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THE EFFECT OF OXYGEN ON LEWIS ACIDITY OF ALUMINUM ALKYL COMPOUNDS AND ITS PROMOTING EFFECT ON COCATALYSTS IN METATHESIS

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Summary

The acidic properties of $EtAlCl_2$ are significantly enhanced by the addition of O_2. O_2 interaction with $EtAlCl_2$ initiates the cationic polymerization of *cis*-2-butene, the oxidation of naphthalene to the corresponding radical cation; it also favors the complexation of the Lewis acid to the metathesis catalyst $W(CO)_5PPh_3$, and thus promotes the catalytic activity of this complex in metathesis reactions. It is suggested that O_2 increases the electron affinity of alkylaluminium compounds. The promoting effect of O_2 in metathesis, observed by various authors, is therefore explained on the basis of Lewis acidity.

Introduction

The promoting effect of oxygen (or of oxygen-containing compounds) in the metathesis of *cis*-2-pentene in the presence of W, Mo or Re complexes and of cocatalysts such as aluminum alkyl compounds has already been reported [1—4]. This effect is particularly important in the systems $WCl_6-(C_2H_5)_3Al$, $ReCl_5-(C_2H_5)_3Al$ and $W(CO)_5P(C_6H_5)_3-(C_2H_5)AlCl_2$. For instance, in an oxygen-free solvent (chlorobenzene or hexane), the system $W(CO)_5P(C_6H_5)_3-(C_2H_5)AlCl_2$ exhibits almost no catalytic activity for *cis*-2-pentene metathesis, whereas upon addition of oxygen the system becomes instantaneously very efficient. In a previous publication [4] we have shown that the effect of O_2 on the catalytic system $W(CO)_5P(C_6H_5)_3-C_2H_5AlCl_2$ was to produce an active aluminum species which, complexed to the *trans* carbonyl of the tunsten complex, labilized the carbonyls in the square plane. We report here some experiments which try to clarify the role played by O_2 with $C_2H_5AlCl_2$.

Experimental

1. Materials

$W(CO)_5P(C_6H_5)_3$ was obtained according to the procedure described by Poilblanc et Bigorgne [5]. The purity was determined by chemical analysis and IR spectroscopy. $(C_2H_5)AlCl_2$ ($EtAlCl_2$), supplied by Ethyl Corporation, was purified by vacuum sublimation, diluted in anhydrous chlorobenzene (or in hexane) and stored under argon. R.P. grade chlorobenzene was distilled twice from P_2O_5 under Ar and was stored under Ar. *cis*-2-Pentene had a purity of 95%, with about 5% of the *trans* isomer. It was distilled from Na and stored under Ar. *cis*-2-Butene had a purity of 99% (Matheson). Naphthalene was purified by vacuum sublimation, was dissolved in benzene and stored in sealed ampoules.

2. Apparatus and procedure

All the reactions were carried out in a Pyrex batch reactor fitted with an injection valve for chromatographic analysis of the gaseous phase. The reagents were driven from gas syringes or burettes into the reactor by argon pressure. In some cases, reagents were stocked in sealed ampoules. For UV, IR and ESR studies, the liquid phase was circulated from the reactor to spectroscopic cells. All the apparatus was carefully degassed and purged with dry argon in order to eliminate any trace of O_2 or H_2O.

Analysis of the olefins was performed using a flame ionization chromatograph IGC 15. A 9 m column of 25% weight fractonitrile deposited on embacel was used at 25° C with nitrogen as the carrier gas but analysis of ethylene, ethane, CO, O_2 and Ar required a catharometer as detector with three Porapak columns and molecular sieves at 25° C and —78° C.

IR spectra were recorded on a Perkin—Elmer 125 spectrophotometer from 4000 to 400 cm^{-1}. The spectra were measured using a KBr variable-path cell with solvent (C_6H_5Cl or hexane) in the reference cell. Electronic spectra were recorded from 200 to 1000 nm with an Optica (Milano) CF4DR double beam spectrophotometer, using either CaF_2 (UVF) variable-path cells or 1.0 mm spectrosil cells. During the reaction, liquid was circulated from the reactor to the spectroscopic cells (carefully purged with dry argon) by means of a peristaltic pump. ESR measurements were carried out on frozen solutions at —196° C with a Varian V 4502 equipped with a 100 Kc field modulation unit (V 4560). Diphenylpicrylhydrazyl was used as reference.

During the metathesis reaction, $W(CO)_5P(C_6H_5)_3$ was usually introduced first into the reactor, which was evacuated and then purged with argon before the solvent was introduced. The order of introduction of the various reagents was varied and caused very drastic changes in catalytic activity.

