3. On narrow-pore zeolites (Pentasil and erionite) below 200°C, isobutylene is selectively dimerized and trimerized mainly on active centers localized on the outer surface of the crystallites, since the zeolite channels are blocked by strongly chemisorbed oligomers.

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CATALYTIC CONVERSIONS OF C_3 CYCLIC OLEFINS IN THE PRESENCE OF Ni(0) COMPLEXES.

COMMUNICATION 1. (η^2-METHYLENECYCLOPROPANE)BIS(TRIPHENYLPHOSPHINE)NICKEL: CATALYTIC ACTIVITY AND ROLE IN DIMERIZATION AND TRIMERIZATION OF METHYLENECYCLOPROPANE

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In the catalytic cycle of dimerization and trimerization of methylenecyclopropane (MCP) on Ni(0) complexes, including complexes modified with phosphines [1-3], η^2-methylenecyclopropane complexes of Ni(0) have been suggested as the primary intermediates [4, 5]. However, no direct data have been available for confirmation of this hypothesis.

Here we are reporting on a study of conversions of MCP in the presence of (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel (Kt-1), the synthesis of which was described in [6], and also an investigation of the behavior of the Kt-1 itself under conditions of catalysis, with the aim of elucidating its role in MCP conversion reactions.

DISCUSSION OF RESULTS

In the presence of $Ni(COD)_2 - PR_n^1R_{3-n}^2$ (COD = 1,5-cyclooctadiene; n = 1-3; series of compounds includes PPh_3), MCP is subjected to dimerization, trimerization, and oligomerization, trimers or oligomers being formed preferentially [3].

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TABLE 1. Dimerization and Trimerization of MCP in the Presence of Kt-1 or Ni(COD)$_2$ with Added PPh$_3$

Experiment No.	Complex	[Ni]$_0$, mM	P/Ni	[MCP]$_0$, M	τ, h	Conversion, %	Activity, moles MCP/mole Ni·h
1	(PPh$_3$P)$_2$Ni (MPC)	7.8	2	3.2	5	57	47
2	Same	2.4	2	1.4	5,5	45	48
3	Ni(COD)$_2$; PPh$_3$	9.1	2	1.0	5	37	8
4	Same	22.8	1	11.5	9	60	34

TABLE 2. Distribution of Products from Catalytic Conversion of MCP in the Presence of Kt-1 or Ni(COD)$_2$ with Added PPh$_3$*

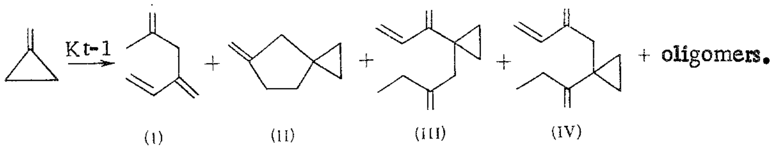
Experiment No.	Complex	Dimer, %				Trimer, % †			Oligomer, %
		Σ	(I)	(II)	(V)	Σ	(III)	(IV)	
1	(Ph$_3$P)$_2$Ni (MCP)	26	17	83	Trace	70	32	65	4
2	Same	22	15	85	»	72	27	61	6
3	Ni(COD)$_2$; PPh$_3$	41	24	76	»	58	30	61	1
4	Same	19	1,9	96,5	1,6	63	30	55	18

*See Table 1 for conditions.

†Remaining trimers unidentified.

We have established that Kt-1 brings about reactions of MCP similar to those with Ni(COD)$_2$–PPh$_3$:

Scheme 1

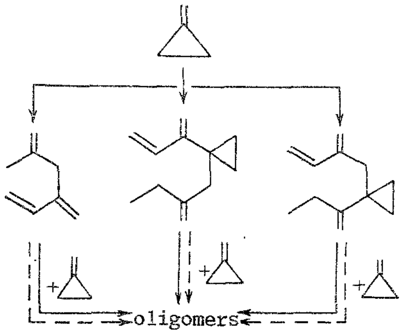


However, significant differences are noted in the catalytic conversions of MCP in the two systems (Tables 1 and 2). For example, when using Kt-1, we detected 2-methyl-4-methylene-1,5-hexadiene (II), which was not observed in the products formed from MCP on Ni(0) complexes [1-3]; as a rule, along with the (II), dispiro[2.1.2.1]octane (V) is formed. The complex Kt-1 is considerably more active than the Ni(COD)$_2$–PPh$_3$ system (see Table 1).

