CATALYTIC CONVERSIONS OF CYCLIC C_3-OLEFINS IN THE PRESENCE OF METAL COMPLEXES.

6. EFFECT OF $P(NEt_2)_3$ LIGAND ON THE PROPERTIES OF COMPLEX Ni(0) CATALYST IN OLIGOMERIZATION OF METHYLENECYCLOPROPANE

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547.512

Preferential formation of di- or trimers of methylenecyclopropane (MCP) under the influence of Ni(0) complexes is determined by the nature of ligands, additions of modifiers, and the reaction conditions. The Ni(0) complex with coordinated $P(NEt_2)_3$ was synthesized via a proposed intermediate catalytic system $Ni(COD)_2$–$P(NEt_2)_3$ by the interaction between $Ni(\eta^3{-}C_3H_5)_2$ and $P(NEt_2)_3$. The composition of the complex: $\{Ni[P(NEt_2)_3]_2\}_x$ (K-1) was established by ^1H and ^{31}P–$\{^1H\}$ NMR, EPR spectroscopy, IR diffuse reflectance spectroscopy, and GLC. In the range 20-60°C complex K-1 only brings about trimerization of MCP. The catalytic properties of K-1 were described earlier by a proposed scheme for the catalytic conversion of MCP under the influence of Ni(0) complexes.

The direction (di-, tri- or oligomerization) of methylene cyclopropane (MCP) conversions in the presence of Ni(0) complexes can be regulated by the use of various ligands, modifiers, or variation in the experimental conditions [1, 2]. The following ligands and modifiers of Ni(0) complexes have been studied in detail: $PR^1R^2R^3 (R_1, R^2, R^3 = Alk, Ar, OAr)$. Additions of these, particularly to $Ni(COD)_2$, result in preferential formation of linear and cyclic trimers [1]. There is no information in the literature about the influence of alkylsubstituted aminophosphines $P(NR_2)_3$ as ligands for Ni(0) complexes on the catalytic reactions of MCP.

In this study the zero valent Ni complex (K-1) has been synthesized with the $P(NEt_2)_3$ ligand and its catalytic properties in MCP conversions have been studied.

EXPERIMENTAL

The ^1H, ^{31}P–$\{^1H\}$ NMR, IR diffuse reflectance, and EPR spectra were recorded by methods described in [3, 4].

Hexaethyltriamidophosphine $P(NEt_2)_3$ (bp 120-122°C at 10 mm Hg, n_D^{25} 1.4712) was synthesized as in [5].

(Bis-η^3-allyl)nickel (K-2) was obtained by the interaction between anhydrous $NiBr_2$ and an ether solution of allylmagnesium bromide [6]; the complex content was determined by complexometric titration [7]. An ether solution of $P(NEt_2)_3$ (24 mmoles) was added to the ether solution of K-2 (8 mmoles) at 22°C. The reaction mixture which had changed in color from yellow to red was evacuated to remove the solvent and the tarry residue was treated with 10 ml acetone. The precipitated crystalline residue was filtered off, washed with acetone and dried in vacuo. The yield was 3.52 g (74%) $\{Ni[P(NEt_2)_3]_2\}$, decomposition temperature 77-79°C (acetone). Experimental analysis: C 52.30, H 10.63%. $C_{26}H_{60}N_6NiP_2$. Calculated values: C 52.09, H 10.93%.

The synthesis of MCP, the catalytic experiment, and monitoring of the reaction path were carried out by GLC as in [3].

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TABLE 1. Catalytic Conversions of MCP in the Presence of Various Complexes (benzene, $[MCP]_0$ = 1.11 moles/liter; 7 h)

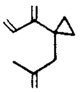
No. of experiment	Complex	$[Ni]\cdot 10^3$, mole	T. °C	Conversion, %	Initial activity, mole MCP / mole Ni·g	Selectivity, %		
						dimers	$\sum C_{12}$	$\sum C_{12}+$
1	$Ni(COD)_2+P(NEt_2)_3$	2,1	60	18	15		7	92
2	$Ni(COD)_2$	2,1	60	37	33	11	8	81
3	$\{Ni[P(NEt_2)_3]_2\}_x$ $(x \geqslant 1)$	2,1	60	35	30	0	100	0
4	»	4,8	60	84	32	4	84	12
5	»	2,4	95	16	12	4	88	8
6	$Ni(PPh_3)_3$ [10]	2,7	60	52	33	32	61	7

TABLE 2. Composition of Trimer Fractions Formed during Catalytic Conversions of MCP under the Influence of Ni(0) Complexes Containing the Ligand $P(NEt_2)_3$ (benzene, $[MCP]_0$ = 1.11 moles/liter; 7 h)

No. of experiment	Trimer composition*		
	(I)	(II)	(III)+(IV)
1	37	27	36
2	30	69	1
3	39	24	37
4	37	27	36
5	36	21	43
6	35	56	9

*In experiments 3 and 4, 4% of dimer (V) was also formed; in experiment 2 a mixture of (VI) and (V) (41:59 % respectively); in experiment 6 (VII) and (V) (29:71 % respectively).

