LITERATURE CITED

1. J. Gloede, Z. Chem., 22, No. 4, 126 (1982).
2. J. Michalski, J. Mikolajczak, M. Pakulski, and A. Skowronska, Phosphorus Sulfur, 4, 233 (1978).
3. D. Dakternieks, G.-V. Rochenthaler, and R. Schmutzler, J. Fluorine Chem., 11, 387 (1978).
4. L. N. Markovskii, A. V. Solov'ev, V. E. Pashinnik, and Yu. G. Shermolovich, Zh. Obshch. Khim., 50, No. 4, 807 (1980).
5. J. Michalski, M. Pakulski, and A. Skowronska, J. Chem. Soc., Perkin Trans. 1, No. 4, 833 (1980).
6. J. Gloede and H. Gross, J. Prakt. Chem., 321, No. 6, 1029 (1979).
7. F. Ramirez, A. J. Bigler, and C. P. Smith, Tetrahedron, 24, No. 14, 5041 (1968).
8. H. Gross and U. Karsch, J. Prakt. Chem., 29, Nos. 3-6, 315 (1965).
9. J. Gloede and H. Gross, Phosphorus Sulfur, 7, No. 1, 57 (1979).

OLIGOMERIZATION OF TRIMETHYLSILYLACETYLENE IN THE PRESENCE OF CATALYTIC SYSTEMS BASED ON GROUP III-VI TRANSITION METAL HALIDES

R. Kh. Mudarisova, I. R. Mullagaliev, A. V. Karaseva,
L. I. Ol'khovskaya, Yu. B. Monakov, and G. A. Tolstikov

UDC 542.97:547.1'128

The features of the reaction of oligomerization of trimethylsilylacetylene in the presence of group III-VI transition metal compounds combined with triisobutylaluminum were investigated. The effect of the nature of the transition metal, cocatalyst, and conditions of conducting the oligomerization reaction on the yield and composition of the products of the reaction were studied. It was shown that it is possible to obtain either linear products of oligomerization or the cyclic trimer, or a mixture of both by varying the nature of the catalyst.

Substituted alkynes can form cyclic trimers (derivatives of benzene) [1] or linear polymers [2] in the presence of Ziegler—Natta catalytic systems as a function of their structure and the reaction conditions. Disubstituted acetylenes tend to form cyclic trimers to a greater degree than monosubstituted acetylenes [3] due to the greater steric hindrances in constructing linear chains. The data on the effect of the nature of the transition metal in the catalytic system and the conditions of conducting the reactions on the direction of the oligo- or polymerization processes are very contradictory [4, 5], and this especially concerns mono- and disubstituted organosilicon acetylenes. For example, obtaining a linear polymer from trimethylsilylacetylene (TMSA) is reported in [6] and oligomeric products were obtained in [7]. Different mechanisms of oligomerization (OM) of acetylenic compounds are also described in the literature: organometallic, coordination, and ion-coordination [8, 9].

The features of oligomerization of TMSA in the presence of compounds of group III-VI transition metals in association with triisobutylaluminum (TIBA) were investigated in the present study. In the presence of catalytic systems (CS) based on $TiCl_4$, $VOCl_3$, $NbCl_5$, and $MoCl_5$, TMSA forms an insoluble polymer and an oligomeric fraction. The CS based on difficultly reduced trivalent metal halides (VCl_3, $LnCl_3 \cdot 3L$, $CrCl_3$) can only yield oligomeric products under the conditions studied. Disubstituted silicon-containing alkynes: trimethylsilylphenylacetylene and trimethylsilylbutylacetylene form an insignificant amount (2-5%) of oligomers in the presence of all of the CS studied, probably due to steric hindrances in coordination of the acetylene on the active site (AS) of the catalyst. In this respect, the basic features of the process of OM were investigated on the example of TMSA.

Institute of Chemistry, Bashkir Scientific Center, Ural Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2823-2828, December, 1989. Original article submitted July 29, 1988.

