**** $K^H_{ML2} = [ML_2]/[ML_2OH][H]$, with $[M]_{total}$ = 0.15 M

* Received September 13, 1974.
** For more details refer to the Ph. D. thesis of F. Chastellain[7].

Results and discussion

The results which were calculated for the HIMDA protonation constants, the rare earth-HIMDA 1 : 1 and 1 : 2 formation constants, and the $[M(HIMDA)_2OH]^{2-}$ protonation constants are listed in the Table.

The formation constants of $[M(HIMDA)]^+$ determined in concentrated solutions are smaller by 0.45 to 0.84 log K unit for the light rare earths and by approximately 0.9 unit for the heavy rare earths with respect to those[3] determined at an ionic strength of 0.1. Though the absolute values of the stability constants are not comparable, the media being too different, the relative change in the stability along the rare earth series is maintained. Thompson and Loraas[3] admit that HIMDA is tetradentate in these complexes with the hydroxyethyl group coordinated to the metal.

The formation constants of $[M(HIMDA)_2]^-$ are smaller by at most 0.32 log K unit with respect to those established in dilute solution. They increase steadily with the charge density of the cation from lanthanum to dysprosium (2.33 units) and decrease from dysprosium to ytterbium as the result of steric hindrance.

The protonation constants of the ternary complexes $[M(HIMDA)_2OH]^{2-}$ may be classified into two groups. In the first group (La to Gd) the constants vary less than 0.2 log K unit, while for the second group (Tb to Lu) they decrease by 1.7 unit. Gupta and Powell[14] showed a similar decrease of the protonation constants of $[M(HEDTA)OH]^-$, where HEDTA = hydroxyethylethylenediaminetriacetate, in the middle of the rare earth series. In both cases it is not possible to decide whether the reacting proton is exchanging with a coordinated hydroxyethyl group, or a coordinated water molecule.

We acknowledge the generous support of the Fonds national suisse de la recherche scientifique through grant 2.0490.73.

F. Chastellain and André E. Merbach

Institut de chimie minérale et analytique
Université de Lausanne, Place du Château 3,
CH-1005 Lausanne

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The Hydroformylation of 2-Pentene-5,5,5-d_3*

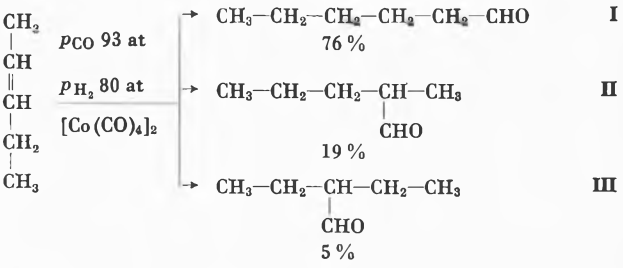
Summary

In the title reaction, at low p_{CO} (5 at), rapid isomerisation of the substrate occurs and a random distribution of deuterium in the reaction products has been found. At 100 at p_{CO}, about $^2/_3$ of *n*-hexanal arises from formylation at position 1 and $^1/_3$ from formylation at position 5.

In the cobalt catalysed hydroformylation of 2-pentene [mixture of *cis* (43 %) and *trans* (57 %) isomers] under conditions in which no isomerisation of the olefinic substrate can be detected[1], 76 % of *n*-hexanal, 19 % of 2-methylpentanal and 5 % of 2-ethylbutanal are obtained (Scheme 1).

In principle *n*-hexanal can be formed by attack of CO either at position 1 or 5 and 2-methylpentanal can be formed by attack of CO either at position 2 or 4, but up to now these alternatives have not been investigated.

This aspect of hydroformylation is possibly connected with isomerisation of the olefin-catalyst complex[3, 2] which might influence the isomeric composition of the reaction products and has therefore not only theoretical but also practical interest. In order to monitor the formation of *n*-hexanal from 2-pentene, hydroformylation of 2-pentene-5,5,5-d_3 was investigated at low and high carbon monoxide partial pressure[5]. The content and distribution of deuterium in the reaction products was investigated by mass and nmr spectroscopy.



* Received September 16, 1974

Table 1. Hydroformylation of 2-pentene-5,5,5-d_3[a] at different CO partial pressures
[Olefin (2 g); $[Co(CO)_4]_2$ (0.3 g); mesitylene (20 ml); p_{H_2} 100 at; temperature 100°C]

p_{CO}(at)	Reaction Time (hrs.)	Carbonyl compounds yields, %[c]	Pentane, yield, %[c]	Aldehydes	Distribution	
				I	II	III
5.5	2	76	22	70	25	5
100	4.5	85	4	75	19	6
400[b]	6	79	2	59	29	12

[a] 58% *trans*, 42% *cis*
[b] 0.9 g $[Co(CO)_4]_2$ were used
[c] Determined by g.l.c.