Results and interpretations

1. The effect of O_2 on the interaction between olefin and $(C_2H_5)AlCl_2$

In a typical experiment *cis*-2-butene was added to $EtAlCl_2$ in C_6H_5Cl solution with the ratio olefin/$EtAlCl_2$ = 2. Slight *cis*—*trans* and 2—1 isomerization was observed. A rapid disappearance of the olefin occurred upon O_2 introduction, probably due to oligomerization since no alkylated products were detected by

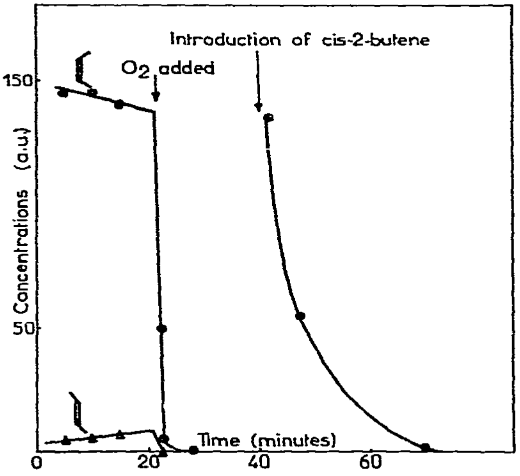


Fig. 1. Influence of O_2 on the *cis*-2-butene concentration in the presence of $EtAlCl_2$.

chromatographic analysis. A further introduction of *cis*-2-butene induced a slower but marked oligomerization (Fig. 1). Such an oligomerization of *cis*-2-butene with $EtAlCl_2$ must be compared with the recent results of Hirata et al. [6] who found that O_2 was a necessary cocatalyst of Et_2AlCl during the cationic polymerization of isobutyl vinyl ether.

UV spectra of the olefin—$EtAlCl_2$ solutions showed that in the absence of O_2 no characteristic UV band was present. But, upon O_2 introduction, an intense band at ~ 305 nm appeared instantaneously. A second band at 380 nm was also observed, the intensity of which increased with time (Fig. 2). The same bands were obtained when *cis*-2-pentene was used instead of *cis*-2-butene and were independent of the solvent (n-hexane of C_6H_5Cl) and the order of introduction of the reagents. Moreover, the electronic bands observed during the oxidation of $EtAlCl_2$ in C_6H_5Cl [4] disappeared instantaneously upon olefin introduction and, even for olefin/$EtAlCl_2$ < 1, were replaced by the 305 and 380 nm bands. In the absence of aluminum alkyl, the action of O_2 on olefins induced no such bands.

By analogy with the results obtained when olefins are adsorbed on solids [7, 8]

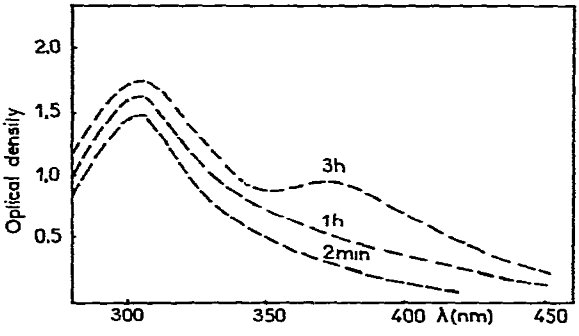


Fig. 2. UV spectral change during the reaction of $EtAlCl_2 + O_2$ with *cis*-2-butene. [Al] = 5.5×10^{-2} mol/l; alkene/$EtAlCl_2$ = 1: O/Al = 4.

one could ascribe the 305 nm transition to a carbonium ion produced by interactic between the olefin and a Lewis acid site. However, in solution, such species would be stable only in a superacid medium [9] . It seems that the electronic transitions reported here must result from a charge transfer complex formed between the olefin and the peroxidic form of $EtAlCl_2$. But we cannot reject the possibility of having secondary oxidized products, arising from the peroxide decomposition, although we could not detect any alcohol by chromatographic analysis. Whatever the interpretation of the electronic spectra, it appears, from the above experiments that O_2 promotes the cationic polymerization of the olefin, probably because it increases the Lewis acidity of the aluminum alkyl.

2. The effect of O_2 on the interaction between naphthalene and $EtAlCl_2$

The oxidizing power of acidic catalysts may be characterized by treating them with polynuclear aromatic compounds to give positive radical cations easily detected by ESR [10]. In a typical experiment, naphthalene, which has a relatively high ionization potential (8.2 eV) was added to $EtAlCl_2$ in the absence of O_2, in degassed chlorobenzene. No ESR signal was detected. Upon O_2 introduction, the ESR signal of the naphthalene radical cation was observed, indicating the presence of a paramagnetic charge transfer complex (CTC) between the aluminum alkyl, activated by O_2, and the aromatic compound. UV spectroscopy confirmed the existence of such a CTC in the presence of O_2 [11].