Identification of Di- and Trimers of MCP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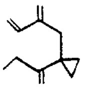
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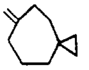
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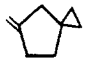
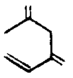
(IV)


(V)


(VI)


(VII)

The catalyst content of the dimers (VII), (V), and (VI) and the trimers (I) and (II) was determined from GLC as in [8]. The methylenespirocyclanes (III) and (IV) formed together with the trimers (I) and (II) were separated from the MCP reaction products in the form of a mixture. The EPR spectra of the (III) and (IV) mixtures were found to be in satisfactory agreement with the data [1].

RESULTS AND DISCUSSION

Dimers and oligomers (~1:1) are known to be formed from MCP in the presence of $Ni(COD)_2$ [9]. Under our experimental conditions the same catalyst gave 81% oligomers with relatively small amounts of dimer (11%) and trimers (8%) (Table 1, expt. 2). However the composition of MCP conversion products changes markedly under the influence of the catalytic system $Ni(COD)_2$ $P(NEt_2)_3$ when $P(NEt_2)_3$ is used as a modifier: dimers are almost absent and the fraction of oligomers increases from 81 to 92%, the trimer content remaining practically the same (7%) (Table 1, expt. 2). This change in the reaction products composition indicates the formation of new intermediates compared to the case of $Ni(COD)_2$, which correspond to the MCP conversion. The most likely are Ni complexes containing $P(NEt_2)_3$ in their coordination spheres, formed during the stage of interaction of the components of the catalytic system. The most convincing support for this assumption is given by the change in composition of the trimers for the catalytic systems being compared (Tables 1, 2). In fact in the presence of $Ni(COD)_2$ 99% of trienes (I) and (II) are formed. Preferential formation of (I) and (II) is also observed in $Ni(COD)_2$ systems modified by tertiary phosphines [1]. However under the influence of our system, $Ni(COD)_2$–$P(NEt_2)_3$, the fraction of cyclic trimers (III) and (IV) increased from 1 to 37%. Even in comparison with $Ni(PPh_3)_3$ there is about a four-fold increase in the amount of (III) and (IV) (see Table 2, expts. 1, 6 and [1]).

The proposed assumption concerning the formation of Ni complexes in the system $Ni(COD)_2$–$P(NEt_2)_3$ with the $P(NEt_2)_3$ ligand is confirmed by investigations into catalytic conversions of MCP under the influence of the system $\{Ni[P(NEt_2)_3]_2\}_x$ (K-1; Tables 1, 2 expts. 3-5). The complex K-1 at 20-60°C only brings about trimerization of MCP whereas in the presence of $Ni(PPh_3)_3$ or $Ni(PPh_3)_n$ ($n = 3, 4$) [7] dimers are formed together with the trimers (Table 1, expt. 6). As distinct from $Ni(PPh_3)_n$ [10] the experimental conditions had little effect on the reaction selectivity. Raising the temperature or increasing the Ni concentration caused a marked increase in the fraction of oligomers formed mainly from trimers, as was shown in [2]. Variation in the conditions merely resulted in an insignificant change in the reaction product composition: 4% MCP dimers were formed (Table 1, expts. 3-5). The main products of MCP trimerization were compounds (I) and (II) (Table 2). However as in the case of $Ni(COD)_2$–$P(NEt_2)_3$ the trimers contained significantly more of the methylenespirocyclanes (III) and (IV). From the data in Table 2 it can be seen that the ratio (I):(II) is not very dependent on the catalytic system or the reaction conditions and is very close to the ratio of these trimers (36-39%):(21-27%) formed when $Ni(COD)_2$–$P(NEt_2)_3$ is used as the catalyst.

Thus Ni(0) complexes containing the ligand $P(NEt_2)_3$ bring about tri- and oligomerization of MCP with a significant methylene spirocyclane content of the trimers.

It is obviously of interest to analyze these characteristics taking into account the donor–acceptor properties of the ligands introduced into the Ni coordination sphere. In accordance with [11, 12] the $P(NEt_2)_3$ ligand occupies an intermediate position in the series of phosphine $P(OR)_3 < PPh_3 < P(NEt_2)_3 \leq P(Alk)_3$. However Bodner et al. [12] did not think it possible for there to be any connection between the catalytic properties of the system $Ni(COD)_2)$–$P(NEt_2)_3$ and K-1 and the basicity of the ligand [11] or its donor–acceptor properties. It is most likely that the determining influence on the catalytic properties of k -1 is produced by steric factors, in particular the volume of the ligand, as was noted in [1]. In fact just like $P(cyclo\text{-}C_6H_{11})_3$ and $P(i\text{-}Pr)_3$ the ligand $P(NEt_2)_3$ favors not only preferential tri- and oligomerization of MCP but also sharply increases the fraction of the spirocyclanes (III) and (IV). In addition dimerization of MCP is almost completely supressed in the presence of Ni complexes containing $P(NEt_2)_3$.

