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Catalysis

Cationic Oligomerization of 3-Methyl-1-Butene Catalyzed by BF_3-Protonic Donor Complexes

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SUMMARY

The oligomerization of 3-methyl-1-butene was carried out in the presence, as catalysts, of BF_3 complexes with different protonic donors (CH_3OH, H_2O, CH_3CH_2COOH, H_3PO_4) in a 1:1 molar composition. By working in n-hexane solution at temperatures between 0 and 70°C only unsaturated low MW oligomers (dimers to hexamers) were obtained. Each oligomer was a complex mixture of isomeric olefins as revealed by GLC and GLC-MS analysis. The presence of some fragmentation products containing one carbon atom more or less than the oligomer was pointed out.

The results obtained show that the MW of the oligomers decreases by increasing the acidity of the protonic donor used as complexing agent of BF_3. By increasing the temperature a decrease of the MW and an increase of the presence of fragmentation products was obtained.

INTRODUCTION

Cationic oligomerization of olefins is an interesting research field in which we can take advantage of the easy chain transfer reactions typical of the cationic polymerization in order to obtain, in high yield, dimers, trimers,... useful as synthetic lubricants, plasticizers, reactive oligomers,.... Several studies showed the importance of the catalyst system and of the experimental conditions in controlling the molecular weight, the molecular weight distribution and the structure of the obtained oligomers. HIGASHIMURA and co-workers studied the selective oligomerization of aromatic (HIGASHIMURA et al., 1979) and of aliphatic olefins (HIGASHIMURA et al., 1982) with different oxo-acid catalysts and $AlCl_3$ complexes. Recently a great deal of work has been done by American researchers on the controlled oligomerization of α-olefins (mainly 1-decene) to dimers and trimers, useful, after hydrogenation, as synthetic lubricants (BRENNAN, 1980; SHUBKIN et al., 1980; NELSON et al., 1983; ONOPCHENKO et al., 1983).

In order to increase the knowledge of the parameters which control the MW and MWD in the cationic oligomerization of olefins, we have taken into consideration the oligomerization of a branched α-olefin, namely 3-methyl-1-butene, by using BF_3 complexes with different protonic donors. Branched α-olefins are more reactive than the linear α-olefins and moreover there is the possibility of formation of preferential structures which are more regular compared with the complex structures obtained with linear α-olefins (ONOPCHENKO et al., 1983).

It is well known that 3-methyl-1-butene can be polymerized at low temperatures with Lewis acids (mainly Al halides) to high MW polymers with different structures due to the possibility of hydride migration (KENNEDY et al., 1965). As far as the control of the MW is concerned, BF_3 complexes with protonic donors seem to be the more suitable catalysts (BRENNAN, 1980; SHUBKIN et al., 1980): such control cannot be obtained with Al halides catalysts (CORNO et al., 1979).

In this work we used BF_3 complexes with protonic donors of different acidity as catalysts, and studied the influence of the catalyst and experimental conditions on the MW and the MWD of the obtained oligomers.

EXPERIMENTAL

Reagents. 3-Methyl-1-butene (Fluka, purity > 99%) and n-hexane (BDH, purity > 99%) were dried over CaH_2 and distilled under N_2. BF_3 (Matheson) and complexing agents (H_3PO_4, CH_3CH_2COOH, CH_3OH, H_2O) were pure products used as received. BF_3 complexes were prepared according to the literature (TOPCHEV et al., 1959) by bubbling BF_3 gas from the pressure cylinder through the complexing agent, which was stirred and maintained at about 0°C, until a constant weight of the system was obtained. The complexes of BF_3 with CH_3CH_2COOH and H_3PO_4 were prepared at higher temperature (50°C). The obtained liquid products were handled under N_2 and stored in a refrigerator (0°C). The composition of BF_3 complexes, obtained on the basis of the weight increase of the system, was 1:1 molar with CH_3OH and H_2O, while a small excess of BF_3 (1.05:1 molar ratio) was present in the case of the complexes with H_3PO_4 and propionic acid.

Procedure. The oligomerization experiments were carried out in glass flasks equipped with screw cap and magnetic stirrer by introducing firstly solvent and monomer and then, when the temperature was stabilized, the catalyst by means of a hypodermic syringe. The typical adopted reaction conditions were: monomer conc. = 1.8 M; BF_3 complex conc. = 0.1 M in hexane solution. To monitor the reaction progress samples were withdrawn periodically and examined by GLC (SE 30 column, 10%, length 2 m, T 80°C) with n-heptane as internal standard, in order to determine the monomer conversion. The reaction was stopped by adding a small amount of water when the monomer conversion was high (over 80%). The reaction mixture was then washed several times with distilled water and dried over anhydrous $MgSO_4$. The solvent was separated by fractional distillation and the oligomers distilled under vacuum. In any case there was practically no unvolatile residue.

