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THE TRANSITION METAL-CATALYZED DISPLACEMENT REACTION BETWEEN ORGANOMETALLIC COMPOUNDS AND OLEFINS

III*. ON THE KINETICS OF THE DISPLACEMENT REACTION BETWEEN (+)TRIS[(*S*)-2-METHYLBUTYL]ALUMINIUM AND (*RS*)-4-METHYL-1-HEXENE CATALYZED BY BIS(*N*-METHYLSALICYLALDIMINE)NICKEL

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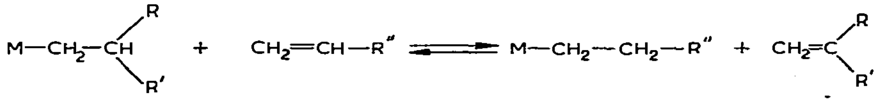
SUMMARY

The kinetics of the displacement reaction between (+)tris[(*S*)-2-methylbutyl]-aluminium and (*RS*)-4-methyl-1-hexene in the presence of soluble nickel catalyst has been investigated under homogeneous conditions. The reaction is kinetically complex and it is characterized by an induction period after which the reaction shows a first-order dependence on the concentrations of the dissolved nickel, of the olefin and of the aluminium linked 2-methylbutyl groups.

In recent years there has been a renewed interest in the study of the mechanistic aspects of the transition metal-catalyzed displacement reaction [eqn. (1)] between olefins and organometallic compounds of Groups I, II and III elements[1-5].



$$M{-}CH_2{-}CH(R)(R') + CH_2{=}CH{-}R'' \rightleftharpoons M{-}CH_2{-}CH_2{-}R'' + CH_2{=}C(R)(R') \qquad (1)$$

In order to get a deeper insight in the proposed mechanism[1], we have undertaken a kinetic investigation of the homogeneous "displacement reaction" between (+)tris[(*S*)-2-methylbutyl]aluminium ($M{=}Al$, $R{=}Me$, $R'{=}Et$) and (*RS*)-4-methyl-1-hexene ($R''{=}CH_2CH(CH_3){-}C_2H_5$) in the presence of bis(*N*-methylsalicylaldimine)-nickel ($Ni\ Mesal_2$)[1,5].

In this reaction 2-methyl-1-butene and racemic tris(4-methyl-hexyl)aluminium are formed and, as the reaction is not stereoselective[1], no optical activity can arise from the 4-methylhexyl groups or from the 2-methylbutyl groups, derived from 2-methyl-1-butene, because of the reverse reaction which occurs very slowly with respect to the direct one[1]. For this reason, the observed optical rotation of the mixtures is

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* For part II see ref. 1.

proportional to the actual concentration of the aluminium-linked 2-methylbutyl groups, and the course of the reaction [eqn. (1)] (from left to right) can be followed by measuring the decrease with time of the optical activity of toluene solutions of the reactants.

Since under the experimental conditions adopted (AlR$^*_3$ 0.1–0.4 M; olefin 0.5–3.0 M; nickel complex 0.8–4.0 × 10^{-4} M) the reaction, which proceeds to completion, is relatively fast, the optical rotation at 589 nm was measured on a Cary Mod. 60 recording spectropolarimeter.

Initially, the reaction is rather slow, then the rate increases to a maximum and finally decreases with time (Fig. 1). The induction period, measured by the time required to reach the maximum reaction rate, is increased by an increase in the initial molar ratio of [AlR$^*_3$] to [NiMesal$_2$]; furthermore, the half-life period, measured from the end of the induction period, decreases as the initial AlR$^*_3$ concentration is decreased (Table 1, runs 1–3). However in each individual experiment, in which the total concentration of aluminium alkyls remains constant [eqn. (1)], the rate in the presence of excess olefin, decreases after the induction period via a first-order dependence on the concentration of the aluminium-linked 2-methylbutyl groups (alR*)(Fig. 1, Table 1).

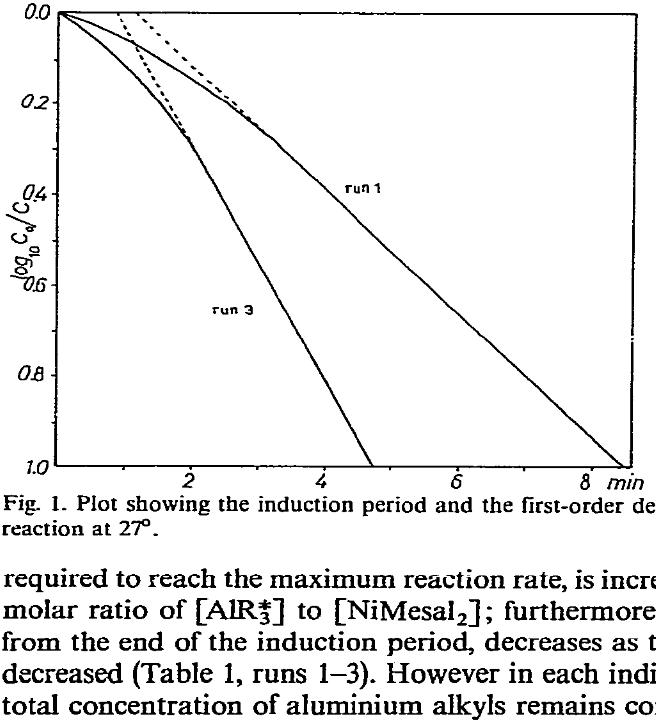


Fig. 1. Plot showing the induction period and the first-order dependence on alR* for the displacement reaction at 27°.

