Kinetics and Catalysis, Vol. 41, No. 4, 2000, pp. 451–456. Translated from Kinetika i Kataliz, Vol. 41, No. 4, 2000, pp. 499–505.
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Influence of the Olefin Structure on the Rate of Hydroformylation and C=C Bond Hydrogenation in the Presence of $Co_2(CO)_8$ as the Catalyst Precursor

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Received October 22, 1998

Abstract—The rate of C=C bond hydrogenation and the yield of paraffins increase in the order 1-hexene < propylene dimers < propylene trimers < propylene tetramers. The kinetic equation of the reaction was derived on the basis of the Breslow–Heck mechanism. The equation is consistent with the experimental data. The ratio between the rates of hydroformylation and hydrogenation correlates to the polar and steric effects of substituents in olefin molecules.

INTRODUCTION

Hydrogenation of the π-bond in olefin molecules

$$RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3 \qquad (I)$$

is the only side reaction in oxo synthesis. It proceeds in parallel to the main reaction of hydroformylation

$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO \qquad (II)$$

and results in additional losses of target products due to the formation of paraffins RCH_2CH_3. Only fragmentary data on the influence of the particular factors on C=C bond hydrogenation in olefin molecules under hydroformylation conditions have been published [1], and a reaction mechanism has been assumed [2]. Data on the hydrogenation of the π-bond in the C_6, C_9, and C_{12} propylene oligomers and in 1-hexene are scarce. This study aims to fill this gap.

EXPERIMENTAL

1-Hexene (reagent grade), distilled in a Würtz flask with KOH to remove peroxides, contained 99.5% of the main substance. After analogous distillation over KOH, propylene dimers (AO Nizhnekamskneftekhim) contained 99.0% 4-methyl-2-pentene and 0.8% 2-methyl-2-pentene. Propylene trimers and tetramers had the same origin and were distilled over KOH on a rectification column with an efficiency of 20 theoretical plates. The fractions of trimers with b.p. 142–146°C (0.101 MPa) and tetramers with b.p. 50–55°C (800 Pa) were collected. The composition and structure of the obtained C_9 and C_{12} olefins are presented in Tables 1 and 2.

To study the parallel reactions of the hydroformylation and hydrogenation of the C_6, C_9, and C_{12} olefins, we used a 0.5-l closed gradientless well-stirred reactor [3] with a water-cooled jacket and a detachable 0.01-l vessel for sampling the liquid phase. The installation

Table 1. Composition and structure of the fraction of propylene trimers

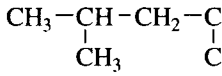
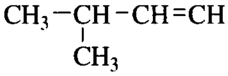
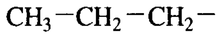
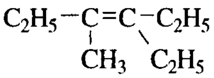
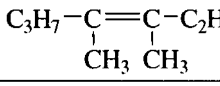
Olefin	Concentration, wt %
 $CH_3-\underset{CH_3}{CH}-CH_2-\underset{C_2H_5}{CH}-CH{=}CH_2$ (3-ethyl-5-methyl-1-hexene)	0.4
 $CH_3-\underset{CH_3}{CH}-CH{=}CH-CH_2-\underset{CH_3}{CH}-CH_3$ (2,6-dimethyl-3-heptene)	0.4
 $CH_3-CH_2-CH_2-\underset{C_2H_5}{C}{=}CH-C_2H_5$ (4-ethyl-3-heptene)	98.9
 $C_2H_5-\underset{CH_3}{C}{=}\underset{C_2H_5}{C}-C_2H_5$ (3-methyl-4-ethyl-3-hexene)	0.2
 $C_3H_7-\underset{CH_3}{C}{=}\underset{CH_3}{C}-C_2H_5$ (3,4-dimethyl-3-heptene)	0.1

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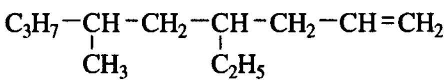
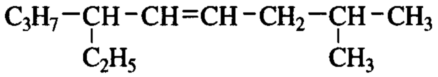
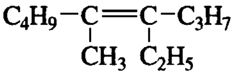
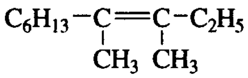
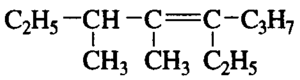
Table 2. Composition and structure of the fraction of propylene tetramers