The reaction was carried out as previously described[1] and gave the results reported in Table 1. As it is already known, the percent of linear isomer increases with increasing p_{CO} from 5.5 to 100 at[1], but remarkably at 400 at p_{CO} it is smaller than at 100 at.

The deuterium content of the reaction products mixture was determined by mass spectroscopy on the anilide derived from *n*-hexanal, *via* *n*-hexanoic acid, and is compared in Table 2 with that of the starting 2-pentene.

Table 2. Deuterium content (%)[a] in the n-hexanoanilide

p_{CO}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	D.N.[b]
5.5	1.5	1.7	10.0	80.0	5.9	0.8	0.2	2.90
100	2.1	0.5	4.3	91.8	~ 0	1.2	0.1	2.91
Initial pent-2-ene	2.2	0.3	2.3	95.4	–	–	–	2.91

[a] Value uncertain to ± 2%
[b] D.N. = average number of deuterium atoms per molecule

The results show that at low partial pressure of CO, relatively high intermolecular deuterium/hydrogen transfer takes place, while at high CO partial pressure it is much lower. In no case was a decrease of total deuterium content noticed, showing that practically no exchange between deuterium of the substrate and gaseous hydrogen takes place.

The methyl esters of the acids obtained from the aldehydes by an already described procedure[4] were separated by g.l.c. and analysed by nmr [in the presence of $Eu(dpm)_3$] to determine the average deuterium content at each carbon atom of the 2-pentene backbone.

In Table 3 the results obtained for the esters derived from deuterated *n*-hexanals are reported.

The spectrum of the products obtained at low partial pressure of CO shows no resolved signals and the deuterium location approximates a random distribution. On the contrary, for the product obtained at high partial pressure of CO, the signals are well resolved. As the intensity of the signal of the methyl group corresponds to 1 proton, the amount of aldehyde formed by formylation at position 1 of the starting olefin is about twice as large as the one arising from formylation at position 5*. The formylation rate at position 5 is higher than that at each of the three positions 2,3 or 4. This confirms that, probably for steric reasons, the catalytic complex largely prefers the two terminal positions of the substrate. Assuming that the catalyst migration along the substrate backbone occurs by an 1,2-hydrogen shift[8], the fact that, within the limits of errors, no deuterium has been found at position 4 of the ester indicates that the catalytic complex migrates along the substrate backbone substantially only once before formylation occurs. This is also confirmed by the rather low deuterium content found for the methylene group at position 5. The percent of deuterium at position 2 in the ester is also in line with this interpretation.

This work confirms that the identical isomeric composition of the reaction products formed at low p_{CO} starting with terminal or internal olefins depends on the fact that, at low p_{CO}, isomerisation of the olefin-catalyst complex is much faster than hydroformylation.

Table 3. NMR-analysis of methyl *n*-hexanoate: mean number of hydrogen atoms at each carbon atom[a]

p_{CO} (at)	CH_3—	CH_2—	CH_2—	CH_2—	CH_2—	COOR
5.5	1.91	1.63	1.66	1.40	1.40	–
100	1.04	1.91	2.00	1.53	1.53	–
Calculated for a product resulting from attack of CO at position 1 of the substrate[b]	0	2	2	2	2	–
Calculated random distribution	2.18	1.45	1.45	1.45	1.45	–

[a] Values uncertain to ± 5%
[b] Only one isomerisation step

* Similar results were briefly reported for the 1-butene-4,4,4-d_3 hydroformylation by M. Bianchi, U. Matteoli and F. Piacenti at a recent meeting (International Symposium on Metals in Organic Chemistry, Venice, 2 to 5 September, 1974).

The different isomeric composition of the reaction products starting with 1-pentene and 2-pentene[1] at high p_{CO} (100 to 400 at) is in keeping with the competition between formylation and olefin-catalyst complex isomerisation occurring, under high p_{CO}, at similar overall rates.

As previously stated[5] the above mentioned differences in hydroformylation at low and high p_{CO} are probably connected to the existence of an equilibrium, influenced by p_{CO}, between different catalytic complexes.

We are continuing our investigation in order to clarify the structure of the catalytic complexes prevailing at high and low p_{CO} respectively and the factors influencing the rate of isomerisation of the catalyst-substrate complex and hence the isomeric composition of the hydroformylation products.

Denis A. von Bézard, Giambattista Consiglio and Piero Pino

Eidgenössische Technische Hochschule Zürich
Technisch-Chemisches Laboratorium
Universitätstrasse 6, 8006 Zürich
Switzerland

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