The hydrogenation of oligomers was carried out in a stainless steel autoclave in n-hexane solution by using as catalyst 5 w% of Pd on charcoal (10%) at 180°C for 4 hrs with an H_2 pressure of 9 Atm measured at room temperature. The hydrogenation was practically complete as revealed by MS measurements.

Analyses. The oligomers (either hydrogenated or not) were analyzed by

GLC with a Varian model 3700 gas chromatograph equipped with a flame ionization detector and a Varian 4270 integrator by using a SE 30 2% column, length 2 m, programmed from 70 to 220°C at 10°C/min, T detector 300°C. The composition was given as the area % of the sum of peaks in each oligomeric fraction. Some calibration experiments showed that, in the adopted conditions, the area % of each oligomer was very near to the weight %.

The MW of the products was obtained by GLC-MS Instrument (Hewlett Packard type HP-5985 B) equipped with a capillar OV1 column (length 25 m).

IR measurements were performed by a Perkin Elmer 457 Instrument.

RESULTS AND DISCUSSION

Different protonic donors were used as complexing agents of BF_3, namely CH_3OH, H_2O, CH_3CH_2COOH and H_3PO_4. The molar ratio BF_3/donor was very near to 1/1 with a small excess of BF_3 in the case of the complexes with H_3PO_4 and CH_3CH_2COOH (see Experimental). All the complexes showed a good catalytic activity in the oligomerization of 3-methyl-1-butene in n-hexane solution at 0 and 70°C.

In Fig. 1 the monomer conversion curves obtained in n-hexane at 0°C in the presence of BF_3 complexes with CH_3OH, H_2O and H_3PO_4 are reported. It can be seen that $BF_3.CH_3OH$ shows less activity than the other ones. At 70°C we observed higher monomer conversions for all the catalysts.

Some experiments were also performed in the presence of a molar excess of the donor with respect to BF_3: a drastic decrease of the catalytic activity was obtained. In the same conditions of Fig. 1 the $BF_3.2H_2O$ complex shows no catalytic activity either at 0 or at 70°C.

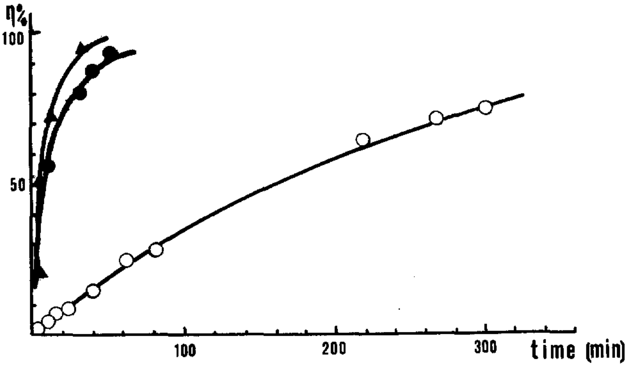

Fig. 1 - Time conversion curves in the oligomerization of 3-methyl-1-butene with different BF_3 complexes in n-hexane at 0°C. $[M]_o$ = 1.8 M; catalyst conc. = 0.1 M; (○) $BF_3.CH_3OH$; (▲) $BF_3.H_2O$; (●) $BF_3.H_3PO_4$

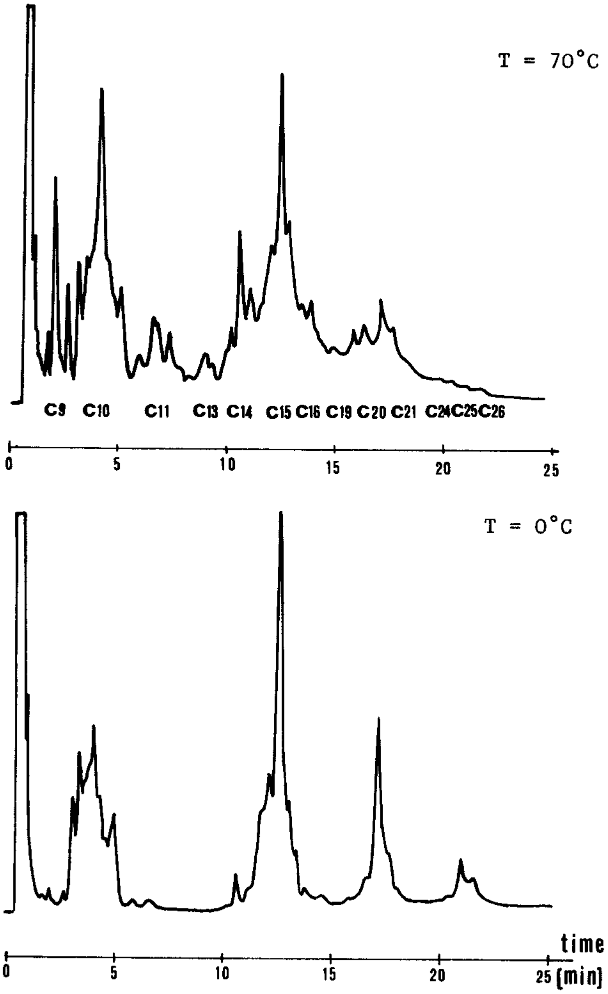

Fig. 2 - Typical chromatograms of the products obtained in the oligomerization of 3-methyl-1-butene at 0 and 70°C with $BF_3.H_3PO_4$ complex.