The characteristics of the catalytic action of the Ni(0) complex having the $P(NEt_2)_3$ coordinating ligand can be satisfactorily explained in terms of the scheme for di-, tri-, and oligomerization of MCP in the presence of triphenylphosphine complexes which we proposed earlier [7, 10]. Evidently formation of MCP dimers via the intermediate trimethylenemethane biradical  $-Ni[P(NEt_2)_3]_2$ is almost nonexistent. According to [2] addition of a MCP molecule to this complex results in subsequent formation of the dimers 2-methyl-4-methylenehexa-1,5-diene and 3-methylenespirol[2,4]octane. An alternative path probably exists for the conversion of MCP which calls for π-bonding of the second substrate molecule with the proposed initial intermediate of the reaction $Ni[P(NEt_2)_3]_2(MCP)$. In fact elevated temperatures, which usually favor MCP dimerization in the case of $Ni(PPh_3)_2(MCP)$, had hardly any effect on dimer formation in the cases studied by us.

In this scheme for the catalytic cycle of MCP conversion under the influence of Ni(0) phosphine complexes the formation of the highly unsaturated coordinated particle $Ni(PPh_3)_2$ was proposed [2, 10]. According to [13] stabilization of such particles which possess neither 16- nor 18-electron structures can be brought about by solvent molecules. In the case of Pt a crystalline dimer $[Pt(PPh_3)_2]_2$ is known [14]. Results obtained by us [2, 10, 15] indicate the possibility of formation of $[Ni(PPh_3)_2]_x$ ($x = 1$) both during synthesis of the triphenylphosphine Ni(0) complexes and in the course of the catalytic reaction of C_3-cyclic olefin under their influence.

An attempt to synthesize the Ni(0) complex by reduction of $NiCl_2 \cdot 6H_2O$ by $NaBH_4$ in the presence of $P(NEt_2)_3$ by the method described in [10] was unsuccessful. The Ni(II) was reduced to the metal. Interaction between $Ni(COD)_2$ and $P(NEt_2)_3$ did not produce the corresponding complex either. Monitoring the reaction by ^{31}P NMR spectroscopy showed that it only occurred with an eightfold excess of $P(NEt_2)_3$. However the Ni complex with the coordinating ligand could not be separated from the reaction mixture.

In this present study the complex $\{Ni[P(NEt_2)_3]_2\}_x$ ($x \geq 1$) was synthesized by the action of $(NEt_2)_3$ on $Ni(\eta^3{-}C_3H_5)_2$. Complex K-1 was a yellow powdery substance extremely sensitive to even a trace of oxygen. In the $^{31}P{-}\{^1H\}$ spectrum of the product (toluene, −80°C) two signals were observed at 146.2 and 145.5 ppm with relative intensities ~1:0.9 respectively. The ^1H NMR spectra of this complex (C_6D_6, 22°C) contained two broad signals for the CH_3 and CH_2 groups (1.18 and 3.38 ppm; ratio of intensity integrals 3:2) belonging to the protonic ligand $P(NEt_2)_3$. When the signals were allowed to build up over a period of time rather poor permitted multiplets with centers at 2.25; 2.55, and 4.69 ppm (corresponding integral intensities 2:2:1) were detected, which evidently correspond to protonic allyl groups. The ^1H NMR spectra confirmed the presence of a nickel complex containing the η^3-allyl group in the sample being analyzed.

The IR diffuse reflectance spectra of K-1 contained absorption bands in the region 3100-2800 cm^{-1} characteristic of C—H bond vibrations: 2975, 2935, and 2870 cm^{-1} (ν_{as} and ν_s CH_3 and CH_2 groups in ethyl fragments). The band at 3025 cm^{-1} is typical for H atoms linked to a C=C bond. Some information about the nature of this bond can be obtained from EPR spectra. The main component of solid K-1 is diamagnetic although it also contains admixed Ni^+ ions ($\sim 10^{-17-18}$ spin/g). At 20°C the spectrum contains broad lines, typical for solid samples, with $g_{cp} > 2.0023 \approx g_e$ which are characteristic for ions with $d > 5$. The same sample of K-1 at 77 K gives rise to an EPR signal with splitting of $g_\perp$ and $g_\parallel$ in three lines (ratio ~1:2:1): $g_\perp = 2.121$; $g_\parallel = 2.393$; $^{31}PA_\perp = 76$ Oe, $^{31}PA_\parallel = 63$ Oe. Biaxial anisotropy of the g-factor and $g_\parallel > g_\perp$ can be characteristic for Ni^+ complexes with oblate octahedron or elongated tetrahedron coordination. It is most likely that the splitting is caused by equivalent ^{31}P nuclei in a Ni(I) complex. It can be assumed that the paramagnetic impurity ($\sim 10^{-17-18}$ spin/g) in K-1 is a nickel complex having σ-bonded allyl group. The GLC data of the K-1 decomposition products support this assumption. Hexa-1,5-diene was detected in the solution, a dimerization product of the allyl ligand. However its molar ratio with respect to Ni was extremely low (~1:135). This indicates that only an insignificant fraction of the Ni η^3-allyl complex is present in the K-1 complex.

