SURFACE COMPOUNDS OF TRANSITION METALS, XIII.[*]
NATURE OF THE POLYMER TO CHROMIUM BOND IN PHILLIPS CATALYSTS

H. L. Krauss and H. Schmidt

Institut für Anorganische Chemie, Freie Universität Berlin
1 West Berlin 33, Fabeckstrasse 34

Two independent experiments show that in polymerization catalysts of the Phillips type the growing hydrocarbon chain is attached to the metal via a σ bond.

Два независимых ряда экспериментов указывают на то, что при использовании катализаторов типа Филипса в процессе полимеризации, растущая углеводородная цепочка присоединяется к металлу связью σ.

The identification of the "active center" in the Phillips polyethylene process as a coordinatively unsaturated Cr^{2+} surface compound [2,3] suggests that the primary step in the polymerization reaction is the attachment of the C_2H_4 monomer to the metal by a π bond — in analogy to the starting reaction in the Ziegler-Natta-process [4, 5, 6]. The growing polymer chain in supposed to be fixed to the metal by a σ bond, but experimental proof of this assumption is lacking. For example, a termination reaction with formation of Cr-H and a π-complexed polymer (in equilibrium with a σ bond chain)
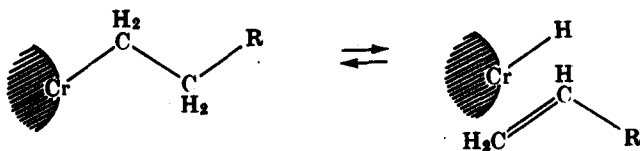
may not be excluded [7].

[*]Part XII: Ref. [1]

6*

We used two independent experiments to solve this problem:

(A) Cleavage of the Cr-polymer bond by $HgCl_2$, both in the "living polymer"

(i. e. in the Cr-polymer complex on the surface) (A_1) and in the corresponding organometallic Cr species /8, 9/ in solution (A_2).

(B) Pulsed reaction of the "living polymer" with CO/C_2H_4 cycles (B_1), and preparation of the organometallic species with or without addition of CO (B_2).

The first reaction (A) is known to form RHgCl and/or R_2Hg if a $Cr-C$ σ bond is present /10/, while similar products from π-bonded olefins are not obtained.

Reaction (B) makes use of the well known competition of C_2H_4 polymerization and CO complex formation /11/: even moderate concentrations of CO in the ethylene atmosphere ($\geq 20\%$) prevent any further growth of polymer chains. Whilst the exchange of π-bonded olefins by CO and vice versa is well known /12/, $Cr-C$ σ bonds react via insertion, if at all /13/. Therefore, CO may act here by occupying the necessary coordination site for π addition of a further monomer, and/or by substitution of π-bonded chains. When we compare a one-step addition of C_2H_4 with a repeated cycle of C_2H_4/CO additions using the same gross amount of monomer, in the latter case CO should "bite off" the shorter polymer chains formed in each single pulse of C_2H_4 if π fixation of the chain occurs. This would result in a lower molecular weight product with respect to the one-step polymerization. Sigma-bonded chains would remain unaffected or undergo insertion (formation of keto groups). Similarily, the cleavage of a possible π-bond between Cr and the polymer chain by CO would reduce the yield of the organometallic species, obtained by splitting the support-to-chromium bond of the "living polymer" /8, 9/.

EXPERIMENTAL

In the following experiments we used the "low polymer" technique described elsewhere /8/, allowing a mass spectroscopic identification of the products. The gross amount of monomer used for polymerization was limited therefore in such a way that hydrocarbon chains of less than ~ 24 C atoms were produced.

All operations were carried out under strict exclusion of oxygen.

Ethylene was purified from traces of oxygen according to Ref. /14/.

(A_1) A chromium(II) contact (1.30% Cr, oxidation number 2.35) was reacted with a known amount of ethylene in argon, as described earlier /8/. One half of the product was extracted at 60 $^{\circ}$C with a 10% solution of $HgCl_2$ in THF. From the resulting liquid phase the solvent was removed almost completely by evaporation. Cylcohexane was then added, the resulting solution was filtered and the solvent evaporated completely. The white residue (which slowly turns black on contact with air) was used directly for mass spectroscopy (Atlas CH 4 instrument, sample temperature 60 — 80 $^{\circ}$C, 10 eV). The appearing masses proved the presence of the ions HgCl (C_nH_{2n+1}) and Hg(C_nH_{2n+1}) with n = 4... 10 (maximum in intensity at n = 6).

(A_2) From the second half of the product mentioned above the organochromium species was removed by extraction with CH_3OH/HCl and transferred into cylcohexane, as described earlier /8/. To 0.05 mmol of the organometallic species in cyclohexane a solution of 0.37 mmol of $HgCl_2$ in THF was added. After vigorous stirring at 60 $^{\circ}$C for 24 hrs, the solvents were removed almost completely by evaporation. The subsequent steps were carried out as in (A_1).

