

EFFECT OF REACTION CONDITIONS ON THE ACTIVITY OF THE $WCl_6 + (CH_3)_4Sn$ CATALYTIC SYSTEM IN THE METATHESIS OF METHYL 10-UNDECENOATE

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Received February 12th, 1985

In contrast to published data, metathesis of methyl 10-undecenoate is found to proceed with a good yield even if the ester is present in a high excess with respect to the catalyst, if the former is first reacted with WCl_6 to form a complex (owing to which the reaction mixture acquires red colour), and only then the metathesis is started by adding $(CH_3)_4Sn$. Moreover, satisfactory degrees of conversion are only attained if the catalyst concentration is low enough so that the deactivation of the active centres is slowed down.

Published data show that metathesis of functionalized olefins (esters of unsaturated acids, alkenyl esters of acids, unsaturated amines, *etc.*) occur with reasonable yields only if catalyst is present in relatively large amounts with respect to substrate¹⁻³. This is explained so that a high fraction of catalyst is deactivated by interaction with the polar substituent. This fact is a serious obstacle to the application of metathesis of functionalized olefins in synthesis on an industrial scale. Ester-to- WCl_6 ratios in excess of 100 have been probably never used in homogeneous metathesis of esters of unsaturated acids; ratios of 20–70 are mostly employed.

We have shown⁴ that, in agreement with the results of Otton and coworkers concerning the co-metathesis of methyl oleate with 2-hexene⁵, the final degree of conversion in the metathesis of methyl 10-undecenoate catalyzed by the $WCl_6 + (CH_3)_4Sn$ system can be affected favourably by allowing tungsten hexachloride to react with the ester before tetramethyl tin is added. This reaction of WCl_6 with methyl 10-undecenoate in benzene proceeds rather slowly and is accompanied by marked colour changes (from dark violet to red and later to green). Infrared spectra revealed that the first stable intermediate, responsible for the red colour, is the WCl_6 -ester complex⁶. The dependence of the resulting conversion on the time of the preceding reaction of WCl_6 with the ester has a maximum which probably corresponds to the formation of the complex mentioned. At the ester-to- WCl_6 ratio 45, the maximum degree of conversion was attained if the preceding reaction was allowed to proceed for 3 h at 60°C (the colour of the reaction mixture changed to wine-red). The aim of the present work was to seek how the preceding reaction of WCl_6 with ester affects the metathesis if the ester is present in a high excess with respect to the catalyst.

EXPERIMENTAL

The reactants were added to the reactor and all the reactions were conducted under argon or in vacuum. All reaction components were perfectly dried and degassed. The acid value of the ester never exceeded 0.03. The solvent (benzene), methyl 10-undecenoate and the components of the catalyst were purified as previously⁴. The course of the metathesis was followed by monitoring the amount of ethylene evolved. The reaction products were analyzed gas chromatographically⁴.

RESULTS AND DISCUSSION

The major products of metathesis of methyl 10-undecenoate are ethylene and dimethyl 10-eicosene-1,20-dioate (C_{22} diester). C_{10} through C_{14} monoesters and C_{18} through C_{21} diesters are also formed in minor quantities due to isomerization of the starting ester.

Fig. 1 shows the conversion curves (amounts of gas evolved *vs* time) for three experiments with the ester-to-tungsten ratio 180. Different mixing procedures and catalyst concentrations were used in the experiments. Their conditions and the reaction yields are given in Table I. The highest catalyst activity was observed for experiment No 1. In this experiment, WCl_6 was allowed to react with the ester (initial tungsten concentration $c_w^0 = 12.5 \text{ mmol l}^{-1}$) for 30 min at room temperature; the solution turned red. Then the solution was additionally diluted with benzene and $(CH_3)_4Sn$ was added to start the metathesis. In experiment No 2, the reaction of WCl_6 with ester virtually could not occur because the reactants were present in lower concentrations and the reaction time was too short. (It should be noted that this reaction does not occur to an appreciable extent after $(CH_3)_4Sn$ has been added because its rate is several orders of magnitude lower than that of the reaction of $WCl_6 + (CH_3)_4Sn$, ref.⁷). The effect of the preceding reaction on the metathesis is documented by the differences in the reaction rates and the maximum degrees

