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Cyclotrimerization of Phenylacetylene Catalyzed by Halides of Niobium and Tantalum

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Halides of niobium and tantalum (NbX_5, TaX_5; X=Cl, Br, F) catalyzed the cyclotrimerization of phenylacetylene in hydrocarbon and chlorinated hydrocarbon solvents at 0—90 °C. When $NbCl_5$ and $TaCl_5$ were used as catalysts, two cyclic trimers, 1,2,4- and 1,3,5-triphenylbenzenes were exclusively formed, and their ratio varied from 17:83 to 94:6 depending on reaction conditions. The cyclotrimerization was more selective than those by other known catalysts. The cyclotrimerization by $NbBr_5$ and $TaBr_5$ occurred in a similar manner, but the reaction was less selective than that catalyzed by $NbCl_5$ and $TaCl_5$. Not only cyclotrimerization but also linear oligomerization proceeded by NbF_5 and TaF_5 as catalysts. The results obtained were discussed together with the linear polymerization of phenylacetylene catalyzed by $MoCl_5$ and WCl_6.

The cyclotrimerization of acetylenes is catalyzed by various transition-metal complexes to give benzene derivatives.[1] The best known catalysts for this reaction are Ziegler-type catalysts and Ni(0) complexes. The catalysts for the cyclotrimerization of acetylenes are usually either mixtures of a transition-metal compound and a reducing agent, or organo-transition metal complexes in which the metals are in a reduced state.

The cyclotrimerization of phenylacetylene by Ziegler-type catalysts gives a mixture of comparable amounts of 1,2,4- and 1,3,5-triphenylbenzene (1,2,4- and 1,3,5-TPB's).[2] The reaction catalyzed by Ni(0) complexes mainly provides a mixture of 1,2,4-TPB and linear oligomers.[3] A cobalt complex is reported to afford mainly 1,2,4-TPB in high yield.[4] In general, most catalysts so far reported for the cyclotrimerization of phenylacetylene show no high selectivity with respect to both cyclization and substituent position. Pure 1,3,5-TPB has been obtained by the acid-catalyzed condensation of acetophenone,[5] and pure 1,2,4-TPB by the reaction of 2,5-diphenylthiophene 1,1-dioxide with phenylacetylene.[6]

There has been a patent on the cyclotrimerization of acetylene and 1-alkyne by use of $NbCl_5$ and $TaCl_5$. The selectivity, however, has not been examined in detail.[7]

We have found that phenylacetylene is polymerized by the chlorides of molybdenum and tungsten to give selectively a linear high polymer (*MW* 5000—15000).[8] From this point of view, it is of great interest what reactions of phenylacetylene take place in the presence of the halides of niobium and tantalum.

The present paper describes the cyclotrimerization and linear oligomerization of phenylacetylene catalyzed by halides of niobium and tantalum (NbX_5, TaX_5; X=Cl, Br, F).

Experimental

Reagents. Phenylacetylene was prepared by the bromination of styrene and the subsequent dehydrobromination, according to the literature method.[9] The halides of niobium and tantalum (Alfa-Ventron, purity >99%) were used without further purification. Solvents were purified by the usual methods.

Procedures. Cyclotrimerization was carried out under a dry nitrogen atmosphere in a 30 ml Erlenmeyer flask equipped with a three-way stopcock, at $[PA]_0=1.0$ mol dm^{-3} and [Cat]=10 mmol dm^{-3} (PA: phenylacetylene, Cat: catalyst). The reaction was started by adding the monomer solution to the catalyst solution at a given temperature, and terminated by adding ammoniacal methanol. The consumption of monomer was determined by gas chromatography. The catalyst residue was removed by washing the reaction mixture with aqueous hydrochloric acid and water, and volatile materials were evaporated. The product obtained was dried under vacuum.

The number-average molecular weight of the products was measured on a Hitachi 117 molecular weight apparatus. The gel permeation chromatograms of the products were observed on a JASCO FLC-A700 chromatograph (column JSP 101, polystyrene gel, xl; eluent $CHCl_3$). The IR spectra of the produts were measured on a Shimadzu IR 27G spectrophotometer in KBr disks. The ratio of 1,2,4-TPB to 1,3,5-TPB in the products was determined from the ratios of D_{1600}/D_{1070}, D_{1495}/D_{1070}; and D_{1475}/D_{1070} in the IR spectra. Here, the absorption at 1070 cm^{-1} appears commonly in both 1,2,4- and 1,3,5-TPB's, while the absorptions at 1600, 1495, and 1475 cm^{-1} are characteristic of either 1,2,4- or 1,3,5-TPB. The ^{1}H NMR spectra were recorded on a JEOL JNM-MH 60 spectrometer.