As can be seen from Table 3, variation of the reaction conditions (temperature and concentrations of Ni and MCP) has a considerable effect on the selectivity and rate of MCP conversion in the presence of Kt-1. Thus, the activity of Kt-1 varies from 11 to 233 moles MCP/mole Ni•h, and the yield of dimers may reach 32%, the content of oligomers dropping to zero. Let us note that with the catalytic system Ni(COD)$_2$–PPh$_3$, the yield of dimers was no greater than 13%, and oligomers accounted for 45-56% 3 .

With increasing temperature, the mole ratio of dimers to trimers increases rapidly (Fig. 1, curve 1), symbatic with the change in mole ratio of the dimers (I)/(II). Along with this, there is an increase in the content of oligomers (see Table 3). An increase in MCP concentration lowers these ratios but increases the yield of oligomers. The increase in content of oligomers is accompanied by a simultaneous drop in the relative amounts of dimer (I) and trimers (III) and (IV) in the MCP reaction products. The course of the kinetic curves (Fig. 2) for the accumulation and consumption of the indicated products is characteristic for consecutive reactions (scheme 2). According to this scheme, the unusually low yield of oligomers formed in the presence of Ni(COD)$_2$–PPh$_3$ (Table 2, experiment 3) in secondary reactions of oligomerization (or cooligomerization with the MCP) of compounds (I), (III), and (IV) is apparently due primarily to the low concentrations of these latter compounds.

Scheme 2



At 100% MCP conversion, the color of the reaction mixture changes from yellow to dark red, without any precipitation of metal. The same process is observed in the action of MCP on Kt-1 (Kt-1:MCP ≅ 1:4). Upon concentration of the solution, a brown crystalline product separated out; this was designated Kt-2. In the reaction of Kt-2 with O_2 or with trans-stilbene, MCP trimers were found, with yields of 15-18%. This fact suggests that the Kt-1 changes into Kt-2, which also contains a mixture of nickel acycloalkanes, predecessors of the MCP trimers that were found in [6].

The $^{31}P\{^1H\}$ NMR spectrum of Kt-1, taken in toluene at −80°C after a period of 4 days, contains the following signals (δ, ppm): 41.34 and 40.59 (doublet), 24.20 (singlet), and 21.15 and 20.46 (doublet), with a ratio of integral intensities 2:2:4:1:1; after 18 days, the spectrum is unchanged, and there are no signals of the original Kt-1. Obviously, the composition of the product Kt-2 includes not only the previously noted predecessors of trimers, but also other phosphine complexes of nickel. It is highly probable that solutions of Kt-2 contain, along with nickel acycloalkanes, the highly active, coordination-unsaturated species $Ni(PPh_3)_2$ (Kt-3), formed by decomposition of unstable metallocycles. Consistent with this hypothesis is the rapid conversion of Kt-2 to Kt-1 by the action of MCP on Kt-2. The subsequent reaction of Kt-1 with MCP leads to MCP dimers and trimers and to Kt-2.

Interconversions of Kt-1 and Kt-2 were also observed by means of transmission electronic spectroscopy. The spectrum of Kt-2 in the UV and visible regions contains an absorption maximum at 372-376 nm with shoulders at 460 and 536 nm, and also continuous absorption in the region below 295 nm.

In the spectrum of the Kt-2, continuous absorption is observed at 295 nm, and a shoulder at 340 nm. Addition of MCP to the Kt-2 solution brings about the disappearance of the band at 372 nm and the appearance of a spectrum that is characteristic for Kt-1. When the MCP conversion approaches 100%, bands typical for Kt-2 appear, regardless of which of the complexes was used as a catalyst.

