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Abstract

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PHYSICAL CHEMISTRY

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ON THE MECHANISM OF CYCLIC TRIMERIZATION OF ACETYLENES ON COMPLEX ORGANOMETALLIC CATALYSTS

(Presented by Academician A. A. Grinberg, 11 XI 1963)

The method of cyclic polymerization of acetylenic hydrocarbons and their derivatives is of great practical interest, since it makes it possible to obtain numerous difficultly accessible derivatives of benzene, cyclooctatetraene, and other cyclic hydrocarbons with conjugated systems of double bonds.

Table 1

Starting monomer	Amount of monomer, g	Amount of catalyst, mmol. Al (iso-$C_4H_9)_3$	Amount of catalyst, mmol. $TiCl_4$	Temp., °C	Trimer yield, g	Trimer yield, %
n-C_4H_9C CH(8)	3.6	1.52	0.49	20—40	3.3	92
n-C_8H_{17}C CH	3.9	1.32	0.46	20—40	3.52	90.3
C_6H_5C CH	6.96	1.24	0.43	20—40	6.26	90

If the low-efficiency thermal methods are not counted (1), until recently the catalysts used for the reaction under consideration have been distinctive systems including complex nickel compounds (2-4), carbonyls of iron, cobalt, and manganese (5), and coordination compounds of aryls and alkyls of chromium, nickel, and cobalt with tetrahydrofuran (6). Common to all the catalysts listed is the obligatory presence of a transition metal capable of forming π-complexes with unsaturated compounds. Therefore all investigators of acetylene cyclopolymerization reactions are inclined toward a coordination mechanism, and in a number of cases very elegant experimental evidence has been obtained.

Table 2

Trimerization product	Trimer yield, g	Trimer yield, %	Relative molar yield, %
Tri-*n*-butylbenzene	3.20	12.4	16.7
Dibutyldiphenylbenzene	7.95	30.9	38.7
Butyldiphenylbenzene	7.0	27.2	31.7
Triphenylbenzene	3.06	11.9	12.9

In the last several years, Ziegler-type catalysts ([7], [8]) have been proposed for the cyclotrimerization of acetylenes. In studying cyclotrimerization in the presence of these catalysts, we obtained facts that provide grounds for developing ideas about the coordination mechanism of action of this class of complex catalysts.

First, acetylenes with various substituents, *n*-C_4H_9, C_6H_5, C_8H_{17}, under identical conditions give yields close to quantitative (Table 1).

Second, in the joint trimerization of different acetylenes, for example, *n*-butyl- and phenylacetylenes ([9]), with an initial molar ratio of monomers of 1 : 1, all four possible trimerization products are obtained in an almost statistical ratio of 1 : 3 : 3 : 1 (Table 2).

It was further found that the cyclotrimerization reaction proceeds with identical results in various solvents that are inert with respect to to the catalyst (benzene, *n*-heptane, cyclohexane, isooctane). At the same time, the addition of substances capable of serving as electron donors strongly affects the results of the process, up to its complete cessation (Table 3). It is interesting that when an excess of silvan is introduced into the system, in which the unshared electron pair of the oxygen atom is conjugated with double bonds, the yield of trimer decreases only slightly.

Table 3

Solvent	Electron-donor additive	Amount, mmol: $TiCl_4$	Amount, mmol: Al(iso-$C_4H_9)_3$	Amount, mmol: additive	Trimer yield, %
Benzene	None	0.43	1.27	–	92.1
Isooctane	»	0.43	1.21	–	93.0
Same	Tetrahydrofuran	0.39	1.25	0.37	65
» »	»	0.435	1.35	1.84	0
» »	Silvan	0.222	0.663	3.0	78
» »	Pyridine	0.24	0.68	1.0	0