Olefin	Concentration, wt %
 $C_3H_7-\underset{CH_3}{CH}-CH_2-\underset{C_2H_5}{CH}-CH_2-CH=CH_2$ (4-ethyl-6-methyl-1-nonene)	0.3
 $C_3H_7-\underset{C_2H_5}{CH}-CH=CH-CH_2-\underset{CH_3}{CH}-CH_3$ (2-methyl-6-ethyl-4-nonene)	0.4
 $C_4H_9-\underset{CH_3}{C}=\underset{C_2H_5}{C}-C_3H_7$ (4-ethyl-5-methyl-4-nonene)	98.7
 $C_6H_{13}-\underset{CH_3}{C}=\underset{CH_3}{C}-C_2H_5$ (3,4-dimethyl-3-decene)	0.4
 $C_2H_5-\underset{CH_3}{CH}-\underset{CH_3}{C}=\underset{C_2H_5}{C}-C_3H_7$ (4-ethyl-5,6-dimethyl-4-octene)	0.2

also contained high-pressure buffer vessels for synthesis gas, hydrogen, and carbon monoxide and a 0.25-l high-pressure loading vessel for olefins. A high stirring rate (2800 rpm) was used to perform the reaction in the kinetic region. With the same goal, the reactor was loaded with a liquid phase by 2/3 of the autoclave volume [4], and the composition that provided a homogenous mixture was used. Before the experiment, carbon monoxide was blown through the reactor, and a solution of $Co_2(CO)_8$ in pentane was poured into the reactor in an argon atmosphere. Next, synthesis gas was supplied to a pressure of 6.0 MPa, the heating and stirring were switched on, and an olefin was poured into the loading vessel. When the specified temperature (180°C) was achieved, the olefin was transferred into the reactor by the pressure of synthesis gas. The moment of transfer was considered to be the beginning of the reaction. The liquid phase was sampled during the experiments. The reaction was performed under isobaric and isothermic conditions: the temperature was maintained constant to within ±2°C, and pressure changes due to the absorption of CO and H_2 and sampling were compensated by adding from the buffer vessel.

Dicobalt octacarbonyl $Co_2(CO)_8$ used as the catalyst precursor was synthesized from cobalt acetate and acetaldehyde in a rocking autoclave under the total pressure of the CO + H_2 mixture of 29.4 MPa at 160°C during 3 h by the procedure described in [5]. The products of the hydroformylation and hydrogenation of the C_6, C_9, and C_{12} olefins were analyzed by GLC on packed columns [6–8]. The fractions of propylene trimers and tetramers were analyzed under identical conditions using the same stationary phases and solid supports as those in [7, 8] but on capillary columns with a length of 25 m and a diameter of 0.2 mm.

RESULTS AND DISCUSSION

Table 3 summarizes the experimental data on the rate, selectivity, and composition of the products of the parallel hydroformylation and hydrogenation reactions of the examined olefins. With an increasing chain length and branching, that is, upon the transition from 1-hexene to C_6, C_9, and C_{12} propylene oligomers, the selectivity for the hydroformylation products (aldehydes and alcohols) decreased from 85 to 77% at an olefin conversion of 80%, and the degree of hydrogenation of the starting olefin, by contrast, increased from 2.8 to 17.0%. The same situation was observed for the olefin conversions of 25 and 50%. Similar behavior was observed by Marko [2], who compared the composition of the hydroformylation and hydrogenation products of propylene, cyclohexene, isobutylene, and diisobutylene in the presence of $Co_2(CO)_8$ as the catalyst precursor. The overall rate of olefin hydroformylation and hydrogenation was determined by numerically differentiating the experimental kinetic curves of olefin consumption using the Lagrange interpolation polynomial [9]. The individual rate of C=C bond hydrogenation was found by a similar method from the kinetic curves of paraffin buildup. The hydroformylation rate was found by difference between the overall rate and the rate of paraffin formation and from the rate of absorption of the synthesis gas CO + H_2 according to the stoichiometry of reaction (II). Both methods gave almost the same rates of reaction (II). With an increasing molecular weight and branching of the olefin carbon chain, the rate of hydroformylation decreased in conjunction with the kinetic data [10], whereas the contribution of C=C bond hydrogenation to the overall rate increased.