Thus, the catalytic conversions of MCP evidently include the formation, as intermediates, of the corresponding nickel acycloalkanes [3, 6] and complexes of Ni(0) (product Kt-2), including $Ni(PPh_3)_2$ (Kt-3), the formation of which is also suggested in the catalytic conversions of aliphatic olefins [7-10]. The Kt-3, thus, if no MCP is present, is one of the final products in the chain of consecutive conversions of Kt-1. Simultaneously, the highly reactive Kt-3 reacts with MCP forming as the primary intermediate Kt-1. Consistent with this hypothesis are the practically identical selectivities of the process with Kt-1 and Kt-2, and also the activity of these complexes in MCP conversions (see Table 3).

The construction of a more detailed scheme of catalytic dimerization, trimerization, and oligomerization of MCP requires an examination, in the first place, of the possible paths of doubling of MCP into the dimer (I) that we found, the formation of which is not taken into account in the reaction scheme adopted in [3, 4]. Within the framework of that scheme, it is likewise impossible to explain our observation that the composition of the MCP conversion products is dependent on temperature and on the concentration of the original hydrocarbon. Dimerization of MCP into (I) by Ni(0) complexes can be explained satisfactorily on the assumption that under the conditions of reaction, Kt-1 is converted into a complex of Ni(0) containing as the ligand the trimethylenemethane biradical; the formation of a similar compound was postulated in [11] in the reaction of cross-combination of MCP with olefins containing elec-

TABLE 3. Influence of Conditions of Experiment on Course of Dimerization and Trimerization of MCP in the Presence of Kt-1 or Kt-2 (benzene, $[MCP]_0$, M: 3.0-3.2 in experiments 1-5 and 8; 7.6 and 9.8 in experiments 6 and 7, respectively)

Experiment No.	Catalyst	T, °C	$[Ni]_0$, M	Activity, moles MCP/mole Ni·h*	Selectivity, %			Composition, %				
								dimer‡		trimer		
					C_8	C_{12}	oligomers	(I)	(II)	(III)	(IV)	unidentified
1 †	Kt-1	20	7.1	11	6	94	0	0	100	31	65	4
2	»	40	10.8	22	19	79	2	6	94	33	64	5
3	»	60	7.8	64	26	70	4	18	82	32	66	2
4	»	80	7.5	79	29	43	18	34	66	45	43	12
5	»	95	7.2	236	24	38	38	35	65	44	40	16
6	»	60	10.9	84	22	66	12	16	84	43	51	6
7	»	80	10.2	233	32	50	18	20	80	44	37	19
8	Kt-2	60	4.1	66	22	66	8	20	80	34	58	8

*At the moment of reaching 30% MCP conversion.

†In experiments 1-3 and 8, conversion after 5-6 h < 60%; in experiments 4-7, ≥60%.

‡Together with dimers (I) and (II), traces of (V) are present.

Note. Initial concentration of Ni is given in M in this table, but in mM in Table 1; activity is given per mole of Ni in both cases — Translator.

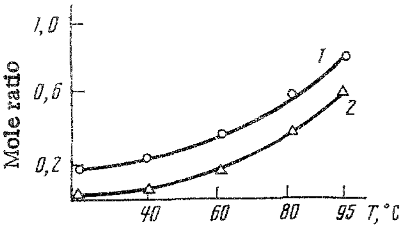


Fig. 1

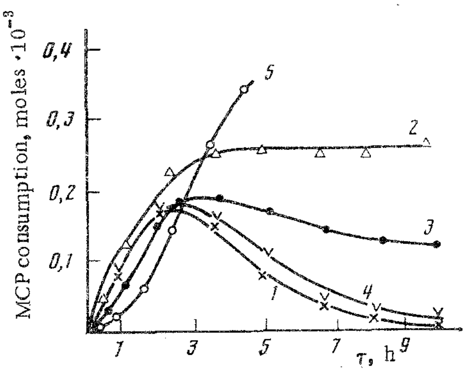


Fig. 2

Fig. 1. Temperature dependence of mole ratio of MCP dimers and trimers: 1) Σ dimers/Σ trimers; 2) (I)/(II).

