Journal of Organometallic Chemistry, 284 (1985) 149–158
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ETHER CLEAVAGE BY ACTIVATED METALS

I. CLEAVAGE OF TETRAHYDROFURAN BY TRANSITION-METAL ACTIVATED MAGNESIUM

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(Received October 2nd, 1984)

Summary

Transition metal complexes obtained by reduction of transition metal chlorides with magnesium catalyze a slow insertion reaction of magnesium into carbon–oxygen bonds of tetrahydrofuran and other ethers. The order of reactivity of the transition metals tested is Ti ≈ Co > V > Cr > Zr > Rh > Mn > Nb > Fe ≈ Ni. The effects on the reaction of modifications of the catalysts are discussed.

Introduction

The reduction of transition metal halides with magnesium in ethereal solvents very often does not give the elements but highly reactive magnesium transition metal complexes [1], which form black solutions if the reduction is carried out in tetrahydrofuran [2] (eq. 1):

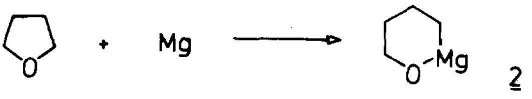
$$\mathrm{MCl_n} \xrightarrow[\mathrm{THF}]{\mathrm{Mg}} \underset{\underline{1}}{[\mathrm{M\,Mg_oCl_p(THF)_q}]_x} \quad (+\,\mathrm{MgCl_2}) \qquad (1)$$

$$\left.\begin{array}{l}\underline{1a}:\ \mathrm{M = Ti}\\ \underline{1b}:\ \mathrm{M = V}\end{array}\right\}\ o = p = 2\ ,\ q = 1$$

Very little is known about the structures of these products and (except in few cases like **1a** or **1b**) even about their stoichiometry. Nevertheless these complexes have been shown to participate effectively (either as catalysts or as reactants) in many interesting reactions such as nitrogen fixation [3], reduction of carbon monoxide [4] or carbon dioxide [5], hydrogen fixation, hydrogen-transfer to substrates like olefins [2] or to magnesium (i.e. magnesium hydride formation) [2,6], and reductive coupling of carbonyl compounds to give olefins [7] ("McMurry reaction" [8]). These systems

0022-328X/85/$03.30

also attack the coordinating ether: according to Sobota during the preparation of solutions of **1** as well as after hydrolysis small amounts of methane, ethane, ethene, propane, propene, butane, and other products can be detected, and can be accounted for only in terms of decomposition of the solvent [2,9]. However, these somewhat complex decompositions seem to play a minor role compared to the relatively simple cleavages catalyzed by complexes **1**; thus magnesium inserts into a C–O bond of THF with formation of the (presumably) cyclic magnesium alkoxy alkyl compound **2** (eq. 2):



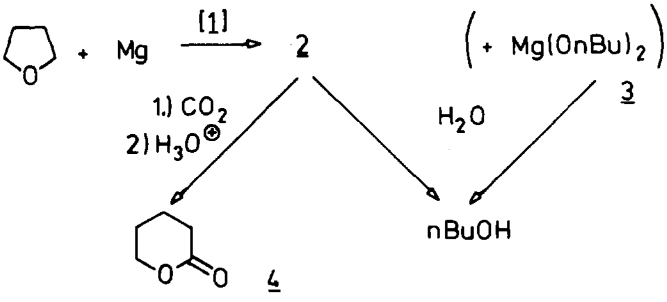
(2)

Normally finely divided "active" magnesium [10] is necessary to bring about this insertion (giving low to moderate yields) [11], and commercial magnesium powder is not active. Addition of transition metal chlorides (or the presence of complexes **1**) sometimes considerably enhances this cleavage. A detailled study of the reaction is described below.

