Generation of Olefin Metathesis Catalysts from $W(CO)_6$ and Group IVa Metal Halides under Photochemical Conditions[1)]

Megumu Nagasawa, Kiyoshi Kikukawa, Makoto Takagi, and Tsutomu Matsuda
Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

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Irradiation of a solution of $W(CO)_6$ and group IV_a metal halides in benzene by UV light gave the olefin metathesis catalysts, of which the combination $W(CO)_6$–$TiCl_4$ was the most effective. Association of the coordinatively unsaturated $W(CO)_5$ and $TiCl_4$ was suggested to be a key step in the formation of a catalytically active complex. A survery was also made for other $W(CO)_6$–MX_n combinations for photo-generation of metathesis catalyst.

Much effort has been made in search for the olefin metathesis catalysts and elucidation of the reaction mechanism.[2,3)] A mechanism involving intermediate formation of carbene complex has been strongly suggested.[3)] However, in view of catalyst preparation, most of the effective catalysts appear to consist of W or Mo compounds in their medium oxidation states. A combination such as WCl_6–R_nAlCl_{3-n} is typical, where the former component is partially reduced by the latter during the course of preparation. As a new access to metathesis-active W species of medium oxidation state, photochemical energy can be used to activate the otherwise inactive combination between W compounds and the cocatalytic oxidizing or reducing components. Two possible combinations can be considered: i) $W(CO)_6$–MX_n, where MX_n is a transition metal halide in high oxidation state, and ii) WCl_6–ML_n, where ML_n stands for the metal complex in low oxidation state. The latter photosystem has so far been unsuccessful, but the former gave a number of new metathesis catalysts, the results of which are given in the present communication. A metathesis catalyst from photosystem has recently been reported by Krausz *et al.*[4)] and by Agapiou and McNelis,[5)] in which $W(CO)_6$–CCl_4 was irradiated.

Results

A solution of $W(CO)_6$ and MX_n, each 4.3×10^{-3} M in benzene, was irradiated by a high pressure mercury lamp at room temperature for 1 h. To the resulting solution was added 260 fold molar amount of 1-octene, and the mixture was stirred at 30 °C in the dark. The product was found to be a mixture of straight-chain internal olefins of carbon number between 3 and 14. It is obvious that the catalysts effected both isomerization and metathesis of the substrate olefin. The result of the analysis of the product after 18—20 h reaction is summarized in Table 1. The yields of C_3 to C_7 olefins are not included, since the determination of these olefins was less reliable under our experimental conditions. $TiCl_4$ was the most effective cocatalyst, followed by $ZrCl_4$ and $HfCl_4$. No metathesis catalyst from $W(CO)_6$-group IVa metal halides has so far been reported. The catalyst mixture before the addition of olefin was brownish and homogeneous for $TiCl_4$, but it was slightly turbid for $ZrCl_4$ and $HfCl_4$ because of their low solubility in benzene. In each case, the turbidity gradually increased in the reaction with olefin. The catalyst activity of $W(CO)_6$–$TiCl_4$ was roughly comparable to that of $W(CO)_6$–CCl_4, the major side reactions being the isomerization of olefin in the former and the addition of CCl_3–Cl component to olefin in the latter system.[6)] It should be emphasized that all these MX_n compounds either alone or as combined with $W(CO)_6$ showed no activity for metathesis unless the mixture with $W(CO)_6$ was irradiated. Among other MX_n compounds tested, $AlCl_3$, $SnCl_4$ and $TaCl_5$ were found effective, but the activity of the resulting catalyst was slight at room temperature. The metal salts, $MoCl_5$, $NbCl_5$, $VOCl_3$, VCl_4, $(C_5H_5)_2TiCl_2$, $FeCl_3$, $ZnCl_2$, and $AgClO_4$ were totally inactive under comparative reaction conditions.