Results and Discussion

Cyclotrimerization of Phenylacetylene Catalyzed by $NbCl_5$ and $TaCl_5$. The cyclotrimerization of phenylacetylene was performed with $NbCl_5$ and $TaCl_5$ in hydrocarbon and halogenated hydrocarbon solvents at 60 °C for 1 h ($[PA]_0=1.0$ mol dm^{-3}, [Cat]=10 mmol dm^{-3}). The reaction was fast and exothermic, and usually proceeded quantitatively. No reaction took place in such solvents as 2-butanone, acetonitrile, ethyl acetate, 1,4-dioxane and nitrobenzene.

The gel permeation chromatogram of the product showed only a peak at the position corresponding to the cyclic trimers. The number-average molecular weight of the product obtained agreed to the value for the trimers (306.4) within an error of 2%. These results indicate that no product other than the trimers was formed. Further, the IR, UV, and ^{1}H NMR spectra of the product were compared with those of authentic 1,2,4- and 1,3,5-TPB's, which revealed that the product was exclusively a mixture of 1,2,4- and 1,3,5-TPB's.

Table 1. 1,2,4-TPB content (%) of product in the cyclotrimerization of phenylacetylene catalyzed by $NbCl_5$ and $TaCl_5$[a)]

	C_6H_6	$C_6H_5CH_3$	n-C_6H_{14}	$\overline{\lfloor\text{-}(CH_2)_6\text{-}\rfloor}$	CCl_4	$CHCl_3$	$(CH_2Cl)_2$	C_6H_5Cl	o-$C_6H_4Cl_2$
$NbCl_5$	90	85	81	80	79	77	86	89	90
$TaCl_5$	70	51	42	45	40	40	48	68	54

a) $[PA]_0 = 1.0$ mol dm^{-3}, $[Cat] = 10$ mmol dm^{-3}, 60 °C (50 °C for $CHCl_3$), 1 h.

Table 2. 1,2,4-TPB content (%) of product in the cyclotrimerization of phenylacetylene catalyzed by $NbBr_5$ and $TaBr_5$[a)]

	C_6H_6	$C_6H_5CH_3$	n-C_6H_{14}	$\overline{\lfloor\text{-}(CH_2)_6\text{-}\rfloor}$	CCl_4	$CHCl_3$	$(CH_2Cl)_2$	C_6H_5Cl	o-$C_6H_4Cl_2$
$NbBr_5$	71	60	62	70	66	65	62	69	71
$TaBr_5$	61	58	50	51	49	60	54	57	69

a) $[PA]_0 = 1.0$ mol dm^{-3}, $[Cat] = 10$ mmol dm^{-3}, 60 °C (50 °C for $CHCl_3$), 1 h.

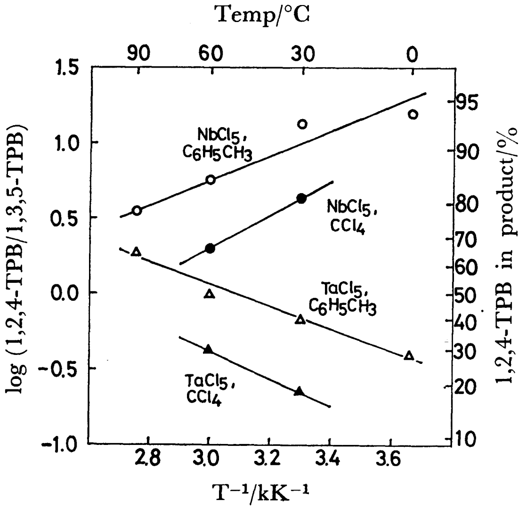


Fig. 1. Arrhenius plots of the ratio of 1,2,4-TPB to 1,3,5-TPB in the cyclotrimerization of phenylacetylene catalyzed by $NbCl_5$ and $TaCl_5$.
$[PA]_0 = 1.0$ mol dm^{-3}, $[Cat] = 10$ mmol dm^{-3}.