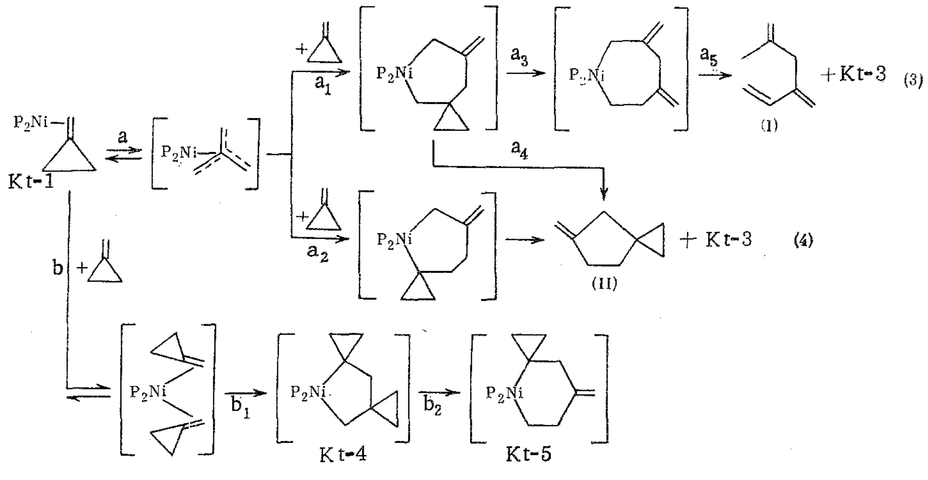
Fig. 2. Kinetic curves for formation and consumption of products of MCP oligomerization in the presence of $(Ph_3P)_2Ni(MCP)$: 1) (I); 2) (II); 3) (III); 4) (IV) 5) higher oligomers. [MCP] = 3.4 M, [Ni] = 7.9 mM; 95°C, benzene.

tron-acceptor substituents. In such a case, the formation of the dimers (I) and (II) can be described by the schemes (top, following page).

Since the oxidative doubling of the MCP molecule in the coordination sphere of Ni can be realized as a symmetry-allowed concerted process [12], we can assume that the occurrence of the reaction along path b requires less activation energy in comparison with dimerization of MCP through the trimethylenemethane complex (path a). In this case, as the temperature is increased, we should expect changes in the ratio of reaction rates toward the formation of the dimer (I). The presence of only traces of the dimer (V) in the reaction products is most probably related to the practically complete conversion of the intermediate Kt-4 into Kt-5 (cyclopropylmethyl/buten-3-yl rearrangement) [13, 14], and mainly to the Kt-7 predecessor of trimers, which are the main products of reaction (5).

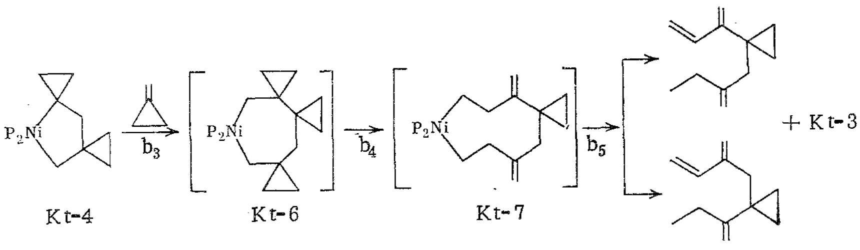
As can be seen from Scheme (5), the formation of trimers includes a stage of insertion of of an MCP molecule at the Ni–C bond of the complex Kt-4 (path b_3). An increase in the reaction temperature, as noted above in the case of dimers, should accelerate the processes going forward along the direction a in accordance with Schemes (3) and (4), and hence should lead to a

Schemes 3-4



P = PPh₃.