0568-5230/89/3812-2587$12.50

TABLE 1. Dependence of the Ratio of Products of the Oligomeric Fraction of TMSA on the Nature of the Transition Metal in the MCl_n–$Al(i\text{-}Bu)_3$ CS*

No.	MCl_n.	Linear		Cyclic trimer (III)	No.	MCl_n	Linear		Cyclic trimer (III)
		dimer (I)	trimer (II)				dimer (I)	trimer (II)	
1	$DyCl_3\cdot 3TBP$	2	1	–	5	VCl_3	2	1	2
2	$TiCl_4$	2	1	0,75	6	$NbCl_5$	–	–	1
3	$VOCl_3$	6	1	1	7	$CrCl_3$	0,5	1	0,25
4	$VO(acac)_2$	2	1	–	8	$MoCl_5$	0,2	1	–

*Conditions of OM: toluene, 25°C (Nos. 1-4), 80°C (Nos. 5-8), 4 h, $C_{TMSA} = 0.5$, $C_{cat} = 10^{-2}$ mole/liter. Conditions of preparation of the catalyst: –78°C, 1 h (Nos. 1-4); 80°C, 15 min (Nos. 5-8).

TABLE 2. Effect of the Nature of the Lanthanide Component of the CS $LnHal_3\cdot 3L$–$Al(i\text{-}Bu)_3$ on the Yield of the Oligomeric Fraction*

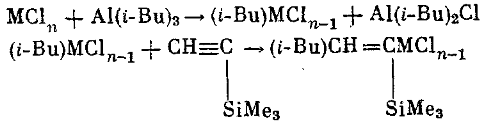
Lanthanide compound	Yield, %		Lanthanide compound	Yield, %	
	(I)	(II)		(I)	(II)
$CeCl_3\cdot 3TBP$	36	18	$LnCl_3\cdot 3TBP$	25	12
$NdCl_3\cdot 3TBP$	21	10	$GdCl_3\cdot 3TBP$	26	13
$NdCl_3\cdot 3DASO$	11	6	$GdBr_3\cdot 3TBP$	21	10
$DyCl_3\cdot 3TBP$	50	25	$GdI_3\cdot 3TBP$	19	10

*Conditions of OM: toluene, 50°C, 4 h, $C_{TMSA} = 0.5$, $C_{cat} = 10^{-2}$ mole/liter, Al/M = 15; conditions of preparation of the CS: –78°C, 1 h.

As a function of the nature and conditions of preparation of the CS, it was possible to obtain either dimers and linear trimers or the symmetric cyclic trimer alone[†] or a mixture of the two, whose ratio is a function of the nature of the transition metal (Table 1). The analysis (IR, PMR, UV spectroscopy, GLC, elementary analysis, mass spectroscopy, and ebulliometry) showed that the dimers and linear trimers formed in the presence of CS based on group III-VI transition metal halides and TIBA contain conjugated C=C double bonds in the chain, an isobutyl radical from the organoaluminum compound (OAC[‡]) and side trimethylsilyl groups. The orders of the OM process in the catalyst are equal to 1 [in the range of concentrations of $(2.5\text{-}10)\cdot 10^{-3}$ mole/liter] and they vary from 1 to 0.5 in the monomer (in the 0.5-2 mole/liter range of concentrations). The products of linear oligomerization of TMSA obtained in the presence of these CS have a different structure from the linear dimers and trimers formed in the presence of Ni(0), as the latter contain both double and triple bonds [11].

The data obtained can be explained by the following mechanism of oligomerization of TMSA in the presence of MCl_n–$Al(i\text{-}Bu)_3$.

Initiation



$$MCl_n + Al(i\text{-}Bu)_3 \to (i\text{-}Bu)MCl_{n-1} + Al(i\text{-}Bu)_2Cl$$

$$(i\text{-}Bu)MCl_{n-1} + \underset{SiMe_3}{CH{\equiv}C} \to (i\text{-}Bu)CH{=}\underset{SiMe_3}{C}MCl_{n-1}$$

[†] The cyclic trimer of TMSA is 1,3,5-tris(trimethylsilyl)benzene which is probably formed similarly to the cyclic trimerization of phenylacetylene on Ziegler–Natta catalysts [10].