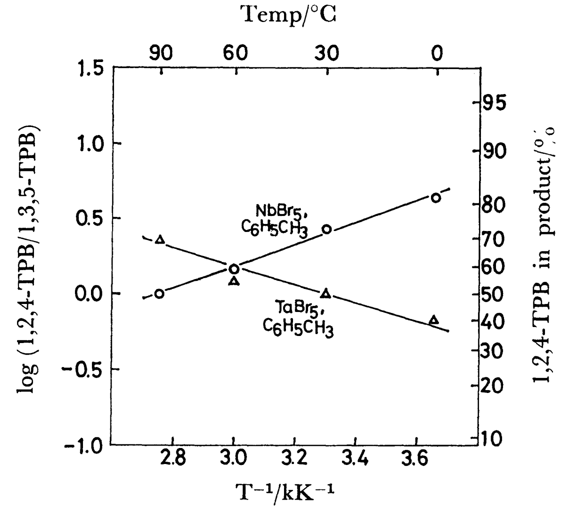


Fig. 2. Arrhenius plots of the ratio of 1,2,4-TPB to 1,3,5-TPB in the cyclotrimerization of phenylacetylene catalyzed by $NbBr_5$ and $TaBr_5$.
$[PA]_0 = 1.0$ mol dm^{-3}, $[Cat] = 10$ mmol dm^{-3}.

Table 1 shows the 1,2,4-TPB content of product expressed in %. In general, $NbCl_5$ gave a product containing more 1,2,4-TPB than $TaCl_5$ did. With regard to solvent, benzene gave a product having the highest 1,2,4-TPB content with both catalyst. On the other hand, 1,2,4-TPB was the least in carbon tetrachloride and in chloroform as solvents. This solvent effect on the product composition is not simply explained, for example in terms of solvent polarity. As seen in Table 1, the 1,2,4-TPB content varied in a range of 40—90% depending on the types of catalyst and solvent.

The dependence of the product composition on reaction temperature was investigated. Toluene and carbon tetrachloride were employed as two different types of solvents. As seen in Fig. 1, good linear relationships were observed in the Arrhenius plots. When $NbCl_5$ was used as a catalyst, the 1,2,4-TPB content of product increased with decreasing reaction temperature. For instance, it was 94% at 0 °C in toluene. $NbCl_5$ is thus an excellent catalyst for the synthesis of 1,2,4-TPB, especially when used at low temperature. On the other hand, the lower the temperature, the less the 1,2,4-TPB content when the $TaCl_5$ catalyst was used. For example, 1,2,4-TPB was 17% at 30 °C in carbon tetrachloride. Thus, the present cyclotrimerizations at low temperature are much more selective than those so far reported. Especially, the cyclotrimerization by $NbCl_5$ at low temperature seems to be a useful method of synthesizing 1,2,4-TPB, though 1,3,5-TPB can be easily prepared by the acid-catalyzed condensation of acetophenone.[5)]

It was confirmed by the following two ways that the product composition in the present cyclotrimerization is kinetically controlled: i) The product composition did not depend on the conversion with both $NbCl_5$ and $TaCl_5$ as catalysts, and ii) 1,2,4-TPB did not isomerize to 1,3,5-TPB in the presence of $TaCl_5$ under the same conditions as those of cyclotrimerization, and *vice versa* with $NbCl_5$.

Cyclotrimerization of Phenylacetylene Catalyzed by $NbBr_5$ *and* $TaBr_5$. Cyclotrimerization of phenylacetylene was performed with $NbBr_5$ and $TaBr_5$ as catalysts in hydrocarbons and halogenated hydrocarbons. The reaction was usually quantitative within 1 h; the reaction rate was similar to or a little slower than that catalyzed by $NbCl_5$ and $TaCl_5$. It was confirmed in the same way as in the case of the chloride catalysts that the product comprised only the two cyclic trimers.

The 1,2,4-TPB content of product is listed in Table 2. Usually $NbBr_5$ produced more 1,2,4-TPB than $TaBr_5$ did. This is the same tendency as observed in the reaction by the chloride catalysts, but the difference in the compositions with $NbBr_5$ and $TaBr_5$ was smaller. The 1,2,4-TPB content only varied in a range of 49—71% in various solvents examined, when $NbBr_5$ and $TaBr_5$ were used.

Figure 2 shows the dependence of the product composition on temperature. As in the chloride-catalyzed reaction, good linear relationships held in the Arrhenius plots. The 1,2,4-TPB content of product obtained with $NbBr_5$ increased with decreasing temperature, whereas the opposite trend was observed with $TaBr_5$. This tendency is also the same as that found in the chloride catalyst systems.

Thus the bromide catalysts behave in a similar manner to the chloride catalysts. The effects of catalyst metal and solvent on the product composition, however, are smaller in the bromide-catalyzed reaction.

Cyclotrimerization and Linear Oligomerization of Phenylacetylene Catalyzed by NbF_5 and TaF_5. The gel permeation chromatogram of the product obtained with NbF_5 and TaF_5 showed many peaks due to oligomers as well as a peak due to the cyclic trimers. Since the molecular weights of these oligomers ranged from 204 (dimer) to several thousands and they are colored dark red, their structure seems to be linear. The ^1H NMR and IR spectra also indicated the formation of not only the cyclic trimers but also of compounds whose structure was similar to that of the linear polymer produced with WCl_6. Consequently, it is concluded that NbF_5 and TaF_5 catalyze not only cyclotrimerization but also linear oligomerization.