Thus it has been established that the interaction between bis(πallyl)nickel and $P(NEt_2)_3$ proceeds mainly with complete substitution of the allyl group and results in the formation of complex K-1

$$(\eta^3\text{-}C_3H_5)_2 + P(NEt_2)_3 \rightarrow \underset{(K\text{-}1)}{\{Ni[P(NEt_2)_3]_2\}_x} \quad (x \geqslant 1).$$

According to [16] interaction of $Ni(\eta^3{-}C_3H_5)_2$ with donor ligands such as PEt_3, NH_3, $NHEt_2$, piridine, etc. can occur in several ways: complete substitution of the η^3-allyl group, formation of addition products, or π—σ-rearrangement of the allyl group. It has also been established that the specific feature of the complex K-1 is its capacity to bring about preferential trimerization of MCP (84-100%)

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KINETICS OF THE REACTION OF DECANESULFOPERACID WITH SO_2 IN THE PRESENCE OF WATER

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A study has been made of the kinetics of the oxidation of SO_2 by decanesulfoperacid in the presence of water in a medium of CH_3CN. Retardation of the process by acids has been observed, the retarding effect decreasing with decreasing strength of acid. A mechanism for the reaction has been suggested which explains the experimental results obtained.

According to [1], one of the stages in the sulfoxidation of n-paraffins is the reaction of RSO_2OOH with SO_2 and H_2O. In the present work, we have studied the kinetics of this reaction for the example of decanesulfoperacid (298 K, CH_3CN solvent).

EXPERIMENTAL

Acetonitrile was heated to bp over P_2O_5, ozonized, and after distillation again boiled with and then distilled from P_2O_5. Decanesulfoperacid was prepared by the method of [2]; the initial solutions of RSO_4H contained ~10% decanesulfonic acid as impurity.

The concentration of RSO_4H was determined iodometrically [3]. The mixture of sulfonic and sulfuric acids was analyzed by potentiometric titration in ethanol, the titrant being tetrabutylammonium hydroxide in 2:1 (vol.) benzene–ethanol [4]. Sulfur dioxide was determined spectrophotometrically at λ 310 nm. The extinction coefficient of SO_2 in CH_3CN solution was measured over the range 250-310 nm at 298 K, $[SO_2] = (1.8\text{-}3.2)\cdot10^{-3}$ mole/liter; the SO_2 content of the standard solutions was measured over the range 250-310 nm at 298 K, $[SO_2] = (1.8\text{-}3.2)\cdot10^{-3}$ mole/liter; the SO_2 content of the standard solutions was determined by the method of [5]. Values of ε, liters/(mole·cm) (λ, nm): 70 ± 6 (250), 162 ± 13 (260), 282 ± 20 (270), 346 ± 27 (280), 282 ± 24 (290), 136 ± 13 (300), 34 ± 6 (310).

The reaction kinetics were studied by the stopped flow technique on a Spectroscan-182 M instrument. The initial solutions of $RSO_4H–CH_3CN$ and $SO_2–H_2O–CH_3CN$ were mixed for 10^{-2} sec after which the consumption of SO_2 was followed.

RESULTS AND DISCUSSION

The reaction of RSO_4H with SO_2 in the presence of H_2O, with initial concentrations (mole/liter): $[RSO_4H]_0 = (4\text{-}29)\cdot10^{-2}$, $[H_2O]_0 = 0.26\text{-}0.7$, $[SO_2]_0 = (0.7\text{-}4.5)\cdot10^{-3}$, results in a quantitative yield of RSO_3H and H_2SO_4

$$RSO_4H + SO_2 + H_2O \rightarrow RSO_3H + H_2SO_4,$$

which is in agreement with the stoichiometric equation established in [1].

With $[RSO_4H]_0 >> [SO_2]_0$, $[H_2O]_0 >> [SO_2]_0$ the kinetic curves of SO_2 consumption fit a first order equation (conversion of SO_2 ~80-90 mole %)

$$-d[SO_2]/dt = k\cdot[SO_2]. \qquad (I)$$

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