REACTION OF ALKYL DERIVATIVES OF TITANIUM AND ALUMINUM WITH CARBOCATIONS

P. E. Matkovskii, L. I. Chernaya, and L. N. Russiyan UDC 542.91:541.49:547.258.2+ 547.256.2:547.632.2-128

Carbonium ions may react with alkyl derivatives of several transition metals (Fe, Mo, and Mn) [1] and with organometallic compounds of many nontransition metals [2-4]. Such reactions apparently also proceed in the recently discovered bifunctional organometallic complex catalysts for controlled olefin polymerization which contain both active anion-co-ordination and cationic sites [5, 6].

Cationic active sites in organometallic complex catalysts are formed as a result of the introduction of microscopic amounts of water into the system during the generation of the catalysts, reactions of the catalysts with monomer, and upon modification of the complex catalysts with water, SnCl₄, SOCl₂ or alkyl halides [6]. Modification permits the controlled inversion of anion-coordination catalysts to cationic catalysts, obtain bifunctional catalysts, and carry out combined processes. A study of the controlled polymerization of ethylene on bifunctional catalysts and the properties of the products obtained indicated high specificity of the catalyst action and kinetic behavior [5-7]. This indicates the possibility of an interaction of the highly reactive cationic active sites with the anion-coordination active sites. The study of the mechanism of this reaction in real systems on the background of other reactions of the catalyst is extremely difficult due to the low concentration of these species.

In order to overcome these difficulties, we studied the reaction of alkyl derivatives of titanium and aluminum with triphenylmethyl cation in the Cp₂TiEtCl (I) - Ph₃C⁺TiCl₅ (II) Ph₃CCl (III) - EtAlCl₂ (IV), and (III) - Et₂AlCl (V) systems. We assumed that the triphenylmethyl cation in the latter two systems arises a result of the formation of Ph₃C⁺(EtAlCl₃)⁻ (VI) and Ph₃C⁺(Et₂AlCl₂)⁻ ionic complexes. The pairs of compounds were selected to be models for bifunctional catalysts and contain components of the most studied anion-coordination systems (I) - (IV) and (I) - (V). The possibility of interaction of carbocations with anion-coordination active sites in combined catalysis has not yet been examined.

RESULTS AND DISCUSSION

The basis of the active sites of organometallic complex catalysis for olefin polymerization are alkyl derivatives of transition metals. Hence, in the first series of experiments, we studied the reaction of (I) with (II). The data in Table 1 as well as the ESR spectra show that this reaction proceeds at 293°K as follows:

$$Cp_{2}TiEtCl + Ph_{3}C^{+}TiCl_{5}^{-} \rightarrow Cp_{2}TiCl_{2} + TiCl_{4} + Ph_{3}CH + C_{2}H_{4} + Ph_{3}CEt + Ph_{3}C^{+} + C_{2}H_{6}$$
(1)
(I) (II)

In control experiments, we established that (I) does not react with (III) under the conditions studied. In this case, (I), in which the titanium ion, which is a very weak electron acceptor, does not form the $Ph_3C^+(Cp_2TiEtCl_2)^-$ ion pair with (III). This is confirmed by the finding that the conductivity of the solution of (III) in toluene remains virtually unchanged after the addition of equimolar amounts of (I). These observations show that the heterolysis of the C-Cl bond in the complexation of (III) with TiCl₄ facilitates reaction (1).

Salt (II) has limited solubility in hydrocarbon solvents and thus, the direction of the reaction and the composition of the products formed may depend on topochemical factors. In order to determine the nature of this dependence, in some experiments (II) was obtained

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Branch. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 643-650, March, 1984. Original article submitted March 4, 1982.