[‡] In using other OAC as cocatalysts, another radical R from AlR_3, for example, C_2H_5, is found at the end of the molecule of the oligomer if triethylaluminum was the cocatalyst.

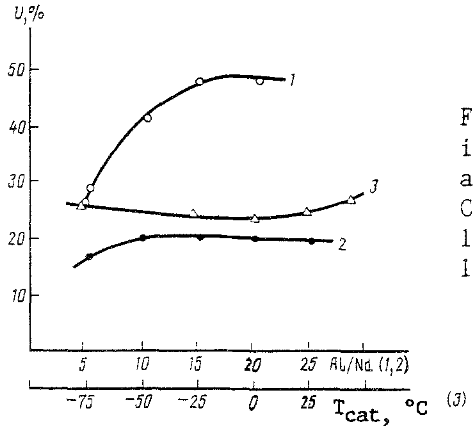
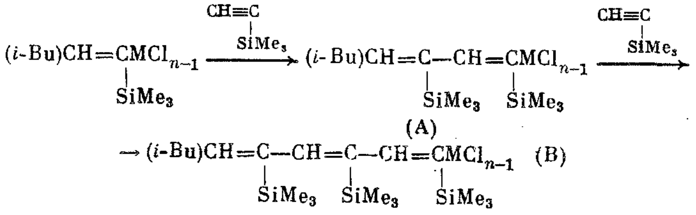


Fig. 1. Dependence of the yield of the oligomeric fraction on the Al/Nd molar ratio (1), (2) and on the temperature of formation of the CS $NdCl_3 \cdot 3TBP{-}Al(i\text{-}Bu)_3$ (3) prepared by the method: 1) separately; 2) in situ. Toluene, 25°C, $C_{cat} = 10^{-2}$, $C_{TMSA} = 0.5$ mole/liter.

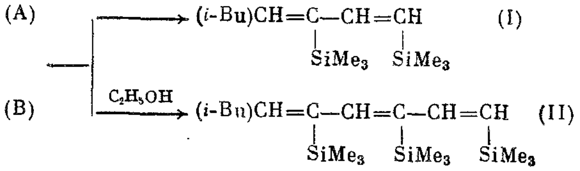
Chain propagation



$$(i\text{-Bu})CH{=}\underset{SiMe_3}{C}MCl_{n-1} \xrightarrow{\substack{CH\equiv C\\ SiMe_3}} (i\text{-Bu})CH{=}\underset{SiMe_3}{C}{-}CH{=}\underset{SiMe_3}{C}MCl_{n-1}\ (A) \xrightarrow{\substack{CH\equiv C\\ SiMe_3}}$$

$$\rightarrow (i\text{-Bu})CH{=}\underset{SiMe_3}{C}{-}CH{=}\underset{SiMe_3}{C}{-}CH{=}\underset{SiMe_3}{C}MCl_{n-1}\quad (B)$$

Chain breaking by ethanol



$$(A) \xrightarrow{C_2H_5OH} (i\text{-Bu})CH{=}\underset{SiMe_3}{C}{-}CH{=}\underset{SiMe_3}{CH}\quad (I)$$

$$(B) \xrightarrow{C_2H_5OH} (i\text{-Bu})CH{=}\underset{SiMe_3}{C}{-}CH{=}\underset{SiMe_3}{C}{-}CH{=}\underset{SiMe_3}{CH}\quad (II)$$

The yield and composition of the oligomeric fraction is very strongly dependent on the nature and conditions of preparation of the CS.

The oligomers obtained on lanthanide catalysts (Table 2) only contain dimers (I) and linear trimers (II) in the ratio of 2:1. The effect of the conditions of preparation of the CS on the total yield of (I) and (II) is illustrated in Fig. 1. The rate of the process is higher in aromatic solvents than in aliphatic solvents. The nature of the cocatalyst also affects the yield of oligomers (Table 3).