Results and discussion

As potential precursors to complexes **1**, a range of transition metal compounds were tested for their catalytic activity in THF cleavage. They were usually used in a 10 mole percent ratio to magnesium, in a large excess of THF. The mixtures were heated to reflux and mostly gave black solutions after an induction period (of a few minutes in the case of $TiCl_4$ but up to several hours in the case of $CoCl_2$). These black solutions are also formed in the reactions of $MnCl_2$, $CoCl_2$, $NiCl_2$, $ZrCl_4$, $NbCl_5$, and $RhCl_3$, which were not previously studied. After a period of refluxing the amount of the cyclic organomagnesium compound **2** was determined by quenching of the mixtures with dilute acid and GLC analysis of the yield of butanol formed. However, the detected butanol might come not only from compound **2** but also from magnesium butoxide **3** (see Scheme 1), which could be formed in a side reaction and so the reaction mixtures therefore were usually filtered before the hydrolysis, and residue and filtrate were worked up separately, since **3**, in contrast to **2**, is almost insoluble in THF at room temperature. Minor amounts of butanol were, in fact, regularly found after hydrolysis of the insoluble portion, but this did not correspond to more than 5% of the total yield of butanol in any experiment.

SCHEME 1



The reaction mixtures were occasionally quenched by introduction of carbon dioxide, which converted **2** into δ-valerolactone, (**4**), which was separated by standard organic work-up procedures. This method reveals a significantly lower

TABLE 1

YIELDS OF THF RING OPENING BY MAGNESIUM UNDER VARIOUS REACTION CONDITIONS AND WITH VARIOUS CATALYSTS

Entry no.	Catalyst precursor	Type of Mg [a]	Reaction time (h)	Yield (%) [b]	
				butanol [c]	δ-valerolactone
1	$TiCl_4$	A	285	72	35
2	$TiCl_4$	B	29	14	–
3	$TiCl_4$	B	67	25	–
4	$TiCl_4$	B	165	50.5	–
5	$TiCl_4$	C	72	13.5	–
6	$TiCl_4$	C	280	21	–
7	$TiCl_4 + 4\ NaI$ [d]	C	70	2.5	–
8	$TiCl_4 + 4\ NaI$ [e]	C	92	9	–
9	$TiCl_4 + 4\ Bu_3P$	C	215	18	–
10	$Ti(OPr)_4$	B	68	4.5	–
11	$Ti(O\text{-}i\text{-}Pr)_4$	C	164	11	6
12	$ZrCl_4$	C	356	11	2.5
13	VCl_4	B	260	35	–
14	VCl_4	C	260	13	10
15	$NbCl_5$	C	120	1.5 [f]	–
16	$CrCl_3$	C	165	8.5	4.5
17	$MnCl_2$	C	405	10	6
18	$FeCl_3$	B	285	25	10
19	$FeCl_3$	C	235	trace	–
20	$Fe(OEt)_2$	C	240	2	–
21	$CoCl_2$	A	24	18	–
22	$CoCl_2$	A	60	26	20
23	$CoCl_2$	A	235	42	–
24	$CoCl_2$	C	42	9	–
25	$CoCl_2$	C	270	20	–
26	$CoCl_2 + 2\ KF$ [e]	C	455	0.5	–
27	$CoCl_2 + 2\ NaI$ [e]	C	165	2.5	–
28	$CoCl_2 + HgCl_2$ [e]	C	165	0	–
29	$CoCl_2 + 2\ Bu_3P$	C	93	21	–
30	$CoCl_2 + 10$ HMPA [h]	C	120	0	–
31	$CoCl_2 + 2\ NaOEt$	C	284	trace	–
32	$CoCl_2 + 2\ KO\text{-}t\text{-}Bu$	C	286	trace	–
33	$RhCl_3$	C	295	10	3.5
34	$NiCl_2$	C	331	trace	–
35	$NiCl_2 + 2\ Bu_3P$	C	380	25	–
36	$NiCl_2 + 2\ Ph_3P$	B	95	8 [g]	–
37	$Ni(OEt)_2$	C	310	9	5.5
38	Cu_2Cl_2	C	380	0	–

[a] Type of magnesium: A = activated magnesium according to Rieke [10], B = activated magnesium according to Bogdanovic [13], C = commercial magnesium powder. [b] Yield based on quantity of magnesium initially taken. [c] Yield of butanol after separation of insoluble material. [d] Halide added after reduction of transition metal chloride. [e] Halide added before reduction of transition metal chloride. [f] Slow polymerization of reaction mixture occurred. [g] Same amount of benzene was found. [h] HMPA = hexamethyl phosphoric acid triamide.