TABLE 1. Yields and Composition of the Products of the Reaction of (I) with (III) in Toluene at 293°K (5 ml toluene, $[I]_0 = 0.026-0.039$ mole/liter, 1 h)

(I), mmoles	Ph ₃ C+TiCl ₅ - (II), mmoles	(II)/(II)	Gas yields		Gas contion,	vol. %	Ph3CX *	Cp2TiCl2
			mmoles	% rela- tive to (I)	C ₂ H ₄	C_2H_6	mmoles	
0,13 0,11 0,12 0,13 0,15 † 0,14 + 0,45 ‡	0,25 0,11 0,12 0,06 0,14 0,14 0,14	0,5 1,0 1,0 2,0 1,0 1,0 1,0 1,0	$\begin{array}{c} 0,073\\ 0,072\\ 0.075\\ 0,063\\ 0,127\\ 0,124\\ 0,220\\ \end{array}$	56,3 65,3 63,0 48,2 84,7 88,6 49,0	82,6 64,0 62,6 65,0 75,0 74,6 86,0	17,4 36,0 37,4 35,0 25,0 25,4 14,0	0,06 0,04 0,05 0,05 - 0,32	0,065 0,050 0,060 0,055 0,060 0,060

```
*99% Ph_3CH and 1% Ph_3CC_2H_3.
+(II) was obtained from TiCl<sub>4</sub> and (III) (1:1) directly dur-
ing the reaction with (I).
+15 ml toluene.
```

TABLE 2. Effect of the Nature of the Components of the Complex Catalysts and the Reaction Conditions on the Composition of the Gaseous Products (GP) ($[MX_n]$, [OAC] = 0.05-0.1 mole/liter)

				GP yield, GP composition, %			
MX _n	OAC	Solvent -	<i>Т</i> , К	per moles/ MXn	$C_{n^{H_{2n+2}}}$	$C_n H_{2n}^{\dagger}$	
TiCl.	(IV)	T etralin Toluene	293-353	0,32-0.68	100	_	
TiCl4	(V)	Tetralin	293-353	0,4-0,9	100	-	
(I)	Et ₃ Al	Toluene	293	0,8-1,4	100	_	
(I)	(V)	»	293	0,8-0,9	6 4–76	24-36	
$(n-C_4H_9O)_4Ti$	Et ₃Al	Xylene, heptane	313	2,7	100	-	
(<i>n</i> -C ₄ H ₉ O) ₄ Ti	Et₃Al	Dibutyl ether	298-353	1,4-4,6	75-93	7-25	
(n-C,H,O),Ti	(<i>i</i> -C ₄ H ₉) ₃ Al	(DBE)	298-343	0.2-3.6	60-87	13-40	
(n-C4H9O)4Ti	Me _s Al	»	313-353	0,3-4,0	100	-	
$\operatorname{Zr}(\operatorname{OC}_{3}\operatorname{H}_{7})_{4}$	Et _{1,5} AlCl _{1,5}	Tetralin	353	0,9-3,5	100	-	

 $C_nH_{2n+2} = CH_4 + C_2H_6$ (from Me₃A1) and C₂H₆ + C₄H₆ (from Et₃A1). +C_nH_{2n} = C₂H₄ + 2C₄H₈.

in the presence of (I). For these experiments, a toluene solution of TiCl₄ was added to a solution of (I) and (III) in toluene. A rapid, homophasic reaction of (III) with TiCl₄ occurs upon mixing of these solutions leading to the formation of orange salt (II) dissolved in toluene, which immediately reacts with (I). The same products are formed in this case as in the reaction of (I) with previously prepared salt (II). This method for carrying out the reaction markedly increases the yield of the gaseous products (to 88.6 mole % relative to (I)) which consist of ethylene and ethane (see Table 1). The ethylene fraction in the gaseous products in all cases is greater than 60 mole %.

It is striking that the composition of the gaseous products of reaction (1) significantly differs from that of the reactions between the components of the organometallic complex catalysts (Table 2). These products consist predominantly of alkanes even when they are completely inactive as catalysts for olefin polymerization [for example, (I) + AlEt₃ or $(n-C_4H_9O)_4Ti + AlEt_3$).