These results are difficult to explain if one assumes an anionic, or in general an ionic, mechanism of cyclotrimerization, which is usually proposed in cases associated with the action of Ziegler-type catalysts. Indeed, the influence of the radicals C_4H_9 and C_6H_5 on the electron density of the triple bond is opposite and unquestionably should have manifested itself in the comparative reactivity of the corresponding acetylenes if the reaction proceeded through ionic structures. This suggests that the cyclotrimerization of acetylenes on these catalysts proceeds by a coordination mechanism, similar to the mechanism of the cyclopolymerization of acetylenes on other catalysts containing transition metals, which was mentioned above. This assumption is also supported by the fact that the catalyst is deactivated by substances capable of forming complexes with the components of the catalyst (Table 3). It could be assumed that in the Ziegler catalyst the coordination center responsible for the formation of cyclic structures is the titanium atom. To verify this, experiments were carried out on the polymerization of *n*-butylacetylene, in which both the titanium and the aluminum component of the system were varied (Table 4). As can be seen from the data in Table 4, replacement of the groups bound to titanium has a considerably stronger effect on the results of the reaction than does a change in the aluminum component. Replacement of $TiCl_4$ by $Ti(OC_2H_5)_4$ deactivates the catalyst, which can be explained by suppression of the ability of the titanium atom in $Ti(OC_2H_5)_4$

Table 4

Aluminum compound	Titanium compound	Al/Ti	T, °C	Yield, %	Nature of polymer
Al(iso-$C_4H_9)_3$	$TiCl_4$	3 : 1	20—40	93	Cyclic trimer
Al(iso-$C_4H_9)_3$	$Ti(OC_2H_5)_4$	5 : 1	20	0	
Al(iso-$C_4H_9)_3$	α-$TiCl_3$	3 : 1	20—40	25	High-molecular-weight linear polymer
Al(iso-$C_4H_9)_2Cl$	$TiCl_4$	3 : 1	20—40	83	Cyclic trimer
Al(iso-$C_4H_9)_2Cl$	$(C_5H_5)_2TiCl_2$	3 : 1	20—40	15	» »

for complex formation through interaction of the unshared electron pairs of the ethoxy group with the vacant *d*-orbitals of titanium (10). Reaction in the presence of $TiCl_3$ leads to the formation only of linear polymers (8). For the preparation of cyclic trimers, however, the presence of a solid phase is not obligatory (experiments with a soluble catalyst based on $(C_5H_5)_2TiCl_2$). From all this it follows that the catalytic activity of the system is associated with the presence of a tetravalent titanium atom.

On the basis of the foregoing, we propose the following scheme for the coordination mechanism of the cyclotrimerization of acetylenes on Ziegler catalysts.

Catalytic complex I is formed upon interaction of an aluminum alkyl with a titanium halide

$$AlR_3 + TiCl_4 \longrightarrow \quad Cl{-}Ti^{\,+}(Cl)(R)\cdots Cl\cdots Al^{\,-}(Cl)(R)_2 \qquad \text{(I)}$$

In this complex the atoms of both metals are connected through a chlorine atom, with the titanium being partially alkylated. Charge separation occurs in the complex: titanium acquires a positive charge, aluminum a negative one. The role of the aluminum alkyl in the catalytic system is reduced to alkylating titanium and imparting to it a formal or potential charge. Alkylation of titanium is of great importance, since upon alkylation there occurs partial rehybridization of the valence electrons of titanium from the d^3s state into the s^3p state (11), which, according to the calculations of Pilcher and Skinner (12), promotes the formation of a stronger bond. In the $d^3s \to sp^3$ transition, the d-orbitals of titanium are freed and can be used for accepting the π-electrons of the triple bond of acetylene molecules.

$$[Cl{-}Ti(R){-}Cl]^{-} + 3\,RC{\equiv}CR \longrightarrow \left[\begin{array}{c}\text{coordination complex of three RC}{\equiv}\text{CR molecules}\\ \text{with TiRCl}_2\end{array}\right] \longrightarrow C_6R_6 + [Cl{-}Ti(R)$$

Fig. 1

Complex I is strongly polarized (according to the data of a number of authors (13)—up to ionization). The active "fragment" (in the limiting case, the cation) of the complex is $[TiRCl_2]$. This "fragment" or ion may retain a tetrahedral structure characteristic of both d^3s and sp^3 hybridization, but without one of the vertices. Since titanium in higher oxidation states is characterized by coordination number 6, the titanium atom in the "fragment" is capable of accepting into its coordination sphere three molecules of acetylene (Fig. 1).

$$\text{coordination complex of } TiRCl_2 \text{ with three acetylene molecules} \longrightarrow \text{substituted benzene}$$

Fig. 2

The complex acquires an octahedral, or nearly octahedral, configuration characteristic of coordination number 6, in which three acetylene molecules can be arranged in one plane. As a result, the subsequent union of the three molecules into a ring is facilitated (Fig. 2), with rehybridization of the carbon atoms of acetylene from the *sp* to the sp^2 state, which is promoted by the formation of a π-complex with the metal $^{(14)}$. The benzene molecule obtained upon ring closure is bound to the central atom of the complex even less strongly than the acetylene ligands, and is readily cleaved off or displaced

new acetylene molecules. Thus, the process proceeds as a π-complex multicenter reaction (according to Schrauzer' s classification).