In Fig. 2 two typical chromatograms of the products obtained in the oligomerization of 3-methyl-1-butene at 70 and 0°C with $BF_3.H_3PO_4$ system are reported. MS analysis coupled with GLC, shows that all the peaks are due to hydrocarbon compounds containing one unsaturation. In Fig. 2 the molecular weight of the more important peaks are reported. It can be seen that the dominant peaks correspond to a MW $(C_5H_{10})_n$ with n = 2...6 and that many isomeric compounds are present.

Small amounts of olefins containing one carbon atom more or less than the olefin $(C_5H_{10})_n$ are also present, together with a very small amount of a C_{13} olefin. Therefore the combined GLC-MS analyses indicated that the oligomers obtained from 3-methyl-1-butene are complex isomeric mixtures and that fragmentation products involving a methyl group abstraction or addition are present. Similar fragmentation product were previously reported in the cationic olefin oligomerization (LACHANCE et al., 1965). By comparing the two chromatograms of Fig. 2, it is evident that the fragmentation products increase sharply by increasing the temperature in agreement with the previously reported data showing that the methyl shift reactions involve a high activation energy (FERRARIS et al., 1977).

The total content of the fragmentation products in the experiments at 70°C was less than 20% while at 0°C it was less than 2%. It can be noted that performing experiments at low or high monomer conversion, very similar oligomer compositions were obtained suggesting that no significant post-modification reactions on the obtained oligomers are operative.

By considering the composition of the obtained products in therms of the groups of peaks as determined by GLC, we have investigated the influence of the type of the catalytic complex, the temperature and the monomer concentration on this parameter. The results obtained are collected in Tab.1.

TABLE 1

Influence of the type of catalyst, temperature and monomer conc. on the composition of 3-methyl-1-butene oligomers [a].

Type of catalyst	$[M]_o$ (M)	Conv. (%)	T (°C)	Composition [b] (wt %) n = 2	3	4	5	6
$BF_3.CH_3OH$	1.8	81	0	2	30	36	22	10
$BF_3.H_2O$	1.8	98	0	6	40	29	18	7
$BF_3.H_3PO_4$	1.8	91	0	22	47	21	7	3
$BF_3.CH_3OH$	1.8	98	70	18	36	26	17	3
$BF_3.H_2O$	1.8	99	70	21	50	24	5	0
$BF_3.CH_3CH_2COOH$	1.8	83	70	37	40	19	4	0
$BF_3.H_3PO_4$	1.8	94	70	37	43	16	4	0
$BF_3.H_3PO_4$	4.5	96	70	37	44	15	4	0
$BF_3.H_3PO_4$	0.9	92	70	50	36	10	4	0

a) Solvent = n-hexane; catalyst conc. = 0.1 M; other conditions as in Fig.1

b) Determined by GLC; n = number of monomeric units in the oligomer.

By increasing the acidity of the protonic donor the average MW decreases and an increase of the content of dimers and trimers is evident. By increasing the temperature a decrease of the average MW is observed according to the general behaviour of polymerization processes.

Finally by working at low monomer concentration the dimer content was highest (50%), while trimers and tetramers increase with increasing monomer concentration. Similar results were obtained in the oligomerization of 1-hexene (HIGASHIMURA et al., 1982).

IR analysis of the products showed the presence of absorptions at 970 cm^{-1} attributable to trans disubstituted double bonds, at 890 cm^{-1} due to vinylidenic groups and at 790 cm^{-1} due to trisubstituted double bonds. With the aim of simplifying the structural analysis of the oligomers we subjected them to complete hydrogenation with Pd catalysts (see Experimental). The chromatograms of the obtained products were not simplified and mixtures of saturated hydrocarbons were obtained whose structure is under investigation.

CONCLUSIONS

The results obtained show that the cationic oligomerization of 3-methyl-1-butene in the presence of BF_3 complexes with protonic donors (CH_3OH, H_2O, CH_3CH_2COOH, H_3PO_4) at low temperature (0°C) allows us to obtain a good control of the oligomer formation (dimers to hexamers) with very low amount of fragmentation products. However each oligomer is a complex mixture of unsaturated isomers which is not simplified even after the complete hydrogenation. By changing the type of the protonic donor in the BF_3 complex, a change of the oligomer composition is observed with a decrease of the MW by increasing the acidity of the protonic donor. This fact suggests an influence of the catalyst structure on the chain transfer constant.

The formation of fragmentation products is favoured at high temperature and involves mainly an intermolecular methyl group abstraction or addition reaction.

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