To explain the observed effect of the olefin structure on the selectivity and rates of hydroformylation and hydrogenation, let us consider the reaction mechanisms

Table 3. Influence of the olefin structure and the contact time on the composition of the reaction mixture, selectivity, formation of target and by-products, and rates of hydroformylation (w_1) and C=C bond hydrogenation (w_2). Reaction conditions: $T = 180°C$; $P = 29.4$ MPa; [Co] = 0.038 mol/l; CO : H_2 = 1 : 1 (vol %); 133.0 g of the olefin and 65.0 g of pentane (solvent) were loaded into the reactor

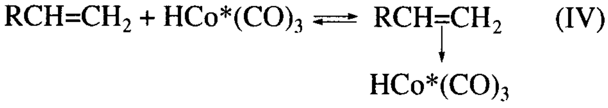
Olefin	Reaction time, min	Olefin conversion, %	Composition of mixture, wt %						Selectivity (aldehydes + alcohols), %	Hydrogenation degree, %	w_1, mol l^{-1} min^{-1}	w_2, mol l^{-1} min^{-1}
			olefins	aldehydes	alcohols	HBP*	pentane	paraffins				
1-Hexene	0	0	67.2	–	–	–	32.8	–	–	–	0.58	0.048
	2.0	25	47.5	20.3	0.4	0.6	31.0	0.2	96	1.2	0.43	0.036
	5.0	50	30.0	34.5	2.0	3.9	29.2	0.4	90	1.3	0.30	0.024
	9.0	80	11.3	48.3	3.7	7.9	27.5	1.3	85	2.8	0.13	0.012
Propylene dimers	0	0	67.2	–	–	–	32.8	–	–	–	0.51	0.065
	4.0	25	47.5	18.2	2.2	0.8	31.0	0.8	94	4.8	0.38	0.048
	7.0	50	30.0	29.6	5.6	4.1	29.2	1.5	87	4.9	0.26	0.034
	12.0	80	11.3	41.8	9.0	8.2	27.5	2.2	83	4.9	0.14	0.017
Propylene trimers	0	0	67.2	–	–	–	32.8	–	–	–	0.20	0.080
	7.0	25	48.3	8.6	9.4	0.6	31.1	2.0	91	12.0	0.14	0.057
	18.0	50	31.0	14.3	18.0	2.0	30.4	4.2	84	13.2	0.09	0.039
	41.0	80	11.9	20.8	27.0	6.4	29.0	5.5	80	11.3	0.04	0.015
Propylene tetramers	0	0	67.2	–	–	–	32.8	–	–	–	0.10	0.120
	11.0	25	48.9	5.2	9.5	0.6	31.8	3.9	90	23.7	0.08	0.087
	25.0	50	31.7	7.8	19.4	3.3	31.0	6.8	86	21.2	0.05	0.057
	58.0	80	12.2	13.0	31.5	4.9	30.0	8.4	77	17.0	0.02	0.024

* High-boiling by-products.

and the corresponding rate equations. In the presence of $Co_2(CO)_8$ as the catalyst precursor, hydroformylation proceeds via the Breslow–Heck mechanism [11], and C=C bond hydrogenation in the olefins, according to [2], has several common steps with hydroformylation. They are (1) the elimination of CO from cobalt hydrocarbonyl $HCo(CO)_4$ to form unsaturated hydrocarbonyl $HCo^*(CO)_3$ (henceforth, coordinative unsaturated compounds are designated by asterisks)

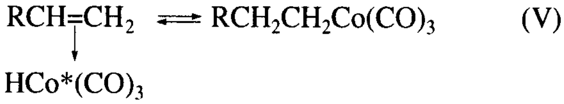
$$HCo(CO)_4 \rightleftharpoons HCo^*(CO)_3 + CO; \qquad (III)$$

(2) the interaction of olefin $RCH{=}CH_2$ with unsaturated hydrocarbonyl $HCo^*(CO)_3$ to form a π-complex



$$RCH{=}CH_2 + HCo^*(CO)_3 \rightleftharpoons \underset{\overset{\downarrow}{HCo^*(CO)_3}}{RCH{=}CH_2} \qquad (IV)$$