Table 1. Catalysis of photosystem $W(CO)_6$–MX_n in the metathesis of 1-octene[a)]

	Yield of olefins, %[b)]					
MX_n	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
$TiCl_4$	12	2	2	4	10	11
$ZrCl_4$	9	1	1	1	5	9
$HfCl_4$	4	tr	tr	tr	tr	2
WCl_6[c)]	24	tr	tr	2	6	7

a) Catalyst solution: Unless otherwise noted, 4.3×10^{-3} M $W(CO)_6+4.3\times10^{-3}$ M MX_n in benzene was irradiated for 1 h by high pressure mercury lamp through a pyrex filter at 20—25 °C. Metathesis reaction: $W(CO)_6$/1-octene (mol ratio) = 260, 18—20 h at 30 °C in the dark after addition of olefin.
b) Yield: (mol product/mol 1-octene added to catalyst solution) × 100; tr, trace. C_n : linear internal olefins in trans coefiguration with n carbon atoms. c) $[W(CO)_6]=4.3\times10^{-3}$ M. $W(CO)_6 : WCl_6$: 1-octene = 1 : 0.5 : 260. The reaction mixture was refluxed for 4 h after addition of olefin.

The $W(CO)_6$–WCl_6 system was studied in some detail. Due to the strong Lewis acidity of WCl_6, this photosystem gave only C_8-substituted benzenes (Friedel-Crafts alkylation, 74%) and oligomers from 1-octene (22%) under the standard conditions. Alkylation of the aromatic solvent was also the major reaction in the absence of irradiation. Even under irradiation, a proper selection of parameters, such as the concentration of catalyst or olefin, was required to suppress the alkylation and to make the metathesis activity observable. Low $WCl_6/W(CO)_6$ ratio (<0.5) combined with high concentration of olefin appeared to favor metathesis. No alkylation was observed under conditions of the run given in Table 1. A competition between alkylation and metathesis depending on the catalyst concentrations as well as on the olefin concentration has been reported by Hocks *et al.*[7] The general trends observed in the present system were similar to those reported. The effect of irradiation time was not critical in our conditions so far as the irradiation time of 40—70 min was adopted. Low pressure mercury lamp could be used instead of the high pressure lamp, but this introduced the formation of hydrogen chloride, and the products became more complex.[8]

In order to reduce the complexity due to isomerization of the terminal olefin, 3-heptene was subjected to metathesis with $W(CO)_6$–TiX_4 catalyst under conditions similar to those in Table 1. The effect of the isomerization could not be eliminated, the products containing the olefins derived from 2-heptene in addition to those from 3-heptene. Figure 1 illustrates a typical conversion-time profile. The reaction is seen to reach some "equilibrium" olefin composition after 6 h. The yields of complementary olefins, *e.g.*, hexene and octene, were in 1 : 1 molar ratio. Similar conversion-time profiles are shown for various catalyst compositions in Fig. 2, where only the combined yields of hexenes and octenes are indicated. The combination, $W(CO)_6$–$TiCl_4$, was more effective than $W(CO)_6$–$TiBr_4$. A change in the ratio $TiCl_4/W(CO)_6$ exerted considerable influence on the rate of metathesis reaction. With the optimum ratio at 1.0, both the increase and decrease in the ratio resulted in lowering the catalyst activity. A similar behavior was also confirmed in the reaction of 1-octene. The increase in the total catalyst concentration increased the reaction rate as expected, but in a complicated manner. The catalyst underwent a considerable temperature effect, the reaction not proceeding below 15 °C. The selectivity of the catalyst defined as per cent molar ratio of the combined yield of octenes and hexenes to the amount of the substrate heptene consumed was dependent on Ti/W ratio. The selectivity increased with the increase in Ti/W ratio, the effect being slight: $TiCl_4/W(CO)_6$ ratio, % selectively; 0.5, 57; 1, 63; 3, 72; 6, 71; 1 ($TiBr_4$ in place of $TiCl_4$), 60.