Modification of the lanthanide catalysts by $TiCl_4$ results in the appearance of a polymer of TMSA together with an oligomeric fraction whose composition and structure virtually do not change. The yields of both the oligomeric and the polymeric products increase with an increase in the Al/Ln ratio (Fig. 2).

TMSA in the presence of $TiCl_4$–TIBA yields a mixture of dimers and linear and cyclic trimers in the ratio of 2:1:0.75 and their yield increases with an increase in the Al/Ti ratio. There are Ti^{3+} and Ti^{2+} compounds in this CS with the Al/Ti ratios studied (2-20) [12] and they apparently also drive linear and cyclic OM of trimethylsilylacetylene; $TiCl_4$ is inactive without a cocatalyst.

CS based on $VOCl_3$ is slightly less active in oligomerization of TMSA than the titanium catalysts. The yield of oligomers of TMSA is a function of the nature of the cocatalyst, conditions of preparation of the CS, ratio of components (Fig. 3), and nature of the solvent (the rates of OM are higher in aromatic solvents). The ligand environment and valence state of the vanadium in the CS affects the composition of the oligomeric fraction (Table 1). Replacement of $VOCl_3$ by VCl_3 also decreases the total yield of oligomers, while preserving the dependence of the yield on the conditions of preparation of the catalyst and nature of the solvent on the whole.

The use of $NbCl_5$ alters the character of oligomerization of TMSA: the process is directed toward the predominant formation of the cyclic trimer (Table 1). An increase in the amount of TIBA up to the ratio of Al/Nb = 10 results in the appearance of dimers and linear trimers together with the cyclic trimer. This effect of the cocatalyst on the composition

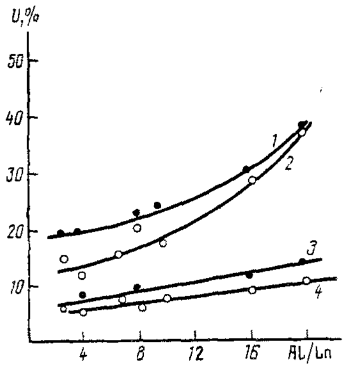


Fig. 2

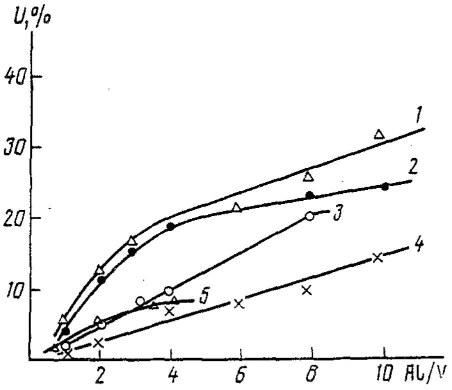


Fig. 3

Fig. 2. Dependence of the yield of oligo- (1), (2) and polyTMSA (3), (4) on the Al/Ln molar ratio in the CS $LnCl_3 \cdot TiCl_4 \cdot TBP$–$Al(i\text{-}Bu)_3$ prepared at −78°C for 1 h: Ln = Dy (1), (3), Nd (2), (4). Toluene, 25°C, 65 h, $C_{cat} = 10^{-2}$, $C_{TMSA} = 0.5$ mole/liter.

Fig. 3. Dependence of the yield of the oligomeric fraction on the Al/Y molar ratio in the CS $VOCl_3$–AlR_3 prepared separately, where $AlR_3 = Al(i\text{-}Bu)_3$ (1), $Al(i\text{-}Bu)_2H$ (2), $AlEtCl_2$ (3), $AlEt_2Cl$ (4), and $AlR_3 = Al(i\text{-}Bu)_3$ (5). Toluene, 25°C, 2 h, $C_{cat} = 10^{-2}$, $C_{TMSA} = 0.5$ mole/liter.

