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Preliminary communication

CATALYTIC REACTIONS INVOLVING BUTADIENE

I. SELECTIVE DIMERISATION TO 4-VINYLCYCLOHEXENE WITH POLYMETALLIC PRECURSORS

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Summary

The products of the metathetical reactions of $Na[Fe(CO)_3NO]$ with metal halides such as $[M(NO)_2X]_2$ (M = Fe, Co; X = Cl, Br, I) are active catalysts for the selective dimerisation of butadiene to 4-vinylcyclohexene.

The selective cyclooligomerisation of butadiene has led to the production of new intermediates for industrial organic chemistry [1]. 4-Vinylcyclohexene (I) is often reported as a by-product in these reactions, but only few catalytic systems are really selective, e.g., cobalt-[2], rhodium- [3] and platinum-based systems [4] However, the most interesting are the nitrosyliron-based systems. Thus, $Fe(CO)_2(NO)_2$ and $Fe(\eta\text{-}C_3H_5)(CO)_2NO$ [5], $Fe(NO)_2Cl + C_3H_5MgBr$ [6], $Fe(NO)_2Cl + (C_3H_5)_4Sn$ [7] are highly selective catalysts for the cyclodimerisation of butadiene to I.

The observation of thermally-induced dismutation of $Na[Fe(CO)_3NO]$ and $Hg[Fe(CO)_3NO]_2$ [8] according to eqns. 1 and 2 prompted us to study the catalytic behaviour of these compounds with butadiene.

$$2\,Na[Fe(CO)_3NO] \rightarrow Fe(CO)_2(NO)_2 + Na_2[Fe(CO)_4] \qquad (1)$$

$$Hg[Fe(CO)_3NO]_2 \rightarrow Fe(CO)_2(NO)_2 + Hg[Fe(CO)_4] \qquad (2)$$

The catalytic activity is low (see Table 1). Although there have been no mechanistic studies of reaction 2, splitting of Fe—Hg bonds in an appropriate intermediate seems reasonable. Thus, weaker metal—iron bonds would favour the formation of the true catalytic species. This assumption is supported by the observation that $Cd[Fe(CO)_3NO]_2$ exists only in solution and by the lack of evidence for $Zn[Fe(CO)_3NO]_2$ [8].

The catalytic ability of mixtures of $Na[Fe(CO)_3NO]$ with $HgCl_2$, $Hg(CN)_2$,

TABLE 1

CATALYTIC CYCLODIMERISATION OF BUTADIENE TO VINYLCYCLOHEXENE (I)

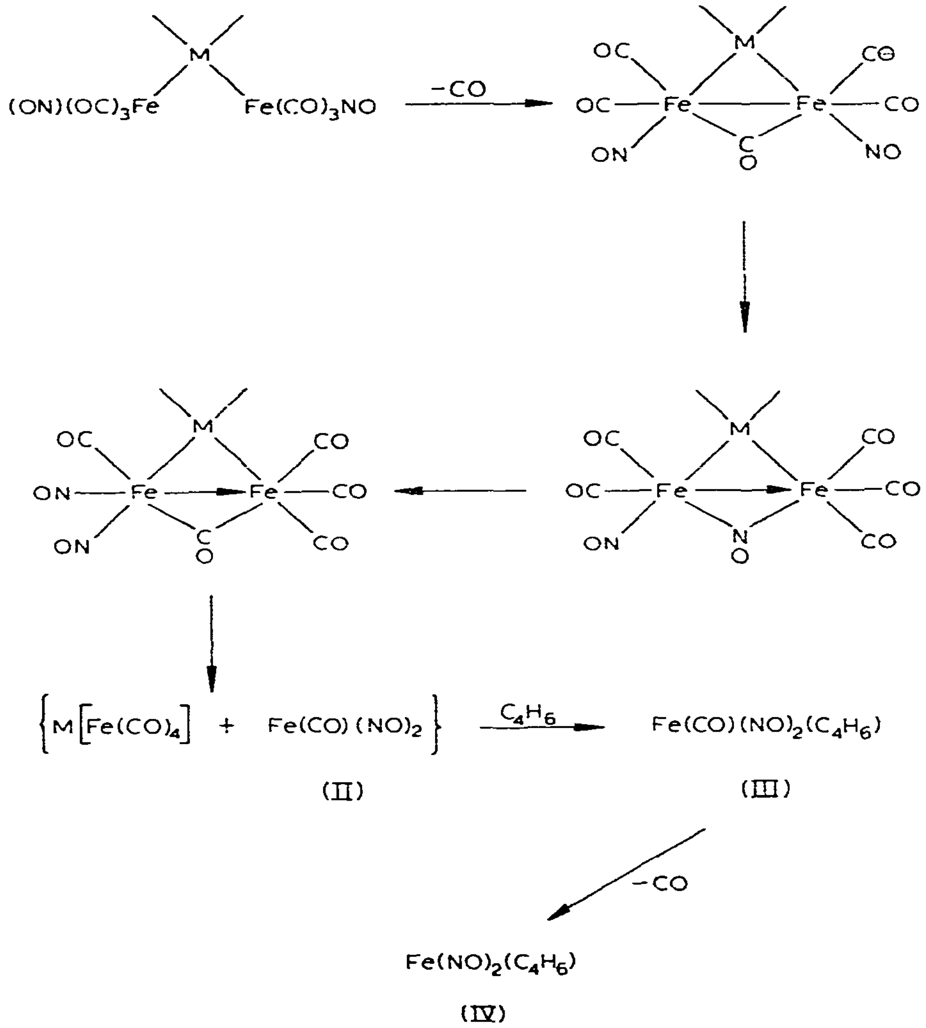
(Solvent: toluene (10 ml); catalyst to butadiene molar ratio: 1 to 300 m*M*)