Scheme 5



relative decrease in the yield of trimers. And indeed, the mole ratio of yields Σ dimers/Σ trimers and the mole ratio of yields of dimers (I)/(II) increase symbatically with temperature (see Fig. 1).

Thus, the new data that have been obtained give us grounds for considering that in the presence of (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel, catalytic conversions of MCP proceed through a scheme with more stages than had been assumed previously for [3, 4]. In particular, in the first stage, a trimethylenemethane complex of Ni is formed (stage a); this is possibly an equilibrium stage. The formation of nickel acycloalkanes by means of π-bonding of a second molecule of MCP (path b), judging from the quantities of dimers (I) and (II) that are formed, plays a less important role in the catalytic cycle of MCP conversions into dimers.

CONCLUSIONS

1. In the presence of (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel (Kt-1), methylcyclopropane (MCP) undergoes dimerization, trimerization, and oligomerization, the formation of trimers being predominant. In catalytic conversions of MCP under the influence of Kt-1, we have found for the first time in the composition of the dimers 2-methyl-4-methylene-1,5-hexadiene. It has been established that this dimer is also formed in the case of the catalytic system $Ni(COD)_2$–PPh_3.

2. Dimers and trimers of MCP that are formed, containing diene fragments, are the principal predecessors of higher oligomers. Conditions have been found for reducing the yield of oligomers from 45-56% to 4-6%, thus increasing the selectivity of the process in the direction of monoolefins and triolefins with cyclopropyl substituents.

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MECHANISM AND KINETICS OF THE NITRATION OF METHANOL.

COMMUNICATION 1. KINETICS OF THE NITRATION REACTION

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The nitration of alcohols in acid media has been studied by many workers [1-3]. However, our understanding of the mechanism of this reaction and role of the different species present is not yet complete. In the present work, we studied the kinetics of the nitration of alcohols in a broad nitric acid concentration range in order to elucidate the nature of the individual reaction steps.

EXPERIMENTAL

The kinetics of the nitration of methanol by aqueous nitric acid with HNO_3 concentration (C_{HNO_3}) from 65.86 to 79.01 mass % and HNO_3–H_2SO_4 with C_{HNO_3} from 5.31 to 23.71 mass % was studied on a calorimetric device analogous to that described by Eremenko et al. [4]. A sample of 100% HNO_3 was prepared and analyzed according to Karyakin and Angelov [5]. A sample of 100% H_2SO_4 was prepared and analyzed according to Bass et al. [6]. The applicability of the calorimetric method for the study of the kinetics of methanol nitration was justified by Eremenko et al. [4]. The selection of the upper limit for C_{HNO_3} in aqueous nitric acid was determined by the time constant of the measurement scheme (4 sec). For the HNO_3–H_2SO_4 system, the rates could not be measured (fast reaction). The initial alcohol concentration C_{CH_3OH} was about 0.037 mole/liter The HNO_3 concentration in the systems used was about 400 times greater than the CH_3OH concentration and hardly changed during the nitration. Bimolecular nitration under these conditions follows first-order kinetics. The rate constant retains its value to conversions of about 0.85 (Table 1).

We also studied the kinetics of the nitration of CH_3OH by HNO_3–H_2SO_4–H_2O with $C^0_{HNO_3}$ = 64.47 mass % (Table 2). This reaction is also described by first-order kinetics.

RESULTS AND DISCUSSION

The major protolytic equilibria in nitric acid solutions are:

$$2HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O \tag{1}$$

$$NO_2^+ + NO_3^- \rightleftarrows N_2O_5 \tag{2}$$

$$HNO_3 + H_2O \rightleftarrows NO^-_3 + H_3O^+ \tag{3}$$

$$HNO_3 + H_2SO_4 \rightleftarrows NO_2^+ + H_3O^+ + 2HSO_4^- \tag{4}$$

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