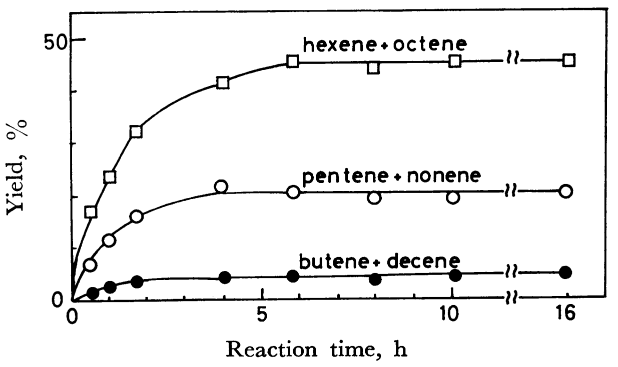

Fig. 1. Metathesis of 3-heptene by photosystem $W(CO)_6$-$TiCl_4$. Reaction conditions are similar to those in Table 1.
$[W(CO)_6]=4.3\times10^{-3}$ M; W : Ti : 3-heptene = 1 : 1 : 260; yield (%), (combined molar yield of complementary olenfins/mol 3-heptene added to the catalyst solution) × 100.

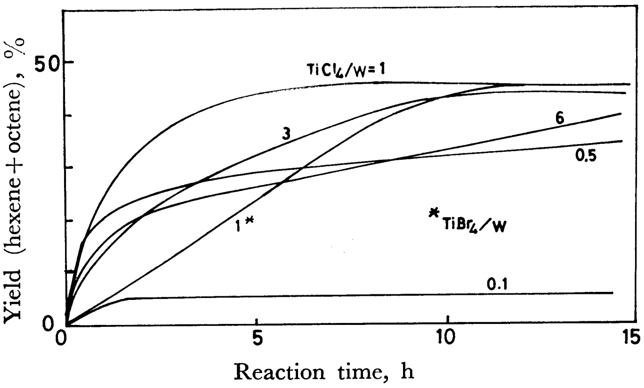

Fig. 2. Effect of catalyst composition on the rate of metathesis. Conditions are similar to those in Fig. 1 and Table 1.
$[W(CO)_6]=4.3\times10^{-3}$ M, 3-heptene/W = 260.

Discussion

One CO molecule dissociates from $W(CO)_6$ to from coordinatively unsaturated $W(CO)_5$ on irradiation by UV light.[9] Examination with a high pressure mercury lamp indicates that exactly one mole of carbon monoxide is evolved per mole of $W(CO)_6$ irrespective of the combination $W(CO)_6$–WCl_6 or $W(CO)_6$–$TiCl_4$. Since no further gas evolution was observed on prolonged irradiation, it is most probable that $W(CO)_5$ is the species involved in the formation of metathetically active complex. The observation that the maximum metathetic activity is obtained for the photosystem with $TiCl_4/W(CO)_6$ ratio of 1 suggests that 1 : 1 molar reaction of $TiCl_4$ and $W(CO)_5$ is essential for the formation of the caralyst. The catalyst solution was also prepared by adding $TiCl_4$ to the irradiated solution of $W(CO)_6$ in benzene, the activity being considerably lower than that by the standard procedure. Krausz *et al.* reported that the reaction of $W(CO)_5$ with CCl_4 produces $W(CO)_5Cl$ and this complex is an essential intermediate in the photochemically induced olefin metathesis (Reaction 1).[4] In our system, the over-all process may be delineated as in reaction 2, since the CO gas escapes out of the system. In reaction 1 the zero-valent tungsten complex $W(CO)_6$ was oxidized by CCl_4 to $W(CO)_5Cl$, in which tungsten is formally in +1 oxidation state. The oxidation state of tungsten in the association complex $W(CO)_5TiCl_4$ in Reaction 2 might be in +1.

