METATHESIS CATALYSTS - II
COMPETITIVE CHARACTER OF METATHESIS AND ALKYLATION REACTIONS CATALYSED BY WCl_6 - $C_2H_5AlCl_2$

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The olefins metathesis catalyst WCl_6 - $C_2H_5AlCl_2$ is a strong Lewis acid which promotes consequently secondary cationic reactions such as prototropic isomerization, alkylation of the aromatic solvent, and oligomerization. All these reactions have an influence on the metathesis thermodynamic equilibrium and, in some cases, can even mask completely the metathesis reaction.

It is therefore interesting to study the factors which influence the relative occurrence of these reactions. In this communication, we report the crucial importance of the molar ratio olefin : catalytic complex in a given solvent. In addition, in an aromatic solvent (benzene), there is a competition between olefin metathesis and aromatic alkylation; in this latter case, the benzene is a reactant : Consequently, the benzene:olefin ratio is also a determining factor which influences the course of these two reactions.

Experimentally, in benzene solution, we observe indeed competitive olefin metathesis and alkylation reactions for molar ratio olefin : catalyst of 70 to 400. For molar ratios greater than 400, olefin metathesis is the main reaction, alkylation being negligible. **Alternatively,**   for a molar ratio less than 70, alkylation is the only effective reaction (Fig. 1); moreover, in this latter case, the WCl_6 - $C_2H_5AlCl_2$ catalyst promotes the formation of monoalkylated products only after a few minutes[1].

Similar results are obtained with variable concentrations of the catalyst
system in a solution of olefin in benzene, or variable concentrations of the
olefin in a given solution of catalyst in benzene, at a benzene:olefin molar
ratio lower than 10; consequently, the molar ratio olefin:catalyst is an impor-
tant variable which influences the course of the two competitive metathesis and
alkylation reactions.

However, in the presence of increasing amounts of benzene (for an
olefin:catalyst ratio of 400) we observe again a competition between metathesis
and alkylation and, for very large benzene:olefin molar ratio, alkylation
prevails completely over the metathesis reaction (Fig. 2).

These results indicate clearly the essential importance of the relative
concentrations of the reactants on the course of the two metathesis and
alkylation reactions; they allow also a better understanding and a rationali-
zation of a number of data scattered in the recent literature[1,2,3,4]. This
behaviour can be explained in two complementary ways :

1°) Alkylation and metathesis are two parallel reactions. Absolute concentrations
    of catalyst, olefin and benzene influence the velocity of these two reactions
as indicated in the following kinetic equations :

$$v_A = k_A \text{ (catalyst)}^u \text{ (olefin)}^v \text{ (benzene)}^w$$
$$v_M = k_M \text{ (catalyst)}^x \text{ (olefin)}^y$$

were v_A, k_A and v_M, k_M are the rates and the rate constants for alkylation and
metathesis reactions, respectively. But these kinetic equations alone cannot
explain all the results of the figure 2; the variations of absolute concentra-
tions and consequently the expected variations of rates, are indeed too small
to explain such an increase of the alkylation reaction.

2°) On the other hand, we can postulate a competitive coordination of benzene
    and olefin on the active catalyst center. This coordination of benzene
would favour the alkylation reaction, maybe by hindering further coordination
of the second olefin necessary for metathesis reaction. Moreover, the formation
of such a benzene complex from the olefin complex is strongly supported by the
very high transalkylation rate [1] of the alkylated products by the tungsten
catalyst, which has to be formed by observing a given order of reagents addition;

it would fit very well the $WCl_4(olefin)_2$ active center proposed recently by Pampus[5] for the metathesis reactions.

More kinetic and structural studies are necessary to afford detailled mechanistic conclusions : the problem is indeed a very complex one because yields of alkylation reaction from metathesis products increase with time in the range of olefin : catalyst ratio 70 to 400. Further kinetic investigations are in progress in our laboratory.

Figure 1   Yields of metathesis or alkylation reaction versus molar ratio olefin catalytic system c.c.d.e (molar ratio benzene olefin = 6)
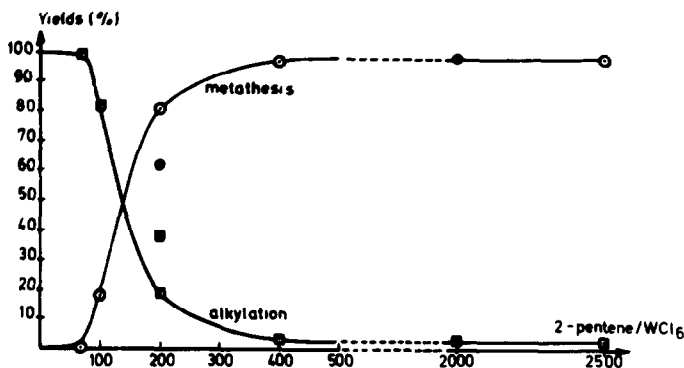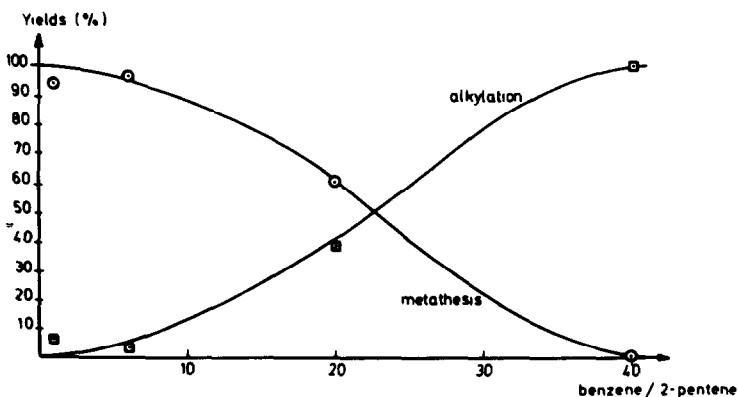

Figure 2   Yields of metathesis or alkylation reaction versus molar ratio benzene olefin b.c.d (molar ratio olefin catalyst = 400)

Caption for the figures 1 and 2.

a) Experimental conditions : 2-pentene = 10^{-2} mole; catalytic system = $2,5.10^{-5}$
   mole; Al/W = 4; variable amounts of benzene; temperature = 25° C; reaction
   time = 1 minute.

b) Experimental conditions : benzene = 6.10^{-2} mole; 2-pentene = 10^{-2} mole;
   variable amounts of catalytic system; Al/W = 4; temperature = 25° C; reaction
   time = 1 minute.

c) Yields are calculated using an internal g.l.c. standard (cyclooctane).
   Conversion of 2-pentene is complete after 1 minute.

d) Yields of the metathesis reaction are defined, in this article, as the sum of
   the olefinic fraction in the mixture of olefin and alkylated products. It
   would be more correct to consider the real ratio of 2-butene or 3-hexene
   versus 2-pentene as the yields of the metathesis reaction, but the thermo-
   dynamic metathesis equilibrium is not always completely established after a
   minute of reaction time; further kinetic studies are in progress on this
   point.

e) The O and ☐ points indicate respectively the yields of metathesis and
   alkylation reactions versus variable concentrations of the catalyst system
   (olefin and benzene concentrations being constant). On the other hand, the
   and ■ points give the same results for variable concentrations in olefin
   with a constant concentration in benzene and catalytic system.

References.

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