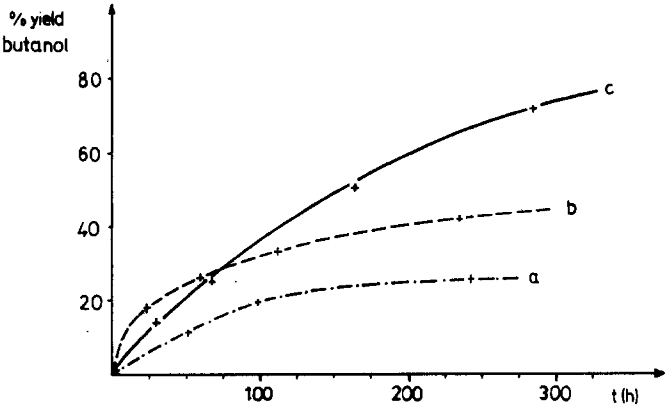


Fig. 1. Yield-time relation of THF cleavage by activated magnesium (a) without catalyst (Ref. 13), (b) with cobalt catalyst, (c) with titanium catalyst.

yield of **2** than that indicated by GLC analysis following simply hydrolysis of the reaction mixtures (especially since **4** tends to polymerize), but it proves the presence of an organometallic compound (such as **2**), since **4** cannot be formed from a simple butoxide (like **3**).

A representative selection of the experiments carried out is given in Table 1.

(a) THF cleavage with catalysts derived from chlorides of first row transition metals

All elements of the first transition metal period (from titanium to nickel) were found to be more or less catalytically active in the THF cleavage reaction, and the activity sometimes almost reached a useable level. However, the effects depend greatly, on the identity of the transition metal used.

It is not surprising that the titanium catalyst **1a** is rather active (see entries 1–6 in Table 1) since titanium is known to be a highly oxophilic metal, and ether cleavage reactions have been observed with other titanium compounds showing reducing properties [12]. Used along with "active" magnesium [10,13], this catalyst gives a 25% yield of butanol (related to the amount of magnesium) after 3 d of refluxing, and 70–75% after 12 d. (Higher yields are hard to achieve since the decomposition of THF gives side-products, as described in the Introduction.) With commercial magnesium powder, yields can be obtained which would require activated magnesium if no catalyst is used [13].

The elements following titanium on the right in the Periodic Table, viz. vanadium, chromium, and manganese, also catalyze reaction 2, but give clearly lower yields (entries 13, 14, 16, and 17), the catalytic efficiency falling along the series. The complexes obtained by reduction of iron or nickel chloride are almost ineffective which was unexpected in view of the fact that nickel so often shows catalytical activity [14]); yields of butanol are only slightly higher than those obtained without any catalyst (entries 18, 19, 34). Also unexpected was the high activity of the cobalt-containing system; after short reaction times the yields of butanol are even higher than those obtained with the titanium catalyst (compare entries 2, 3, 21, and 22). However, although increasing more steeply at the beginning, the yield-/timecurve (see Fig. 1) after longer reaction periods levels out more than in the titanium case; this may be at least partially due to the fact that the catalyst decomposes slowly with formation of a black slurry having ferromagnetic properties, probably elemental cobalt (Similar behaviour is observed with the iron and nickel systems). Nevertheless cobalt catalyzed reaction 2 more effectively than any other transition metal examined except titanium; the reasons for its effectiveness are not clear.

Addition of copper chloride to magnesium/THF mixtures does not accelerate ether cleavage at all (entry 38); in this system none of the characteristic, black, soluble transition metal magnesium complexes **1** is formed, and elemental copper is immediately precipitated by the magnesium. Zinc was not tested: Sumitani et al. observed cleavage of cyclic ethers by aluminum activated by some transition metal chlorides, especially zinc chloride and/or mercury chloride; they reported that these latter activators had no effect on magnesium or other elements in this type of reaction [15].

Thus for transition metals of the first row the reactivities of the complexes **1** in THF cleavage fall in the following order: Ti ≈ Co > V > Cr > Mn > Fe ≈ Ni (> Cu, Zn).

The magnesium also plays an essential role in this type of ether cleavage. Thus a violent reaction occurs between $TiCl_4$ and potassium in THF, but it produces only finely divided "active" titanium [10,16] and no potassium-titanium complexes, and only traces of ether cleavage products are formed. However, as already mentioned, aluminum does cleave THF and other cyclic ethers, even more effectively than magnesium, after activation by transition metal chlorides.