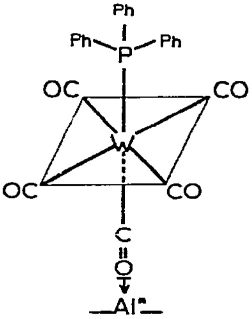
3. The effect of O_2 on the interaction between $W(CO)_5PPh_3$ and $EtAlCl_2$

We have previously shown [4] that there is no interaction between $W(CO)_5PPh_3$ and $EtAlCl_2$ in the absence of O_2. However, when O_2 is introduced into the $W(CO)_5PPh_3$—$EtAlCl_2$ system, CO is slowly given off with the rate of CO evolution first-order with respect to $EtAlCl_2$. If $EtAlCl_2$ is oxidized first and then added to $W(CO)_5PPh_3$ there is no release of CO. It is thus an intermediate produced durin the oxidation of $EtAlCl_2$, which interacts with the tungsten complex. This acid—base complexation could occur at the carbonyl ligand *trans* to $P(C_6H_5)_3$. When added to $EtAlCl_2$ and O_2, $W(CO)_5PPh_3$ of C_{4v} symmetry characterized by three $\nu(CO)$ bands at 2068 (A_1), 1936 (E and A_1) and 1984 (B_1) cm^{-1} was transformed into a new compound with only one $\nu(CO)$ band at 1998 cm^{-1}. The shift of the vibration of the E mode (mainly relative to CO in the square plane) from 1943 to 1998 cm^{-1} indicates a decrease in the backbonding of tungsten d electrons into the π^* orbitals of CO. Moreover, a new band at 1667 cm^{-1} was assigned, by comparison with various literature data [12, 13] to the vibration of the CO *trans*-coordinated to a Lewis acid by the oxygen atom. We postulate the following scheme (Fig. 3), where Al* is the aluminum alkyl activated O_2.

It seems therefore that the effect of O_2 is to enhance the Lewis acidity of the aluminum alkyl so as to favor acid—base complexation with the tungsten carbonyl. Such a complexation is the cause of the slow release of carbon monoxide.

4. The effect of O_2 on the interaction between $W(CO)_5PPh_3$, $EtAlCl_2$ and olefin

$W(CO)_5PPh_3$ and $EtAlCl_2$ were introduced into a reactor with the ratio $Al/W = 4$. Then a known amount of O_2, with $O/Al = 3$, was allowed to react, causing a slow release of CO. *cis*-2-Pentene was introduced into the reactor ($C_5/W = 100$) when a given ratio of CO/W had been attained and the composition



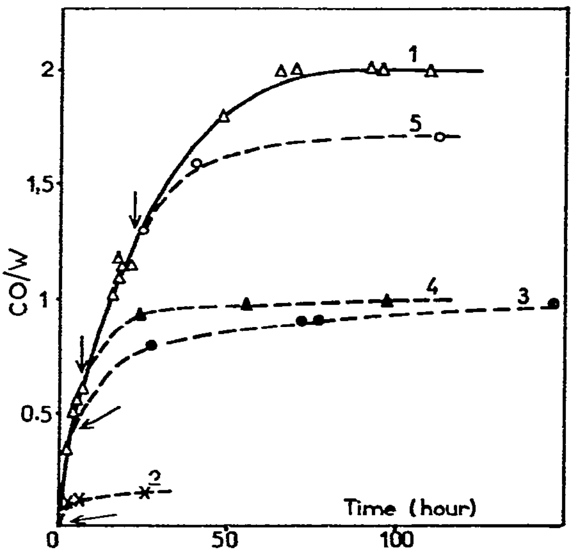


Fig. 3. Possible intermediate produced by $EtAlCl_2 + O_2$ with $W(CO)_5PPh_3$.

Fig. 4. Effect of olefin on CO evolution (the arrow indicates when the olefin has been introduced). Curve (1): the amount of CO released in the absence of olefin; (2): olefin introduced at the beginning of oxidation; (3): olefin introduced after release of 0.4 CO/W; (4) olefin introduced after release of 0.7 CO/W; (5): olefin introduced after release of 1.3 CO/W.

of the gaseous phase was then determined. The results presented in Fig. 4 show a drastic inhibiting effect of the olefin towards the release of CO. Whereas 2 CO/W were evolved in the absence of olefin, only 0.17 CO/W were liberated if pentene was introduced immediately after O_2 introduction. The complexation between the Lewis acid and $W(CO)_5PPh_3$, which is the cause of the release of CO, is therefore inhibited by the presence of olefin. Since O_2 promotes the complexation of $EtAlCl_2$ both with the olefin (probably by means of a charge transfer complex) and with $W(CO)_5PPh_3$, it is logical to observe an inhibition by excess olefin on the tungsten—Al* interaction.