This discrepancy apparently indicates that this reaction involves specific steps. A correct explanation of the results obtained also requires consideration of the finding that solutions of (I) in hydrocarbons under the conditions studied are stable while the spontaneous decomposition of (I) in this medium at a noticeable rate proceeds only above 363° K by a first-order reaction. The rate constant for the decomposition of (I) in tetralin is $3.4 \cdot 10^{9} \exp(-22,700/\text{RT}) \sec^{-1}$ [8]. The ethylene fraction in the gaseous products for the thermal decomposition of (I) does not exceed 50 mole% [9].



Fig. 1. ESR spectrum for the products of the reactions of (I) with (II) (a) and of (III) with (IV) or (V) (b).

These results may be explained assuming that the reaction of (II) with (I) proceeds as a consequence of the attack of a Ph_3C^+ cation on a Ti-C σ -bond. The Ti-C σ -bond in (I) is polarized: $-Ti^{+0} - -CH_2 - CH_3$. Thus, it is natural that the polarized Ti - C σ -bond specifically is the reaction site in reaction (1) with cation Ph3C⁺. One-electron transfer from the Ti-C bond to the carbocation may occur during the attack of Ph_3C^+ on the Ti-C σ -bond of (I). This apparently results in the short-lived zwitterionic biradical pair (C₅H₅)₂Ti⁺Cl- $(\cdot CH_2 - CH_3)[\cdot C(C_6H_5)_3]$ TiCl₅. Subsequent transformations of this pair lead to the formation of all the observed products. This intermediate species is extremely reactive and undergoes monomolecular decomposition as a result of disproportionation and recombination of the triphenylmethyl and ethyl radicals in the titanium coordination sphere. Table 1 indicates that the yields of Ph₃CH and ethylene are similar. Hence, the reaction of the triphenylmethyl and ethyl radicals in the titanium coordination sphere proceed largely toward disproportionation. The recombination product of the ethyl and triphenylmethyl radicals (1,1,1-triphenylpropane) is detected in the liquid phase by gas-liquid chromatography in amounts \leq 1 mole % (see Table 1). In this regard, we should note that specifically this direction for the transformations is characteristic for the reactions of ethyl and triphenylmethyl free radicals with the ethyl group attached to titanium in the case of (I) [9] and in systems containing titanium derivatives (TiCl₄, Cp₂TiCl₂, Ph₃C[•], and organoaluminum compounds (OAC) [10].

On the basis of this mechanism, we should expect in addition to the formation of Ph_3CH , ethylene and the products of the recombination of C_2H_3 and Ph_3C , the escape of some fraction of the triphenylmethyl and ethyl radicals from the titanium coordination sphere as observed in the reaction of Ph_3C^+ with triphenylphosphine hydride complexes of iridium [11]. However, we did not detect the triphenylmethyl radical by ESR spectroscopy in this reaction in toluene at room temperature. The addition of pyridine to the reaction products ($C_3H_3N/Ti \approx 100$) leads to the formation of Ph_3C^+ as indicated by the appearance of paramagnetic species (PMS) in the solution. The ESR spectrum of these species has a hyperfine structure characteristic for Ph_3C^+ in the presence of titanium compounds [10] (Fig. 1). The yield of Ph_3C^+ could not be determined with high precision but a crude evaluation using a standard DPPH sample indicates that its concentration is not greater than 1 mole % relative to starting (I). It is very likely that Ph_3C^+ appears in solution as a consequence of the destruction of Cp_2TiCPh_3C1 which is formed along with the other products (see Table 1) during homolytic displacement by the reaction

$$Ph_{3}C \cdot + (I) \rightarrow Cp_{2}TiCPh_{3}CI + C_{2}H_{5} \cdot$$
⁽²⁾

by pyridine. It is not excluded that Cp_2TiCPh_3Cl is formed as a result of the oxidative addition of Ph_3C to intermediate Ti(III) derivatives as found by Dolgoplosk et al. [12].