These experiments show that the reactivity of the al–R* groups is not essentially influenced by the nature of the other two alkyl groups bound to the aluminium atom.

The results (Table 1) indicate that the reaction [eqn. (1)] is first-order both in olefin (runs 3–5) and in bis(N-methylsalicylaldimine)nickel (runs 6–9). Using an equivalent amount of olefin with respect to the organoaluminium compound (run 5), the reaction is kinetically second order, since a plot of the reciprocal of [alR*] *vs.* t is linear. Over the relatively small range of AlR$^*_3$ concentrations investigated, $1/k^{27}_{\text{expt.}}$ is proportional to the total concentration of aluminium trialkyls [Al(C$_5$H$_{11}$)$_x$-(C$_7$H$_{15}$)$_{3-x}$] (Fig. 2) and the rate at which 2-methylbutyl groups disappear in the dis-

TABLE 1

KINETIC RESULTS FOR THE DISPLACEMENT REACTION AT 27°

Run	Molar concentration of the reactants in toluene solution			Half-life periods[a] (sec)			$V_{max} \times 10^4$ (mole·l^{-1}·sec^{-1})	$k^{27}_{expt.}$ (mole^{-2}·l^{2}·sec^{-1})	k^{27} [b]
	AlR^*_3	Olefin	Nickel complex (×10⁴)	$t_{\frac{1}{2}}$	$t_{\frac{1}{2}-\frac{1}{4}}$	$t_{\frac{1}{4}-\frac{1}{8}}$			
1	0.356	2.877	2.78	130	129	130	3.95	6.68	56.6
2	0.295	2.809	2.78	108	110	108	4.75	8.17	58.7
3	0.163	2.749	2.78	70	70	70	7.33	13.17	58.2
4	0.147	1.688	2.78	110	111		4.75	13.44	54.9
5	0.157	0.486	2.78				1.57	13.35	57.3
6	0.279	2.829	3.74	76	75	72	11.08	8.57	58.8
7	0.266	2.896	2.15	132	133	132	6.33	8.39	55.2
8	0.253	2.896	1.36	196	194	195	4.08	9.01	56.8
9	0.279	2.819	0.88	326	325	325	2.58	8.57	58.8

[a] Measured from the end of the induction period. [b] Average value 57.0.

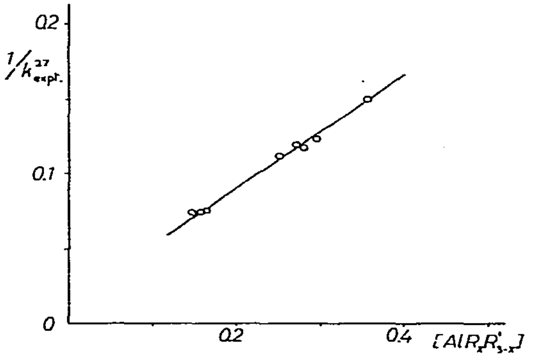


Fig. 2. Linear dependence of the reciprocal of the experimental rate constants on $AlR_xR'_{3-x}$ concentration.

placement reaction [eqn. (1)] after the induction period can be expressed by equation (2):

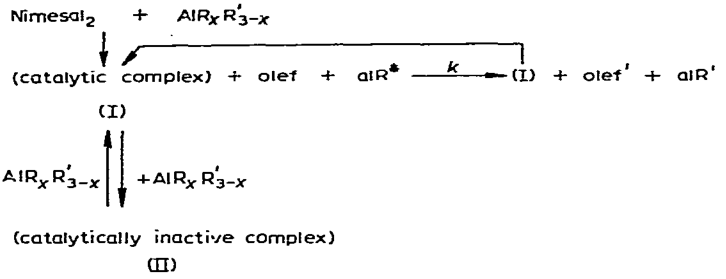
$$-\frac{d[alR^*]}{dt} = \frac{k^{27}\cdot[olef]\cdot[NiMesal_2]\cdot[alR^*]}{1+a\cdot[AlR_xR'_{3-x}]} \tag{2}$$

where $k^{27} = k^{27}_{expt.}\cdot(1+a\cdot[AlR_xR'_{3-x}])$

The above equation is consistent with the following mechanistic Scheme, which is obviously oversimplified and where R is the alkyl group originally present in the aluminium alkyl used, R′ is the alkyl group derived from the olefin (olef) used and (olef′) is the vinylidene olefin formed during the reaction [eqn. (1)]. (I) is in equilibrium with (II) (eqn. 3):

$$\frac{[II]}{[I]\cdot[AlR_xR'_{3-x}]} = K, \tag{3}$$

the latter having little or no catalytic activity in comparison to (I).



Assuming that both (I) and (II) contain only one nickel atom, that after the induction period (which may be reasonably assumed to be connected with the formation of the catalytic complex) practically all the $NiMesal_2$ is transformed into (I) and (II), and that the equilibrium between (I) and (II) is established very rapidly in comparison to the displacement reaction, the rate equation after the induction period may be expressed as:

$$-\frac{d[alR^*]}{dt} = \frac{k\cdot[olef]\cdot[NiMesal_2]\cdot[alR^*]}{1+K\cdot[AlR_xR'_{3-x}]} \qquad (4)$$

which has the same form as the equation determined experimentally [eqn. (2)], provided that $k^{27}=k$ and $a=K$.

Further experiments at different temperatures, as well as attempts to determine the oxidation number of Ni during the reaction, are in progress in order to clarify the reactions occurring during the induction period.

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