The mass spectra showed the presence of the same ions as in (A_1). Blank exper-

iments with $HgCl_2$ refluxed for 24 hrs in n-octene-1 did not show any masses due to the presence of organomercury compounds in the reaction mixture.

(B_1) As a support for the catalysts Vycor plates (Vycor 7930, Thermalquarzschmelze, Mainz, Germany) of 20 mm diameter and 0.05 mm thickness were used. After impregnation with an aqueous solution of CrO_3 and drying at 110 ^{o}C the Cr content was 1.74%. Mounted in a special quartz IR cuvette /14/ they were activated for 5 min at 500 ^{o}C, reduced with CO for another 5 min at 400 ^{o}C, finally flushed with argon for 5 min at 400 ^{o}C and cooled to room temperature. The catalyst plates were then reacted with small amounts of pure C_2H_4, while the relative quantity of reacted monomer was monitored by measuring the $\tilde{\nu}_{CH}$ as at 2926 cm^{-1} of the polyethylene formed. Equal IR absorption intensities were adjusted a) by adding the monomer in a single step, and b) by reaction with five pulses of ethylene, interrupted by flushing with argon (25 ^{o}C, 760 Torr, 5 min) and CO (25 ^{o}C, 760 Torr, 5 min).

The plates were powdered under argon and the resulting samples transferred under inert conditions directly to the mass spectrometer (Varian MAT CH 5 D with data system MS 100, sample temperature 50 — 200 ^{o}C, 18 eV). The mass distributions in the rage of m/e = 200 to 700 were equal for a) and b) within a limit of ± 20%, which is the typical error within the individual a) or b) series. No insertion reaction was observed under our conditions.

(B_2) The preparation of the organochromium compounds was reported earlier /8/. The polymerization was carried out with standardized small amounts of ethylene in a "fluidized bed" reactor, followed by flushing /1/ with carbon monoxide (5 min/25 ^{o}C) or (2) with argon (10 min/25 ^{o}C) to terminate the polymerization. Isolation and purification of the organochromium species was carried out

as usual. The molar yields of (1) and (2) were determined photometrically in a CH_3OH solution ($\bar{\nu}_{max}$ = 16130 cm^{-1}, log ε = 2.54) and shown to be equal within a limit of 7%.

RESULTS

All the experiments described here lead to the same result:

Cleavage of the polymer to chromium bond by $HgCl_2$ forms the corresponding organomercury species — which proves the existence of a chromium to carbon σ-bond for the "living polymer" as well as for the corresponding support-free organometallic compounds.

The "bite-off" cycles with CO leave the molecular weight distribution of the resulting polymer unchanged with respect to a one-step polymerization, excluding a π type chain to metal bond. The equal yield in organometallic species using CO or vacuum for the termination of polymerization again is contradictory to a substitution of π-bond chains by CO.

Thus, we have to conclude that the chains are fixed to the metal by a Cr-C σ-bond. Furthermore, the obvious parallelism between the experiments with supported and support-free species shows that the Cr-C bond is essentially the same in both cases.

Termination of the polymerization by CO (occupation of a coordination site for the monomer) or by lack of monomer (empty coordination site for monomer) are not followed by a β-elimination equilibrium.

87

REFERENCES

1. G. Hierl, H. L. Krauss: Reaction Kinetics and Catalysis Letters, 2, 47 (1975)

2. H. L. Krauss, H. Stach: Inorg. Nucl. Chem. Lett., 4, 393 (1968)

3. H. L. Krauss, H. Stach: Z. Anorg. Allg. Chem., 366, 280 (1969)

4. G. Henrici-Olivé, S. Olivé: Chem.-Ing. Techn., 43, 906 (1971)

5. L. L. van Reijen, P. Coséé: Disc. Faraday Soc., 41, 277 (1966)

6. G. Henrici-Olivé, S. Olivé: Angew. Chem., 83, 782 (1971)

7. R. A. Schunn: Inorg. Chem., 9, 2566 (1970)

8. H. L. Krauss: Proc. Vth International Congress on Catalysis, p. 207, North
   Holland/Amer. Elsevier (1972)

9. H. L. Krauss, H. Schmidt: Symp. on the Mechanism of Hydrocarbon Reactions,
   Siófok, Hungary (1973), in press

10. H. H. Zeiss, P. A. Sneeden: Angew. Chem., 79, 401 (1967)

11. J. P. Hogan: J. Pol. Sci., 8, 2673 (1970)

12. M. Heberhold: Metal π Complexes, II. Elsevier Scientific, Amsterdam 1972/74

13. K. Noak, F. Calderazzo: Inorg. Chem., 7, 345 (1968)

14. H. Schmidt: Dissert. TU München, Germany, 1973