The liberation of ethane in the reaction of (I) with (II) may be attributed to reactions of the ethyl radical with cyclopentadienyl groups. The organotitanium radicals formed may recombine with Ph_3C or undergo decomposition.



Fig. 2. The effect of the sequence for the introduction of components to the cell on the nature of the change in the electrical conductivity of solutions of the $(III) - Et_{1.5}AlCl_{1.5}$ at 313°K in toluene (1, 2) and n-heptane (3) with 10.5 mmole/liter $Et_{1.5}AlCl_{1.5}$, (III)/Al = 1.0. 1) Solvent + $Et_{1.5} - AlCl_{1.5} + (III)$ and 2) solvent + $(III) + Et_{1.5}AlCl_{1.5}$.

Fig. 3. Change in the electrical conductivity of 1:1 TiCl₄ + $Et_{1.5}AlCl_{1.5}$ (1), 1:1 (III) + $Et_{1.5}AlCl_{1.5}$ (2) and 1:2:2 TiCl₄ - $Et_{1.5}AlCl_{1.5}$ - (III) (3) in toluene at 313°K. [TiCl₄ = 5.25 mmole/liter, [$Et_{1.5}AlCl_{1.5}$] = 10.5 mmole/liter.

Some fraction of the ethane may be formed as a result of reactions of the ethyl radical with the solvent in the titanium coordination sphere or in solution after its escape from the cage. This follows from the finding that the formation of monodeuteroethane is formed (2.7-2.9 mole % relative to (I)) upon carrying out the reaction of 0.03 mole/liter (I) with (II) (1:1) at 298°K in octadeuterotoluene. Dibenzyl and butane were not detected by gas and gas-liquid chromatography in the products of these reactions. This finding apparently indicates that the intermediate ethyl and benzyl radicals selectively and rapidly disproportionate with the ethyl group attached to titanium (see our previous work [9, 10]).

However, it is not excluded that other processes also occur in this system in addition to reaction (1). Ethane, in particular, may form in a sequence of reactions beginning with the alkylation of the TiCl₅ anion by starting (I). The EtTiCl₄ anion formed, similar to EtTiCl₃, is unstable and decomposes. This hypothesis is based on the data of Clark and Coles [13] who obtained unstable $R_4N^+TiCH_3Cl_4$ salts.

This hypothesis is also supported by the finding that slow liberation of gaseous products and the formation of TiCl₃ are observed upon mixing a solution of (I) with a solution of TiCl₄ at room temperature. The gaseous products liberated during this reaction consist mainly of ethane.

This system is apparently too complicated for unequivocal interpretation of the mechanisms for the reactions which occur in it. Simpler models for clarification of the mechanism for the reactions of carbocatons with $M - C \sigma$ -bonds are (III) + (IV), (III) + Et_{1.5}AlCl_{1.5}, and (III) + (V), in which the initial components and all the possible intermediate transalkylation products are completely stable at 293-373°K.

(111), mmo les	OAC			Gas yield		Gas compo- sition		(C ₆ H ₅) ₃ CX		
	n	mm	(III)/OAC	mmoles	% rel. to OAC	C₂H₀	C ₂ H ₄	mmoles	Ph ₃ CH fraction	Ph ₃ CEt fraction
2.0 1.0 0,5 2.0 1.0 0.5 1.2 * 1,0 †	(IV) (IV) (IV) (V) (V) (V) (V) (IV) (V)	$ \begin{array}{c} 1,0\\ 1,0\\ 1,0\\ 1,0\\ 1,0\\ 1,0\\ 1,2\\ 1,0\\ \end{array} $	2,0 1,0 0,5 2,0 1,0 0,5 1,0 1,0	0,59 0,67 0,27 0,87 0,50 0.21 0,37 0,26	59 67 27 87 50 21 31 26	15,1 29,2 40,7 17,5 15,2 17,0 59,0 73,0	84,9 70,8 59,3 82,6 84,8 83,0 41,0 27,0	$0,73 \\ - \\ 0,26 \\ 1,39 \\ 1,03 \\ 0,36 \\ - \\ 0,33$	82,0 64,0 88,5 96,3 97,0 97,7 99,7	18,0 36,0 11,5 3,7 3,0 2,3 0,3

TABLE 3. Yield and Composition of Products of the Reaction of (II) with (IV) or (V) in Toluene at 293° K (5 ml toluene, 0.2 mole/liter OAC, 90 min reaction time)

*Hexadecane used as solvent. +(II).