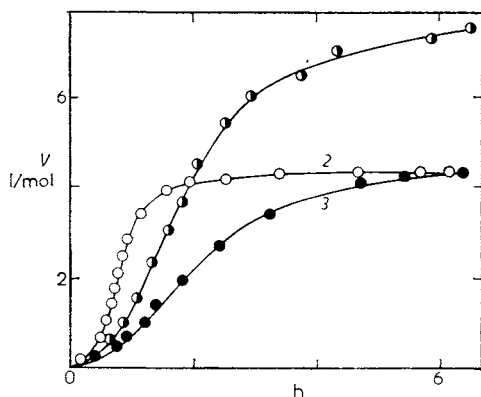


FIG. 1
Time dependence of gas evolution (STP) per unit substrate amount. Ester-to-W-to-Sn ratio 180 : 1 : 4, solvent: benzene, metathesis temperature 60°C, other conditions and curve labelling as in Table I

of conversion in experiments No 1 and 2. In experiment No 3, the components were added at 60°C in order WCl_6 , ester, $(\text{CH}_3)_4\text{Sn}$. Although the time between the mixing of WCl_6 with ester and the addition of $(\text{CH}_3)_4\text{Sn}$ was as short as 5 min, a great amount of the complex was formed as indicated by the red colour of the system.

TABLE I

Characterization of the metathesis of methyl 10-undecenoate preceded by the reaction of the ester with WCl_6 ; ester-to-W-to-Sn ratio 180 : 1 : 4, solvent: benzene, temperature during metathesis 60°C

Experiment No	Reaction of ester with WCl_6			Colour ^a	Metathesis		
	$c_{\text{WCl}_6}^0$ mmol l^{-1}	$t, ^\circ\text{C}$	time min		c_{W} mmol l^{-1}	degree of conversion ^b	selectivity ^c
1	12.5	25	30	red	3.3	59	0.9
2	3.3	25	5	violet	3.3	40	0.9
3	10	60	5	red	10	36	1
4	WCl_6 added as the last component			—	10	20	0.7

^a Colour of solution before addition of $(\text{CH}_3)_4\text{Sn}$; ^b in 6 h; ^c 2 times number of mol of C_{22} diester / number of mol of reacted monoester.

TABLE II

Effect of reaction conditions of the catalyst activity at a high excess of ester. Conditions as in Table I

Experiment No	Ester-to- WCl_6 molar ratio	Ester- WCl_6 reaction ^a		Metathesis		
		c_{W}^0 mmol l^{-1}	time min	c_{W} mmol l^{-1}	degree of conversion ^b %	selectivity
1	360	7.1	10	2.8	43	0.98
2	360	10	5	8.3	8	0.9
3	540	2.9	10	1.8	40	0.75
4	540	WCl_6 added last		2.1	2	—
5	720	2.5	5	1.6	30	0.7

^a at 20°C ; ^b after 6 h.

In contrast to experiment No 1, the mixture was not diluted before the metathesis. The initial metathesis rate was considerably higher than in the two preceding cases, the final degree of conversion, however, was again appreciably lower than in experiment No 1 due to the rapid drop of the catalyst activity. When the reaction preceding the metathesis was omitted (WCl_6 was the last component added) and the metathesis was carried out at higher concentrations, as in experiment No 3, the degree of conversion further decreased (experiment No 4).

The experiments thus indicate that the final degree of conversion can be affected favourably by allowing the reaction of the ester with WCl_6 to precede and by adjusting properly the reactant concentrations for the metathesis itself. The results given in Table II demonstrate that if these conditions are met, reasonable degrees of conversion of methyl 10-undecenoate can be attained even if the ester is present in a high excess with respect to WCl_6 . The reaction of these two components was allowed to proceed at room temperature for a time necessary for the colour to change to red. Then, immediately, the mixture was diluted with an additional portion of benzene and the metathesis was initiated by adding $(\text{CH}_3)_4\text{Sn}$ and performed for 6 h at 60°C . The ethylene evolution curves show that the degree of conversion observed after this time is the maximum attainable in each particular experiment. Table II also includes experiments where the reaction before the metathesis or the additional dilution with solvent was omitted. Clearly, both of the above conditions must be satisfied, *i.e.*, the reaction of ester with WCl_6 must be allowed to proceed to a sufficient degree and the initial concentration of tungsten for the metathesis itself must be held relatively low ($c_w^0 = 1 - 3 \text{ mmol l}^{-1}$).

This is consistent with some results obtained recently. It has been shown that oxygen ligands have a favourable effect on the metathesis yields⁸. The degree of conversion in metathesis of alkenes has been observed to decrease with increasing concentration of $\text{WCl}_6 + \text{R}_4\text{Sn}$ catalyst⁹, which is assumed to be due to bimolecular decay of the catalytically active centres. Since the ester can interact not only with tungsten hexachloride but also with the various products of its reaction with tetramethyl tin, including the catalytically active carbene complexes, and this interaction can hardly be monitored, a comprehensive explanation of the effects observed cannot be thus far presented. Clearly, however, the catalyst-ester interaction need not inhibit invariably the metathesis, and metathesis of esters of unsaturated acids even at high substrate-to-catalyst ratios is in principle not impossible.

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Translated by P. Adámek.