Discussion

The properties of $EtAlCl_2$ are drastically changed upon interaction with O_2 : (a) no complexation is observed between $EtAlCl_2$ and oelfins, O_2 introduction favoring the formation of charge transfer complexes; (b) no paramagnetic CTC is formed between naphthalene and $EtAlCl_2$, O_2 causing the immediate transfer of one electron from the polynuclear compound to the activated form of the aluminum alkyl; (c) no complexation is observed between carbonyl ligands of $W(CO)_5PPh_3$ and $EtAlCl_2$, O_2 causing such a complexation between the terminal oxygen atom of the *trans* carbonyl group and the activated form of the aluminum alkyl; (d) when $EtAlCl_2$ is oxidized in the presence of $W(CO)_5PPh_3$ and olefin, a competition for the activated aluminum alkyl between W and the olefin occurs, resulting in a decrease in the release of CO from the W complex.

It seems that all these phenomena are related to the same property of O_2, which is to enhance strongly the Lewis acidity of the aluminum alkyl. This is quite general: oxygen is known to increase the electron affinity of various Lewis sites [10] and also to promote the catalytic activity of various Lewis acids in isomerization reactions of saturated hydrocarbons [14, 15]. In heterogeneous catalysis, solids which exhibit strong Lewis acidity such as silica—alumina [16—2 and fluorinated [16] or chlorinated alumina [20] are able to oxidize various pol nuclear aromatic compounds of low ionization potential to their positive radical cations. Brönsted sites are not involved in these electron transfer reactions. In solution, typical strong Lewis acids such as BF_3 or $AlCl_3$ [16, 21] exhibit the same behaviour, whereas typical protonic acids are inactive [16]. It is also know that the formation of such paramagnetic CTC's may be induced by oxygen [21] in the presence of compounds of Lewis acidity weaker than those cited above. In the same way, the strength of strong Lewis sites is enhanced upon O_2 interaction so that CTC's are observed with compounds of very high ionization poten When aluminas are contacted with perylene, it is only after O_2 introduction that the cation radical perylene$^{\dot{+}}$ is observed [12]. Chlorinated aluminas which, in the absence of O_2, are able to give paramagnetic CTC's with perylene (IP = 6.94 eV), naphthalene (IP = 8.2 eV) and 2-pentene (IP = 9.06 eV), only show an intense ESR signal for benzene (9.3 eV) in the presence of O_2 [23]. In solution, O_2 is necessary to the formation of such complexes between perylene and $SbCl_3$ but not $SbCl_5$ [21, 24]. Since O_2 is not able to generate these free radical cation on its own, whereas typical Lewis acids can, the effect of O_2 must be to enhance the electron affinity of the Lewis site, and we suggest from our own experiments that we have a similar effect with aluminum alkyl compounds.

These results must be correlated with the data concerning the metathesis reaction itself [4]. To summarise: in the catalytic system $W(CO)_5PPh_3$—$EtAlCl_2$ oxygen is needed to obtain activity, and the maximum activity is obtained at the beginning of the oxidation of $EtAlCl_2$. EtO—$AlCl_2$ is inactive as a cocatalyst, so an intermediate species produced during the oxidation of $EtAlCl_2$ must be the cause of the activation of $W(CO)_5PPh_3$. In this intermediate the Lewis acidity of the aluminum alkyl would be increased just before the insertion of O_2 into the Al—C_2H_5 bond, during the formation of the peroxide $EtOOAlCl_2$ (which is transformed later into inactive $(EtOAlCl_2)_n$ [25]). This increase in the electron affinity of the Al-atom upon addition of O_2 induces the formation of an adduct of the Lewis acid to the *trans* terminal carbonyl of $W(CO)_5PPh_3$, with labilizatio of the other CO molecules in the square plane. The metathesis reaction has been performed with $W(CO)_5PPh_3$ and $AlCl_3$; in this case O_2 was not needed and we obtained a very high activity.

The results of Y. Uchida et al. [2] and A. Uchida et al. [3] concerning the promoting effect of O_2 in the metathesis of 1-octene with WCl_6—Et_3Al can be explained on the same basis. The weak Lewis acidity of Et_3Al is much too low to create a complex with WCl_6, so that metathesis will not be promoted. With other catalytic systems such as $Mo(NO)_2Cl_2(PPh_3)_2$—$EtAlCl_2$, O_2 is not needed, which is accounted for by a stonger reactivity of the ligand towards the alkylaluminum. It is interesting to note that the catalytic system derived from WCl_6—n-butyllithium exhibits a relatively low activity and the rate of metathesis is considerably enhanced by addition of $AlCl_3$ or $AlBr_3$ [26], proving again the importance of Lewis acids as cocatalysts in methathesis. By comparison with Ziegle type catalysts, it has been suggested that the role of the aluminium alkyls (which are the most commonly used cocatalysts [27]) was to create an alkyl—tungsten bond. A reasonable suggestion is that the cocatalyst must be a Lewis acid able to react with a ligand of the tungsten complex.

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