(3) the isomerization of the π-complex to alkylcobalt tricarbonyl

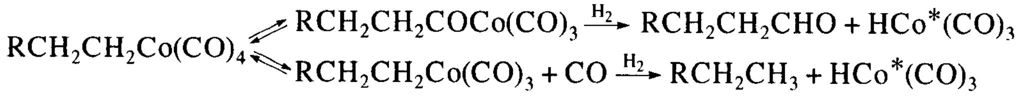


$$\underset{\overset{\downarrow}{HCo^*(CO)_3}}{RCH{=}CH_2} \rightleftharpoons RCH_2CH_2Co(CO)_3 \qquad (V)$$

and (4) the transformation of alkylcobalt tricarbonyl into alkylcobalt tetracarbonyl

$$RCH_2CH_2Co(CO)_3 + CO \rightleftharpoons RCH_2CH_2Co(CO)_4. \qquad (VI)$$

Marko [2] found that the relative rates of C=C bond hydroformylation and hydrogenation depend on the rates of parallel reactions of alkylcobalt tetracarbonyls $RCH_2CH_2Co(CO)_4$ toward the isomerization to acylcobalt tricarbonyls $RCH_2CH_2COCo(CO)_3$ or toward the reverse reaction of the tetracarbonyls to tricarbonyls $RCH_2CH_2Co(CO)_3$ according to the following scheme:



$$RCH_2CH_2Co(CO)_4 \begin{cases} \nearrow RCH_2CH_2COCo(CO)_3 \xrightarrow{H_2} RCH_2CH_2CHO + HCo^*(CO)_3 \\ \searrow RCH_2CH_2Co(CO)_3 + CO \xrightarrow{H_2} RCH_2CH_3 + HCo^*(CO)_3 \end{cases}$$

Therefore, for a more distinct comparison of the hydroformylation and hydrogenation rates, it is reasonable to recognize the steps of the formation and a further transformation of the alkylcobalt tetracarbonyls

Table 4. Initial data and the values of K_1–K_3, k_{hf}, k_h, w_1^c, w_2^c, and $(w_1 + w_2)^c$ calculated by equation (4) for the reaction involving 1-hexene (P_{H_2} = 14.7 MPa, P_{CO} = 14.7 MPa, [Co] = 0.038 mol/l). K_1 = 0.125 l/mol; K_2 = 0.400 MPa; K_3 = 0.247*; k_{hf} = 13.5 min^{-1} MPa^{-1}; k_h = 10.0 min^{-1} MPa^{-1}

[RCH=CH$_2$], mol/l	w_1^e	w_2^e	$(w_1 + w_2)^e$	w_1^c	w_2^c	$(w_1 + w_2)^c$	$\left\lvert\frac{w_1^e - w_1^c}{w_1^e}\right\rvert$, %	$\left\lvert\frac{w_2^e - w_2^c}{w_2^e}\right\rvert$, %	$\left\lvert\frac{(w_1 + w_2)^e - (w_1 + w_2)^c}{(w_1 + w_2)^e}\right\rvert$, %
	mol l^{-1} min^{-1}								
3.70	0.58	0.048	0.63	0.53	0.044	0.58	8.3	8.3	0.7
2.66	0.43	0.036	0.47	0.43	0.036	0.46	0.7	0	0.6
1.71	0.30	0.024	0.32	0.31	0.026	0.33	4.0	8.3	4.4
0.65	0.13	0.012	0.14	0.13	0.011	0.15	5.5	8.3	4.3

* The equilibrium constants K_3 presented in Tables 4–7 are dimensionless because the number of moles remains unchanged upon going from the starting substances to the reaction products in the isomerization reaction (IX).

Table 5. Initial data and the values of K_1–K_3, k_{hf}, k_h, w_1^c, w_2^c, and $(w_1 + w_2)^c$ calculated by equation (4) for the reaction involving propylene dimers (P_{H_2} = 14.7 MPa; P_{CO} = 14.7 MPa; [Co] = 0.038 mol/l). K_1 = 0.109 l/mol; K_2 = 0.366 MPa; K_3 = 0.306; k_{hf} = 11.0 min^{-1} MPa^{-1}; k_h = 17.5 min^{-1} MPa^{-1}