TABLE 3. Effect of the Nature of the Cocatalyst and Conditions of OM on the Yield of the Oligomeric Fractions on the CS $DyCl_3 \cdot 3TBP$–Cocatalyst (see Table 2 for the conditions of OM and preparation of CS)

Cocatalyst	Al/Dy	Temperature of OM, °C	Yield of fractions, %	
			(I)	(II)
TIBA	30	0	40	20
TIBA	30	50	47	23
TEA	30	0	19	9
DEAC	10	0	22	10
DIBAH	30	0	26	13

of the products of the reaction is probably due to a different mechanism of OM. Cyclotrimerization of TMSA takes place on $NbCl_5$ through a metallocyclopentadiene complex similar to cyclotrimerization of alkynes on cobalt catalysts [13]. Oligomerization of TMSA on the $NbCl_5$–TIBA system probably takes place according to an anion-coordination mechanism, as on Ziegler catalysts.

The use of group VI metal halides, in contrast to group III-V metal halides, results in the fact that the oligomeric fraction contains significantly more linear trimers than dimers (Table 1). In addition to a higher concentration of trimers in the oligomeric phase, a distinctive feature of the chromium catalyst is that the cyclic trimer of TMSA is also obtained on $CrCl_3$. The yield of the oligomeric fraction decreases when TIBA is added to $MoCl_5$ and $CrCl_3$ up to a ratio of Al/Mo(Cr) = 10.

EXPERIMENTAL

Oligomerization of TMSA was conducted in glass ampuls in an atmosphere of dry argon using carefully purified solvents.

TMSA was synthesized according to [14] and additionally purified by three distillations in an argon current over calcium hydride. The concentration of basic substance was 98.5-99%.

The complexes of lanthanide halides with tributyl phosphate (TBP) and diamyl sulfoxide (DASO) were prepared according to [15]. Triisobutylaluminum, triethylaluminum (TEA), diethylaluminum chloride (DEAC), and diisobutylaluminum hydride (DIBAH) in the form of 92-95% solutions in heptane were used without additional purification. $TiCl_4$ and $VOCl_3$ were distilled in a current of dry argon. Pure VCl_3, $NbCl_5$, $CrCl_3$, and $MoCl_5$ were used without additional purification. The CS were prepared in situ with separate incorporation of the components in an solution of the monomer or the components of the CS were mixed in a separate ampul, held for a certain time at a given temperature, and then added to a solution of the monomer. OM was stopped by addition of ethanol to the reaction mixture, the products of the reaction were treated with a 5% solution of HCl and water, the solvent was eliminated by evacuation at 25-30°C, the products were dried to a constant weight, extracted with acetone, the acetone was eliminated, and the residue was vacuum distilled. The oligomers of TMSA are light-yellow viscous liquids which are soluble in aromatic and aliphatic solvents, acetone, and alcohol.

1,3-Di-(trimethylsilyl)-6-methyl-1,3-heptadiene (I), bp 34°C (27 mm), n_D^{20} 1.4615. IR spectrum (ν, cm^{-1}): 780, 840, 1260 [$Si(Me)_3$], 990, 1590 (CH=CH), 2950 (Me). PMR spectrum (CCl_4, δ, ppm): −0.03 s [9H, $Si(Me)_3$], −0.06 s [9H, $Si(Me)_3$], 5.61 d (1H), 6.66 d (1H), 5.67 t (1H), 0.77 d (6H), 1.45 m (1H), 2.02 t (2H). UV spectrum (n-C_6H_{14}, λ_{max}, nm): 245. Mass spectrum: 245 (M^+). Found: C, 67.20; H, 10.51; Si, 22.29%. $C_{14}H_{30}Si_2$. Calculated: C, 66.11; H, 11.79; Si, 22.10%.