The first step in the reaction of (III) with Et_nAlCl_{3-n} is complexation leading to the appearance of orange $Ph_3C^+AlEt_nCl_{4-n}$ carbonium salts [14, 15]. In the case of systems containing (III) and $Et_{1.5}AlCl_{1.5}$, we established that the initially formed ion pair undergo significant dissociation into ions. This is seen in the sharp rise in the conductivity of solutions of such systems after the introduction of (III) (Figs. 2 and 3).

The reaction of (III) and OAC (IV) and (V) does not stop at the step involving carbonium salt formation. The liberation of gaseous products consisting of ethylene and ethane begins immediately after mixing solutions of (III) and the OAC (Table 3). As in the case of the (I) + (II) system, the ethylene fraction in the gaseous products of (III) with OAC exceeds 60 mole %. Gas-liquid chromatographic analysis after completion of the reaction showed Ph_3CH and 1,1,1-triphenylpropane (see Table 1). The fraction of Ph_3CEt in the reaction products increases in going from (V) to (IV) and with a decrease in the (III)/(IV) ratio to reach 18-36 mole % relative to starting (III).

In addition to these products, PMS giving a broad ESR signal (see Fig. 1) were detected by ESR spectroscopy in the liquid phase in the case of 2:1-0.5:1 (III) + (I) and 2:1-1:1 (III) + (V). These PMS are apparently products of the reaction of Ph_3C with (III) and its derivatives coordinated with AlCl₃. These complexes have poor solubility in hydrocarbons and separate as a dark red, viscous oil. Pyridine destroys these complexes and gives their dissolution, decoloration of the reaction system, and disappearance of the PMS.

The results obtained in this series of experiments and the literature data on the reaction of (III) and Me_3CC1 with OAC [14, 15] indicate the following mechanism for the reaction of (III) with (IV)

$$\frac{Ph_{3}CCI + EtAlCl_{2} \rightleftharpoons Ph_{3}C^{+}[EtAlCl_{3}]^{-}}{(III)}$$
(3)

$$(VI) \rightleftharpoons Ph_3C^+ + [EtAlCl_3]^-$$
(4)

$$(VI) \xrightarrow{OET} (\overline{Ph_3C})(Et) AlCl_3} (VII)$$
(5)

$$(VII) \rightarrow AlCl_3 + Ph_3CH + C_2H_4 + Ph_3CEt + Ph_3C \cdot + C_2H_6$$
(6)

We assume, that as in the reaction of (I) and (II), the rate-limiting step for the irreversible reaction of (II) with OAC is one-electron transfer (OET) from the Al-C bond to the triphenylmethyl cation leading to the formation of unstable coordinated radical pair (VII) (Eq. (5)). Subsequent decomposition of this pair is accompanied by the formation of all the major gaseous and liquid-phase products.

Relative to reaction (1), the reaction of (III) with OAC have lower selectivity for the disproportionation of C_2H_3 with Ph_3C in the aluminum coordination sphere and is distinguished by side reactions of Ph_3C^+ with ethylene [15] and Ph_3CX with Ph_3C . These processes do not permit a complete balance relative to the C_2H_3 and Ph_3C' groups. In the reactions of (III) with (IV) and (V), as in reaction (1), a significant amount of ethane is found in the gaseous products in addition to ethylene. The ethane fraction in the gaseous products of the reaction of (III) with (IV) decreases with increasing (III)/(IV) molar ratio. The formation of ethane in this system is apparently a result of the reaction of C_2H_3 with unreacted OAC. In the case of 1:1 (II) + (IV) and (II) + (V), the ethane fraction in the gaseous products is markedly greater than the ethylene fraction. The larger yield of ethane relative to the yield of ethylene in this system is attributed to the loss of a significant portion of the ethylene formed as a result of its polymerization at active sites of the highly active two-component systems [16].