[RCH=CH$_2$], mol/l	w_1^e	w_2^e	$(w_1 + w_2)^e$	w_1^c	w_2^c	$(w_1 + w_2)^c$	$\left\lvert\frac{w_1^e - w_1^c}{w_1^e}\right\rvert$, %	$\left\lvert\frac{w_2^e - w_2^c}{w_2^e}\right\rvert$, %	$\left\lvert\frac{(w_1 + w_2)^e - (w_1 + w_2)^c}{(w_1 + w_2)^e}\right\rvert$, %
	mol l^{-1} min^{-1}								
3.74	0.51	0.065	0.57	0.50	0.064	0.56	1.6	1.5	1.6
2.74	0.38	0.048	0.43	0.40	0.052	0.45	5.8	8.3	6.1
1.74	0.26	0.034	0.30	0.29	0.036	0.32	7.8	5.9	8.4
0.68	0.14	0.017	0.15	0.13	0.016	0.14	6.7	5.9	6.5

from the overall mechanism of the process. To simplify the form of the rate equation and to facilitate its analysis, the steps of CO elimination from cobalt hydrocarbonyl, the formation of the π-complex, its isomerization to alkylcobalt tricarbonyls, and the transformation of $RCH_2CH_2Co(CO)_3$ to $RCH_2CH_2Co(CO)_4$ (reactions (III)–(VI)) were united to form a single reaction.

After the above assumptions, the mechanism of the parallel reactions of the hydroformylation and hydrogenation of the C=C bond in olefins can be presented as follows:

$$RCH{=}CH_2 + HCo(CO)_4 \xrightleftharpoons{K_1} RCH_2CH_2Co(CO)_4, \tag{VII}$$

$$RCH_2CH_2Co(CO)_4 \xrightleftharpoons{K_2} RCH_2CH_2Co(CO)_3 + CO, \tag{VIII}$$

$$RCH_2CH_2Co(CO)_4 \xrightleftharpoons{K_3} RCH_2CH_2COCo(CO)_3. \tag{IX}$$

In addition, the step of hydrogen activation by dicobalt octacarbonyl $Co_2(CO)_8$ is assumed to be performed beforehand according to the experimental procedure described above:

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4. \tag{X}$$

The synthesis of aldehydes and paraffins is described by the following reactions:

$$RCH_2CH_2COCo(CO)_3 + H_2 \xrightarrow{k_{hf}} RCH_2CH_2CHO + HCo(CO)_3, \tag{XI}$$

$$RCH_2CH_2Co(CO)_3 + H_2 \xrightarrow{k_h} RCH_2CH_3 + HCo^*(CO)_3. \tag{XII}$$

The catalyst is regenerated in the reaction

$$HCo^*(CO)_3 + CO \xrightarrow{\text{rapidly}} HCo(CO)_4. \tag{XIII}$$

When the balance on cobalt is fulfilled,

$$[Co] = [HCo(CO)_4] + [RCH_2CH_2Co(CO)_4] + [RCH_2CH_2COCo(CO)_3] + [RCH_2CH_2Co(CO)_3], \tag{1}$$

based on the reaction rate equations

$$w_1 = k_{hf}[RCH_2CH_2COCo(CO)_3]P_{H_2}; \tag{2}$$

$$w_2 = k_h[RCH_2CH_2Co(CO)_3]P_{H_2}, \tag{3}$$

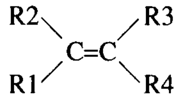
Table 6. Initial data and the values of K_1–K_3, k_{hf}, k_h, w_1^c, w_2^c, and $(w_1 + w_2)^c$ calculated by equation (4) for the reaction involving propylene trimers (P_{H_2} = 14.7 MPa; P_{CO} = 14.7 MPa; [Co] = 0.038 mol/l). K_1 = 0.030 l/mol; K_2 = 0.301 MPa; K_3 = 0.350; k_{hf} = 10.5 min^{-1} MPa^{-1}; k_h = 73.8 min^{-1} MPa^{-1}

[RCH=CH$_2$], mol/l	w_1^e	w_2^e	$(w_1 + w_2)^e$	w_1^c	w_2^c	$(w_1 + w_2)^c$	$\left\lvert\frac{w_1^e - w_1^c}{w_1^e}\right\rvert$, %	$\left\lvert\frac{w_2^e - w_2^c}{w_2^e}\right\rvert$, %	$\left\lvert\frac{(w_1 + w_2)^e - (w_1 + w_2)^c}{(w_1 + w_2)^e}\right\rvert$, %
	mol l^{-1} min^{-1}								
3.71	0.195	0.080	0.275	0.200	0.082	0.282	2.6	2.5	2.5
2.56	0.143	0.057	0.200	0.144	0.059	0.203	0.7	3.5	1.5
1.56	0.094	0.039	0.133	0.091	0.037	0.128	3.2	5.1	3.8
0.57	0.038	0.015	0.053	0.053	0.034	0.048	10.5	6.7	9.4