(b) Effects of modifications of catalysts 1

In addition to the chlorides of the elements of the first transition metal period, some alkoxides of titanium, iron, cobalt, and nickel were examined as catalyst precursors. These alkoxides also give black products on reduction with magnesium; in the case of titanium they are only slightly soluble in THF. However, the catalytic activity of these alkoxide-derived products does not parallel that of the chloride-containing catalysts: Whereas iron(II) ethoxide causes a small and nickel(II) ethoxide a significant increase in ring opening compared to the corresponding chlorides (entries 20, 37), the opposite effect was observed with systems containing titanium or cobalt which are very active as their halides (entries 10, 11, 31, and 32). The cobalt alkoxide systems are, in fact, almost inactive.

A decrease in the extent of THF ring opening is also brought about by additives introduced into the cobalt or titanium chloride systems in order to replace the chloride by other ions. For example, sodium iodide acts in this way (entries 7, 8, and 27) irrespective of whether the halide is added before or after the reduction of the transition metal chloride. The opposite behaviour is shown by "active" (Rieke-) magnesium (in the absence of any catalyst), which is more reactive if prepared in the presence of alkali iodides [17]. The difference suggests that addition of transition metal halide does not cause only a "simple" activation of the magnesium metal (as it is probably the case in the above-mentioned ether cleavage by activated aluminum); instead, the formed complexes must be intimately involved in the ring opening process.

Addition of potassium fluoride to the cobalt system did not give a black solution, only a grey precipitate, and only traces of butanol could be detected after work-up (entry 26). Similarly, added mercury chloride inhibits the formation of the black solution and completely stops the ring opening (entry 28).

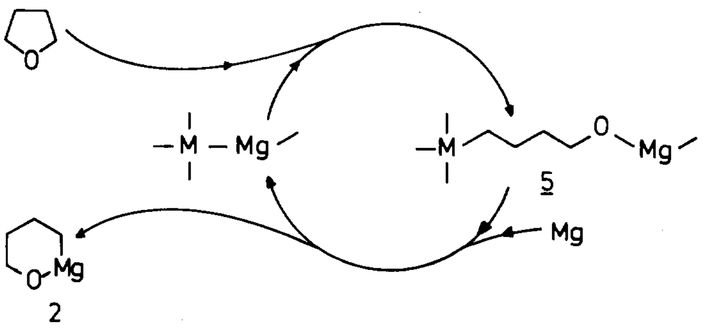
Some experiments were carried out with tributylphosphine added before the reduction of the transition metal chloride. Whereas the titanium system showed no change in effectiveness (entry 9), a remarkable effect was found in case of cobalt and nickel. The addition of the phosphine leads initially, of course, to the formation of complexes of the type $(Bu_3P)_2MCl_2$ [18]; the induction period for the reduction of these complexes by magnesium can be as much as 24 h, and the subsequent reduction itself proceeds slowly. But black solutions are produced, and there is no decomposition of the catalysts and formation of cobalt or nickel slurries such as are observed in the absence of phosphine (see above): the yields of butanol are much higher than in the absence of the phosphine (compare entries 25 vd. 29, and 34 vd. 35). Utilization of these observations is hindered by severe complications in the work-up procedure caused by the phosphines, but the interesting effects of the phosphine on the behaviour of the catalysts call for further investigation. It should be added that with triphenylphosphine instead of tributylphosphine in the nickel case, no rate enhancement of the THF cleavage was found but after aqueous work-up benzene was detected in almost the same quantities as butanol (entry 36) indicating that there had been cleavage of the complexed triphenylphosphine.

(c) THF cleavage with catalysts derived from chlorides of higher transition metals

Compounds of higher transition metals were not examined systematically because it soon became clear that the extent of THF cleavage was rather lower than with halides of the first-row transition metals. Thus $ZrCl_4$, like $TiCl_4$, produces characteristic black solutions on reduction with magnesium in THF but the yield of **2** is considerably lower (entry 12). Similar observations were made for $NbCl_5$ and for $RhCl_3$ (entries 15 and 33). With $TaCl_5$ and $MoCl_5$ total polymerization of the mixture occurred at reflux temperatures.