It is not excluded that some portion of the olefins and Ph_3CH may be formed in these reactions as a result of heterolytic attack of the Ph_3C^+ cation on the alkyl group C-H σ -bond of the organometallic compound

$$Ph_{3}C^{+}+H-CH_{2}CH_{2}-Ti(Al) \rightarrow Ph_{3}CH+CH_{2}-CH_{2}-Ti(Al) \rightarrow \rightarrow Ph_{3}CH + C_{2}H_{4} + Ti^{+}(Al^{+})$$
(7)

The hypothesis of a heterolytic mechanism for these reactions accounts for the formation of Ph_3CH and ethylene but does not explain the paths for the formation of the other products. Thus, the question of the ratio of these reaction pathways is an independent problem which requires the development of special approaches for its resolution.

Thus, the entire body of data obtained confirms our hypothesis of the possible reaction of cationic active sites with anion-coordination sites under conditions of their synchronous functionalization is organometallic complex catalysts. These results have more general significance for metal complex catalysis since they demonstrate the possibility of the activation of Ti-C and Al-C σ -bonds by carbocations.

In conclusion, we note that the possibility of the reaction of anion-coordination active sites with cationic active sites is supported by the kinetic data on the telomerization of ethylene on bifunctional complex catalysts and the formation of a significant amount of alkanes on telomerization conditions.

EXPERIMENTAL

The reaction of 0.026-0.030 mole/liter (I) with (II) was carried out in toluene at 293°K for 1 h. Gaseous products are released which consist of ethane and ethylene. The major portion of the gaseous products (up to 70%) is given off in the first 5 min. At the end of the reaction, the liquid phase (toluene and TiCl₄) was frozen in vacuum. The yield of TiCl₄ was 23-40 mole % relative to (II). A heptane extract and then a toluene extract were obtained from the solid residue. The heptane extract contained Ph₃CH; Ti and Cl were absent from this abstract. The yield of Ph₃CH was determined spectrophotometrically using a calibration curve relative to absorption at 263 nm as well as by gas-liquid chromatographic analysis.

The visible spectrum of the toluene extract corresponded to the spectrum of a toluene solution of Cp_2TiCl_2 . The yield of Cp_2TiCl_2 was found by titration for Ti and Cl. The Cl/Ti ratio in the toluene extract was 2.0 \pm 0.3. The composition of the solid residue (8-20 mass %) relative to the sum of the masses of the components of the (I) + (II) system was not determined. The reaction of (III) with OAC (IV) and (V) proceeds in a homogeneous phase. The composition of the products of the transformations in these systems was determined by gas and gas-liquid chromatographic analysis after the completion of the liberation of the gaseous products and the decoloration of the reaction mass. The reaction mass was hydrolyzed prior to the analyses. Ph₃COH was not detected in the hydrolysis products, which indicated the complete consumption of (III).

The yield of gaseous products was determined volumetrically after their freeze transfer in a calibration vessel while the composition was determined by gas-liquid chromatography on a KhL-4 chromatography by the standard method using a 4×1000 mm column packed with Apiezon L on Al₂O₃ at 293°K. In the homophasic reaction of (I) with (II) the total yield of ethylene and ethane is 84.7-88.6 mole % relative to (I) (see Table 1).

The resistivity of the solutions R_x was measured with an E6-3 terachmmeter in a thermostatted cell with coaxial cylindrical platinum electrodes. The solution was stirred using an electromagnetic stirrer and dry argon bubbling. The specific electrical conductivity (\varkappa) was calculated using the equation $\varkappa = 34.7/R_x$, Ω^{-1} cm⁻¹. The ESR spectra of the paramagnetic reaction products were taken on an EPR-2 spectrometer designed at the Institute of Chemical Physics of the Academy of Sciences of the USSR.