1,3,5-Tris(trimethylsilyl)-8-methyl-1,3,5-nonatriene (II), bp 93°C (27 mm), n_D^{20} 1.4568. IR spectrum (ν, cm^{-1}): 780, 830, 1260 [$Si(Me_3)$], 990, 1580 (CH=CH), 2950 (Me). PMR spectrum (CCl_4, δ, ppm): 0.05 [9H, $Si(Me)_3$], 0.07 [9H, $Si(Me)_3$], 0.13 [9H, $Si(Me)_3$], 5.62 d (1H), 6.7 d (1H), 5.75 t (1H), 2.03 t (2H), 1.5 m (1H), 0.86 d (6H). UV spectrum (n-C_6H_{14}, λ_{max}, nm): 245. Mass spectrum: 352 (M^+). Found: C, 65.19; H, 12.06; Si, 22.75%. $C_{19}H_{40}Si_3$. Calculated: C, 64.77; H, 11.57; Si, 23.86%.

1,3,5-Tris(trimethylsilyl)benzene (III), bp 56°C (27 mm), n_D^{20} 1.0350. IR spectrum (ν, cm^{-1}): 770, 840, 1260 [$Si(Me)_3$], 1130, 1430 [$Si(Me)_3$], 2940 (Me). PMR spectrum (CCl_4, δ, ppm): 0.03 [27H, $Si(Me)_3$], 7.38 s (3H). Mass spectrum: 294 (M^+). Found: C, 61.52; H, 10.17; Si, 28.31%. Calculated: C, 61.23; H, 10.20; Si, 28.57%.

The IR spectra of the oligomers were made on a UR-20 spectrophotometer in thin films prepared by evaporation of CCl_4 from dilute solutions on KBr glass; the PMR spectra were recorded on a Tesla BS-467 instrument (60 MHz) in CCl_4 relative to HMDS; UV: on a Specord M-40 in hexane solution, 2 mm cuvette thickness; mass spectra: on a MX-1303 spectrometer. The chromatographic analysis was conducted on a Chrom-5 chromatograph, columns ℓ = 1.2 m, SE-30 phase, katharometer detector, T = 50-300°C. The molecular weights were estimated by the ebulliometric method on an ÉP-68 ebulliometer.

LITERATURE CITED

1. V. O. Reikhsfel'd and K. L. Makovetskii, Usp. Khim., 35, 1204 (1966).
2. E. M. Smolin and D. S. Hoffenberg, Encyclopedia of Polymer Science and Technology, Vol. 1, Wiley-Interscience, New York (1964), p. 46.
3. B. Franzys, P. I. Canterino, and R. A. Wiculiffe, J. Am. Chem. Soc., 81, 1514 (1959).
4. Y. Tekegami, T. Suruki, and M. Fujii, J. Chem. Soc. Jpn. Industr. Chem. Sec., 70, 1796 (1967).
5. V. O. Reikhsfel'd and K. L. Makovetskii, Dokl. Akad. Nauk SSSR, 155, 414 (1964).
6. Okano Yoshimichi, Masuda Toshio, and Higashimura Toshinobu, J. Polym. Sci., Polym. Chem. Ed., 22, 1605 (1984).
7. M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinshaya, et al., J. Polym. Sci., Polym. Chem. Ed., 18, 57 (1980).
8. T. Yu. Sineva and V. O. Reikhsfel'd, Zh. Org. Khim., 5, 2090 (1969).
9. C. Simionescu, T. Lixcandru, I. Negulescu, et al., Macromol. Chem., 163, 59 (1973).
10. G. I. Bantsyrev, M. I. Cherkashin, and A. A. Berlin, Izv. Akad. Nauk SSSR, Ser. Khim., 2705 (1968).
11. V. P. Yurev, G. A. Gailyunas, F. G. Yusupova, et al., J. Organomet. Chem., 169, 21 (1979).
12. Yu. B. Monakov, S. R. Rafikov, N. Kh. Minchenkova, and A. A. Berg, Dokl. Akad. Nauk SSSR, 244, 918 (1979).
13. D. R. Alister, J. E. Bercaw, and R. G. Bergman, J. Am. Chem. Soc., 99, 1666 (1977).
14. V. Chvalovsky and J. Rathousky, Organosilicon Compounds, 1, 6 (1978).
15. Yu. I. Murinov, Yu. B. Monakov, Z. G. Shamaeva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2790 (1977).