An alternative mechanism of cyclotrimerization may be the incorporation of two acetylene molecules into the coordination sphere of titanium, the intermediate formation of a cyclobutadiene ring, and a peculiar Diels—Alder reaction upon its interaction with a third acetylene molecule (cf., for example, (11)). The difference between this scheme and the one set forth above is small. The Diels—Alder reaction, according to Syrkin (15), also has the character of a multicenter reaction and proceeds through a cyclic transition complex. The decisive argument in favor of one or the other scheme could be provided by data on the kinetics of cyclotrimerization. However, we have not yet been able to obtain such data because of the very high rate and strong exothermicity of the process. For the same reason, the literature contains no data on kinetic studies of cyclotrimerization on other catalysts.

It seems to us that the views developed here could prove useful not only in considering the mechanism of the cyclic trimerization of acetylenes on Ziegler catalysts, but also for interpreting data on the linear polymerization of olefins, diolefins, and acetylenes on the same catalysts. This supposition finds some confirmation in the observations of Bresler, Dolgoplosk, and Kropacheva (16) on the copolymerization of isoprene with divinyl and of Korotkov (17) on the polymerization of styrene, and also has a number of features in common with the views developed by Furukawa (18) on the multicenter coordination mechanism of stereoregular polymerization; however, it still requires serious verification.

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CITED LITERATURE

1. Berthelot, C. R., **62**, 905 (1866). N. Zelinsky, Ber., **57**, 264 (1924); N. D. Zelinsky, ZhRKhO, **55**, 140 (1923).
2. W. Reppe, W. J. Schweckendick, Lieb. Ann. Chem., **560**, 104 (1948).
3. L. S. Meriwether, E. C. Colthup et al., J. Org. Chem., **26**, 5155 (1961).

4. G. N. Schrauzer, Chem. Ber., **94**, 1403 (1961).

5. W. Hübel, E. H. Braye et al., J. Inorg. and Nucl. Chem., **9**, 204 (1959). W. Hübel, C. H. Hoogzand, Chem. Ber., **93**, 103 (1960).

6. H. H. Zeiss, W. Herwig, U. S. Pat., No. 2953610; RZhKhim, **21 96**, 1961. H. H. Zeiss, M. Tsutsui, U. S. Pat., No. 2980741; RZhKhim, **10 96**, 1962.

7. W. R. Smith, Brit. Pat., No. 802510 (1958). Chem. Abstr., **53P**, 8070 (1959). B. Franzus, P. I. Canterino, R. A. Wickliffe, J. Am. Chem. Soc., **81**, 1514 (1959). E. F. Lutz, J. Am. Chem. Soc., **83**, 2551 (1961).

8. B. O. Reikhsfeld, K. L. Makovetskii, L. L. Erokhina, ZhOKh, **32**, 653 (1962).

9. K. L. Makovetskii, B. O. Reikhsfeld, L. L. Erokhina, ZhOKh, **34**, No. 3 (1964).

10. B. O. Reikhsfeld, Dissertation, L., 1949.

11. H. H. Zeiss, Organometallic Chemistry, N. Y., 1960, p. 429.

12. G. Pilcher, H. A. Skinner, J. Inorg. and Nucl. Chem., **7**, 8 (1958).

13. E. Duck, J. Polym. Sci., **34**, 86 (1959); A. Malatesta, J. Polym. Sci., **51**, 45 (1961).

14. G. N. Schrauzer, S. Eichler, Chem. Ber., **95**, 550 (1962).

15. Ya. K. Syrkin, I. I. Moiseev, Uspekhi Khim., **27**, 1321 (1958).

16. L. S. Bresler, B. A. Dolgoplosk, E. N. Kropacheva, DAN, **149**, 595 (1963).

17. A. A. Korotkov, Abstracts of Reports, Conference of the Institute of High-Molecular Compounds, Academy of Sciences of the USSR, L., 1963, p. 39.

18. Yu. Furukawa, Khim. i tekhn. polim., 1963, p. 83.

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