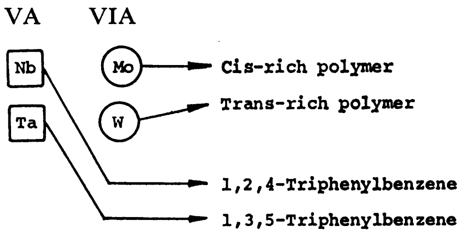
The ratio of the linear oligomers to the cyclic trimers in the product was tentatively determined from peak areas in the gel permeation chromatogram measured with a refractive index detector. As shown in Table 3, the linear oligomer content of product was higher in halogenated hydrocarbons than in paraffinic hydrocarbons. TaF_5 gave a product containing more linear oligomers than NbF_5 did. The conversion ranged from 45 to 100% under the reaction conditions shown in Table 3.

The product obtained with TaF_5 in ethylene dichloride virtually consisted of the linear oligomers. The ^1H NMR and IR spectra of the linear oligomers resembled those of a linear high polymer obtained with WCl_6. The number-average molecular weight was 1400.

TABLE 3. LINEAR OLIGOMER CONTENT (%) OF PRODUCT IN THE REACTION OF PHENYLACETYLENE CATALYZED BY NbF_5 AND TaF_5[a)]

	$n\text{-}C_6H_{14}$	$\overline{\text{-}(CH_2)_6\text{-}}$	CCl_4	$CHCl_3$	$(CH_2Cl)_2$
NbF_5	30	26	55	41	79
TaF_5	59	51	100	91	100

a) $[PA]_0$ 1.0 mol dm^{-3}, [Cat] = 10 mmol dm^{-3}, 60 °C (50 °C for $CHCl_3$), 24 h.



Scheme 1.

When benzene and toluene were used as solvents, the yield of product did not agree with the consumption of reactant, but the former exceeded the latter. The product from a toluene solution proved to have tolyl group according to its ^1H NMR spectrum. These findings indicate that solvent-incorporated linear oligomers were formed. These oligomers seem to have been produced by the Friedel-Crafts alkylation, which suggests that the linear oligomerization proceeds *via* a cationic species. This is expected because the fluorides of niobium and tantalum are stronger Lewis acids than their chlorides and bromides are.

Characteristics of the Present Cyclotrimerization. Two characteristics are pointed out for the present cyclotrimerization.

One is that no reducing agent has to be added though the metals of NbX_5 and TaX_5 are in their highest oxidation state. This contrasts with the case of Ziegler-type catalysts, in which a reducing agent such as triethylaluminum is required for an active species to be formed. The metals of some metal halides such as $NbCl_5$, $MoCl_5$, and WCl_6 can be reduced by olefins and acetylenes.[10)] This reduction occurs through the halogenation of olefins and acetylenes. Thus, it is assumed that NbX_5 and TaX_5 are at first reduced by phenylacetylene in the present reaction.

The second characteristic is the striking contrast to the linear polymerization of phenylacetylene catalyzed by $MoCl_5$ and WCl_6. The relationships between catalyst metals and products (exclusive or principal) are shown in Scheme 1: The chlorides of niobium and tantalum brought about only cyclotrimerization. Further, there was a tendency for $NbCl_5$ to give 1,2,4-TPB as the major product and for $TaCl_5$ to give 1,3,5-TPB. On the other hand, $MoCl_5$ and WCl_6 polymerize phenylacetylene very effectively to give linear high polymers.[8)] The $MoCl_5$ catalyst provides a *cis*-rich polymer, while WCl_6 gives a *trans*-rich polymer. No cyclic trimer is formed in this polymerization at all. It is of great interest that the kind and structure of the product critically depend on the group and period of the metal in these reactions. On the other hand, Ziegler-type catalysts and Ni(0) complexes can catalyze both cyclotrimerization and linear polymerization, and it is often difficult to selectively bring about either of the two reactions with these catalysts.

It has been clarified that the cobalt-catalyzed cyclotrimerization of acetylenes proceeds *via* a metallocyclopentadiene (metallole).[11,12] Since the present cyclotrimerization is also a coordination reaction and behaves in some respects similarly to the cobalt-catalyzed reaction, the present reaction might proceed by a similar mechanism. A further study on reaction behavior, mechanism, and intermediates is in progress.

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