Table 7. Initial data and the values of K_1–K_3, k_{hf}, k_h, w_1^c, w_2^c, and $(w_1 + w_2)^c$ calculated by equation (4) for the reaction involving propylene tetramers (P_{H_2} = 14.7 MPa; P_{CO} = 14.7 MPa; [Co] = 0.038 mol/l). K_1 = 0.027 l/mol; K_2 = 0.272 MPa; k_{hf} = 0.995 min^{-1} MPa^{-1}; k_h = 154.2 min^{-1} MPa^{-1}

[RCH=CH$_2$], mol/l	w_1^e	w_2^e	$(w_1 + w_2)^e$	w_1^c	w_2^c	$(w_1 + w_2)^c$	$\left\lvert\frac{w_1^e - w_1^c}{w_1^e}\right\rvert$, %	$\left\lvert\frac{w_2^e - w_2^c}{w_2^e}\right\rvert$, %	$\left\lvert\frac{(w_1 + w_2)^e - (w_1 + w_2)^c}{(w_1 + w_2)^e}\right\rvert$, %
	mol l^{-1} min^{-1}								
3.65	0.100	0.120	0.220	0.099	0.118	0.217	1.0	1.7	1.4
2.57	0.075	0.087	0.162	0.074	0.090	0.164	1.3	3.4	1.2
1.60	0.050	0.057	0.107	0.050	0.061	0.111	0	7.0	3.7
0.62	0.023	0.024	0.047	0.021	0.025	0.046	8.7	4.2	2.1

Table 8. Polar and steric effects of substituents in the test olefins

Olefin 	Matrix of substituents	Matrix of σ_i (i = 1, 2, 3, 4)	Matrix of $E_{S_i}^0$ (i = 1, 2, 3, 4)	$\sum_{i=1}^{4} \sigma_i$	$\sum_{i=1}^{4} E_{S_i}^0$	$\sum_{i=1}^{4} (\sigma_i + E_{S_i}^0)$
1-hexene (R1 = H, R2 = H, R3 = H, R4 = C_4H_9)	$\begin{pmatrix} H & H \\ H & C_4H_9 \end{pmatrix}$	$\begin{pmatrix} +0.490 & +0.490 \\ +0.490 & -0.130 \end{pmatrix}$	$\begin{pmatrix} +0.25 & +0.25 \\ +0.25 & -0.59 \end{pmatrix}$	+1.34	+0.16	+1.50
Propylene dimers (R1 = CH_3, R2 = H, R3 = H, R4 = $CH(CH_3)_2$)	$\begin{pmatrix} H & H \\ CH_3 & CH\,(CH_3)_2 \end{pmatrix}$	$\begin{pmatrix} +0.490 & +0.490 \\ 0 & -0.190 \end{pmatrix}$	$\begin{pmatrix} +0.25 & +0.25 \\ 0 & -0.85 \end{pmatrix}$	+0.79	−0.35	+0.44
Propylene trimers (R1 = C_3H_7, R2 = C_2H_5, R3 = H, R4 = C_2H_5)	$\begin{pmatrix} C_2H_5 & H \\ C_3H_7 & C_2H_5 \end{pmatrix}$	$\begin{pmatrix} -0.100 & +0.490 \\ -0.115 & -0.100 \end{pmatrix}$	$\begin{pmatrix} -0.37 & +0.25 \\ -0.56 & -0.37 \end{pmatrix}$	+0.175	−1.05	−0.875
Propylene tetramers (R1 = C_3H_7, R2 = C_2H_5, R3 = CH_3, R4 = C_4H_9)	$\begin{pmatrix} C_2H_5 & CH_3 \\ C_3H_7 & C_4H_9 \end{pmatrix}$	$\begin{pmatrix} -0.100 & 0 \\ -0.115 & -0.130 \end{pmatrix}$	$\begin{pmatrix} -0.37 & 0 \\ -0.56 & -0.59 \end{pmatrix}$	−0.345	−1.52	−1.865