$$W(CO)_6 \xrightarrow{h\nu} W(CO)_5 + CO \xrightarrow{CCl_4} W(CO)_5Cl + COCl_2 + \text{other products} \quad (1)$$

$$W(CO)_6 \xrightarrow{h\nu} W(CO)_5 \xrightarrow{TiCl_4} W(CO)_5TiCl_4 \quad (2)$$

If $W(CO)_5X$ species can be a potential precursor for the metathesis catalyst, several other routes to the catalytically active systems can be envisaged. The reaction of $W(CO)_6$ in benzene with halogens (I_2, ICl, ICl_3, and Br_2) in the presence or in the absence of light failed to produce the catalyst. The solution of $W(CO)_6$ in various halogenated organic solvents was irradiated as a possible extension of the photosystem $W(CO)_6$–CCl_4. Tetrachloroethylene, trichloroethylene and chlorobenzene[10] were found to give the catalyst of varying activity and selectivity depending on the irradiation conditions. *In situ* generation of the catalyst in which a $W(CO)_6$–MX_n–olefin mixture in benzene was irradiated, sometimes proved to be much more effective than the standard procedure. This suggests a possibility of improving the catalytic activity by proper selection of irradiation conditions and the catalytic cofactors which trap the photo-generated intermediate such as $W(CO)_5$.

Experimental

Materials. $W(CO)_6$ was purified by vacuum sublimation. Contaminations in WCl_6 were removed by sublimation at 200 °C. Commercial metal halides were used. 1-Octene and 3-heptene were distilled from sodium, and organic solvents were purified by standard methods. All these reagents were kept and handled under dry nitrogen.

Catalyst Solutions. Irradiation of benzene solution containing appropriate catalyst precursor ($W(CO)_6+MX_n$) was achieved either by a 100 W immersion-type high pressure mercury lamp (Riko UVL-100HA) equipped with a water-jacketted pyrex cell of 100 ml content or by an 80 W coil-type low pressure mercury lamp (Ushio UL1-8HQ) with a jacketted quartz cell of 100 ml content which was placed inside the coiled lamp. Eighty milliliters of the solution was utilized. After irradiation the required amount of olefin was added under stirring. Often, aliquots of the catalyst solution were transfered from the photo-cell to another reaction vessel, and the subsequent reaction was conducted in the latter. All the manipulations were carried out under dry nitrogen. Irradiation of the benzene solution containing both olefin and metal compounds, though effective for metathesis reaction, was not employed as a standard procedure, since it sometimes introduced more complexity in the product.

Metathesis Products. The progress of the reaction was monitored by GLC, using octadecane or octane as an internal standard. Metathesis products were isolated from the final reaction mixture and identified by the conventional spectroscopic method as well as by comparison with standard samples of saturated hydrocarbon after the products had been hydrogenated. All of the internal olefins showed a strong IR band at 960 cm^{-1} indicating *trans* configuration. In the work-up of the reaction mixture from 3-heptene, most of the solvent (benzene) had to be removed by refrigeration followed by filtration, before the products were subjected to preparative GLC.

References

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6) Detailed metathesis study with the photosystem $W(CO)_6$–CCl_4 is not available.[4,5] In the present study, $W(CO)_6$–CCl_4 system, in which the latter component was employed either as solvent or as an additive in benzene solution, was irradiated in a manner similar to that described for $W(CO)_6$–MX_n (see Experimental). The conditions were thus different from those reported. The addition of CCl_4 to olefin, which under our conditions proceeded to a comparable extent to metathesis in the reaction of 1-octene, was not described in the literature.[4,5]

7) a) L. Hocks, A. J. Hubert, and Ph. Teyssie, *Tetrahedron Lett.*, **1973**, 2719; b) L. Hocks, A. Noels, A. Hubert, and P. Teyssie, *J. Org. Chem.*, **41**, 1631 (1976).

8) In the following study, the high pressure lamp could be replaced by the low pressure lamp whenever the former proved to be effective, but the nature of the resulting catalyst was generally more complex.

9) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).

10) The reaction in chlorobenzene was possible only under irradiation with a low pressure lamp.