CONCLUSIONS

1. Conditions were found for the reactions of $Ph_3C^{T}TiCl_5$ with $Cp_2TiEtCl$ and of Ph_3CCl with ethylaluminum and diethylaluminum chlorides and the composition of the products of these reactions was determined. A mechanism was proposed.

2. A conductometric study has shown that the reaction of Ph_3CC1 with OAC has a rapid step for the formation of $Ph_3C^+[EtAlCl_3]^-$ and $Ph_3C^+[Et_2AlCl_2]^-$ ionic complexes which dissociate into ions to a significant extent.

3. The rate-limiting step for the reaction of the triphenylmethyl cation with organotitanium and organoaluminum compounds is a one-electron transfer from the M-C σ -bond to the carbocation leading to the formation of highly reactive intermediate biradical complexes.

LITERATURE CITED

- 1. M. L. H. Green and P. L. J. Nagy, J. Organomet. Chem., 1, 58 (1963).
- 2. J. M. Jerkunica and T. G. Traylor, J. Am. Chem. Soc., <u>93</u>, 6278 (1971).
- 3. A. N. Kashin, N. A. Bumagin, I. P. Beletskaya, and O. A. Reutov, J. Organomet. Chem., <u>171</u>, 321 (1979).
- 4. I. P. Beletskaya, G. A. Artamkina, and O. A. Reutov, Usp. Khim., <u>45</u>, 661 (1976).
- 5. A. A. Semenov, P. E. Matkovskii, and F. S. D'yachkovskii, Vysokomol. Soedin., <u>A21</u>, 2749 (1979).
- P. E. Matkovskii, A. A. Semenov, L. N. Russiyan, Z. G. Busheva, L. I. Chernaya, D. B. Furman, F. S. D'yachkovskii, and N. S. Enikolopyan, Proceedings of the Third All-Union Conference on Catalytic Reaction Mechanisms [in Russian], Vol. 2, Novosibirsk (1982), p. 121.
- A. A. Semenov, P. E. Matkovskii, and F. S. D'yachkovskii, Vysokomol. Soedin., <u>A20</u>, 1754 (1978).
- 8. P. E. Matkovskii, L. I. Chernaya, F. S. D'yachkovskii, and N. E. Khrushch, Zh. Obshch. Khim., 47, 1841 (1977).
- 9. P. E. Matkovskii, L. I. Chernaya, and F. S. D'yachkovskii, Dokl. Akad. Nauk SSSR, <u>244</u>, 1351 (1979).
- 10. P. E. Matkovskii and L. I. Chernaya, Zh. Org. Khim., 11, 1503 (1975).
- M. I. Kalinkin, S. M. Markosyan, Z. N. Parnes, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., 2141 (1981).
- 12. S. I. Beilin, N. N. Eliseeva, G. N. Bondarenko, G. P. Karpacheva, and B. A. Dolgoplosk, Izv. Akad. Nauk SSSR, Ser. Khim., 2561 (1976).
- 13. R. J. H. Clark and M. A. Coles, J. Chem. Soc., Dalton Trans., 2454 (1972).
- Kh. Kaar and G. Shvindlerman, Izv. Akad. Nauk Est. SSR, Ser. Fiz.-Mat. Tekh. Nauk, <u>13</u>, 148 (1964).
- 15. A. Priola, S. Cesca, and G. Ferraris, Makromolec. Chem., <u>160</u>, 41 (1972).
- P. E. Matkovskii, A. D. Pomogailo, L. N. Russiyan, A. P. Lisitskaya, F. S. D'yachkovskii, Kh.-M. A. Brikenshtein, and M. P. Gerasina, USSR Inventor's Certificate No. 491,404 (March 18, 1974); Byull. Izobret., No. 42, 17 (1975).