Exp.	Catalyst	Reaction parameters		Conversion of C_4H_6 (%)	Selectivity C_8H_{12} (%)
		t (h)	T (°C)		
1	$Na[Fe(CO)_3NO]$	24	60	37.0	100
2	$Hg[Fe(CO)_3NO]_2$	24	60	43.0	100
3	$Na[Fe(CO)_3NO] + HgCl_2$	24	60	37.0	100
4	$Na[Fe(CO)_3NO] + Hg(CN)_2$	24	60	45.0	> 99.5
5	$Na[Fe(CO)_3NO] + CdCl_2$	5	60	98.0	> 99.5
6	$Na[Fe(CO)_3NO] + ZnCl_2$	5	60	100	> 99.5
7	$Na[Fe(CO)_3NO] + CoCl_2$	5	60	35.5	100
8	$Na[Fe(CO)_3NO] + FeCl_2$	5	60	37.0	100
9	$Na[Fe(CO)_3NO] + NiCl_2$	5	60	41.5	100
10	$Na[Fe(CO)_3NO] + FeBr_2$	5	60	99.5	100
11	$Na[Fe(CO)_3NO] + FeI_2$	5	60	100	100
12	$Na[Fe(CO)_3NO] + FeCl_3$	5	60	98.5	100
13	$Na[Fe(CO)_3NO] + Fe(NO)_2Cl$	3	60	97.0	100
14	$Na[Fe(CO)_3NO] + Fe(NO)_2Br$	3	60	99.0	100
15	$Na[Fe(CO)_3NO] + Fe(NO)_2I$	3	60	99.0	100
16	$Na[Fe(CO)_2Cp] + Fe(NO)_2Cl$	3	40	99.0	100
17	$Na[Co(CO)_4] + Fe(NO)_2Cl$	3	60	92.5	100
18	$Na[Fe(CO)_3NO] + Co(NO)_2Cl$	3	60	95.0	100
19	$Na[Fe(CO)_2Cp] + Co(NO)_2Cl$	3	40	98.5	100
20	$Na[Co(CO)_4] + Co(NO)_2Cl$	3	60	58.0	100

$CdCl_2$ and $ZnCl_2$ effectively follows this stability trend (Table 1, exp. 3—6). These preliminary experiments led us to a detailed examination of other metal halides and $Na[Fe(CO)_3NO]$ mixtures [9]. In every case, 4-vinylcyclohexene is the sole product, as with $Fe(CO)_2(NO)_2$ and $Fe(\eta\text{-}C_3H_5)(CO)_2(NO)$ [5]. However, better catalytic activities are apparent in many cases. This can be explained by (i) the need for $Fe(CO)_2(NO)_2$ and $Fe(\eta\text{-}C_3H_5)(CO)_2NO$ to interact through a dissociative pathway with butadiene and (ii) the facile decomposition of $M[Fe(CO)_3NO]_n$ which directly leads to an unsaturated iron species able to coordinate butadiene.

No evidence for the catalytic species has been put forward in the literature [5]. We tentatively suggest that the $Fe(NO)_2$ moiety is the true catalytic species; this species would be stabilized by butadiene, i.e. $Fe(NO)_2(\eta\text{-}C_4H_6)$. We tested this hypothesis with respect to the proposed nickel-phosphine catalysed cyclodimerisation of butadiene [1, 10]. The formation of this species and its stabilisation by butadiene can be explained according to Scheme 1.

This scheme involves compounds with a Fe—M—Fe angle smaller than 180° and could not explain all the examples. However, Burlitch and Hayes [11] reported the formation of a probably bent compound $Zn_2Co_4(CO)_{15}$ from $Zn[Co(CO)_4]_2$. In Scheme 1 M may thus represent a polymetallic moiety. Scheme 1 accounts for the occurrence of IV through CO and NO migrations between two metallic sites followed by bond-breaking possibly promoted by butadiene. Nitrosyl [12] as well as carbonyl migrations [13] are now well established. A direct proof of such a process is to be found in the work of Hieber and Führling [14], who observed a rearrangement during the attempted metathetical reaction:



SCHEME 1

$$Fe(NO)_2(PPh_3)Cl + Na[Fe(CO)_3NO] \rightarrow Fe(CO)(NO)_2(PPh_3) + \text{other products}$$

The reaction of $[Fe(NO)_2X]_2$ with $Na[Fe(CO)_3NO]$ and similar species [15] also leads to highly active catalysts (Table 1). This is consistent with the last steps of Scheme 1, in which Fe—Fe bond breaking directly gives $Fe(NO)_2(C_4H_6)$.

An analogous reaction is observed with $[Co(NO)_2X]_2$ and $Na[Fe(CO)_3NO]$ and similar salts [15]. The low activity of these systems with respect to the iron catalysts can be attributed to the nature of the true catalyst. We suspect the presence of a $Co(CO)(NO)(\eta\text{-}C_4H_6)$ species, the formation of which needs CO/NO migrations which are in competition with cobalt—metal bond breaking.

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