taking into account quasi-equilibrium steps (VII)–(IX), we obtain the following rate equation of the two-route reaction of olefin hydroformylation and C=C bond hydrogenation:

$$w = w_1 + w_2$$
$$= \frac{K_1 P_{H_2}[Co][RCH{=}CH_2](k_{hf}K_3P_{CO} + k_hK_2)}{K_1[RCH{=}CH_2]\{K_2 + P_{CO}(1 + K_3)\} + P_{CO}}. \quad (4)$$

The concentration of $Co_2(CO)_8$ in expression (1) can be neglected because dicobalt octacarbonyl was almost completely converted into $HCo(CO)_4$ after activation step (X).

Next, using the Nelder–Mead nonlinear optimization method [12], the equilibrium constants K_1–K_3 of quasi-equilibrium steps (VII)–(IX) and the rate constants k_{hf} and k_h were calculated. The initial concentrations of $RCH{=}CH_2$; the corresponding experimental rates w_1^e, w_2^e, and $(w_1 + w_2)^e$; the found numerical values of the constants K_1–K_3, k_{hf}, and k_h; and the values of w_1^c, w_2^c, and $(w_1 + w_2)^c$ calculated by equation (4) and their relative deviations in % are presented in Tables 4–7. The results show that both the rates of individual reactions $(w_1 + w_2)^p$ and the overall rate (w_1^c, + w_2^c), calculated by equation (4), are consistent with the experimental values. The rate constant of aldehyde synthesis k_{hf} decreases on going from 1-hexene to propylene tetramers, and the rate constant of paraffin synthesis k_h increases in the same order; that is, they change in parallel to the rates w_1 and w_2 in accordance with the observed reaction kinetics.

The qualitative explanation of the influence of the olefin structure on the ratio between the rates of reactions (I) and (II) was given in [2], indicating that an increase in olefin branching, that is, on going from 1-hexene to propylene tetramers, facilitates the elimination of a CO molecule from tetracarbonyl to form the tricarbonyl $RCH_2CH_2Co(CO)_3$ via reaction (VIII) and inhibits the isomerization of alkylcobalt tetracarbonyls $RCH_2CH_2Co(CO)_4$ to acylcobalt tricarbonyls $RCH_2CH_2COCo(CO)_3$ according to equation (IX). The influence of the olefin structure on the ratio between the rates of C=C bond hydroformylation and hydrogenation is well described quantitatively by the following correlation equations, which were derived by the least-squares method and are similar to the Taft equations [13]:

$$\log\overline{\left(\frac{w_1^e}{w_2^e}\right)} = 0.2412 + 0.6823\sum_{i=1}^{4}\sigma_i \quad (5)$$

(correlation coefficient $r = 0.98$),

$$\log\overline{\left(\frac{w_1^e}{w_2^e}\right)} = 1.040 + 0.6735\sum_{i=1}^{4}E^0_{S_i} \quad r = 0.98, \quad (6)$$

$$\log\overline{\left(\frac{w_1^e}{w_2^e}\right)} = 0.6433 + 0.3391\sum_{i=1}^{4}(\sigma_i + E^0_{S_i}) \quad r = 0.98, \quad (7)$$

where $\overline{\left(\frac{w_1^e}{w_2^e}\right)}$ is the average ratio w_1^e/w_2^e at the olefin conversions from 0 to 90% calculated as the arithmetic mean from the data in Table 3, σ_i is the polar effect constant of the ith substituent in the olefin molecule according to Taft [13], and $E^0_{S_i}$ is the purely steric effect of the ith substituent in the olefin molecule according to Palm [13]. In the calculations, 4-methyl-2-pentene, 4-ethyl-3-heptene-3, and 2-methyl-6-ethyl-4-nonene were considered as dimers, trimers, and tetramers, respectively (Tables 1 and 2). The polar and purely steric effects of substituents in various olefins are presented in Table 8.

Analysis of correlation equations (5)–(7) shows that not only the olefin chain branching, that is, the purely steric effects of the substituents, but also their polar effects σ_i affect the ratio of the rates of C=C bond hydroformylation and hydrogenation, and none of these factors can be favored.

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