This low activity of catalysts derived from higher transition metals might seem surprising, but can be explained. The catalyzed insertion of magnesium into the C–O bond of the ether can be thought of as involving two steps (see Scheme 2), first the cleavage of the C–O bond by the magnesium-transition metal complex forming a compound with a transition metal–carbon bond (**5**), and second the reductive cleavage of the latter (displacement of the transition metal) with formation of **2** and re-formation of the catalyst.

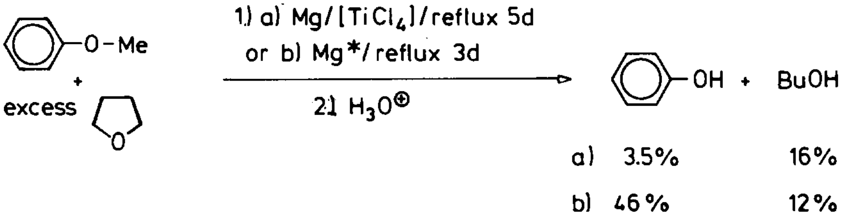
SCHEME 2



The first step can be confidently assumed to be faster with higher transition metals than with the lower ones, but the cleavage of the transition metal–carbon bond involved in the second step will be slower with the heavier metals. It is known that the latter generally form stronger and more stable bonds to carbon than the lighter transition elements [19]. (It will be appreciated that the mechanistic scheme presented here is highly simplified; both the reaction of the intermediate **5** with magnesium followed by desorption of **2** from the catalyst and, as will be shown below, the reaction of THF with the catalyst are probably more complex processes.)

(d) Experiments with open-chain ethers

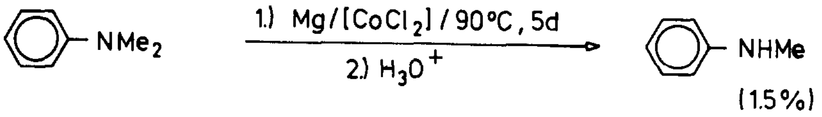
Some results of (preliminary) experiments with anisole are of mechanistic interest. After refluxing of a mixture of equimolar amounts of the ether and (commercial) magnesium powder with the titanium or cobalt catalyst in THF for several days, a small amount of phenol is detected after aqueous work-up. This indicates a small amount of cleavage of the ether at the methyl–oxygen bond (formation of methylmagnesium phenoxide). However, the main reaction remains the ring opening of the THF used as solvent (see eq. 3). This behaviour is completely opposite to that observed in experiments with activated magnesium (prepared by the Bogdanovic procedure [13]) in the absence of any catalyst. Here, after aqueous work-up, phenol is found as main product in moderate yields and the extent of the THF cleavage has been lowered. (In the latter case traces of benzene can also be detected, which suggests a phenylmethoxide cleavage of the anisole alongside the dominant methylphenoxide cleavage.)



(3)

Thus, in the non-catalyzed reaction the ether which is mainly attacked is that possessing the better leaving group, i.e. the phenoxide rather than the aliphatic alkoxide originating from the THF. This corresponds to the behaviour observed in most ether cleavage reactions [20] or more generally in reactions of metals with organic substrates containing potential leaving groups [21]. However, in the catalyzed ether cleavage another feature of the ether seems to be of importance, namely its coordination properties. THF is known to be a better donor and ligand than most other ethers, including anisole [22] and so in the catalyzed reaction coordination of the ether at the catalyst (either at the transition metal or at the magnesium) may play some significant and rate-determining role. (The simplified mechanism depicted in Scheme 2 must be supplemented in this sense.) This suggestion is inkeeping with the fact that the ether cleavage is suppressed if a stronger donor which can displace THF from its coordination site, is added; for example hexamethylphosphoric acid triamide (entry 30 in Table 1). Since, however, the reaction is not prevented by added phosphine (see above), this critical coordination site is likely to be located on the magnesium not the transition metal.

$$\text{Bu–O–Bu} \xrightarrow[\text{2.) } H_3O^+]{\text{1.) Mg/[CoCl}_2\text{]/reflux 5d}} \underset{(2.5\%)}{\text{BuOH}} \qquad (4)$$



(5)

Other compounds with potential leaving groups have also been found to be cleaved by magnesium in the presence of transition metal catalysts, but so far though to a very small extent. For example, in boiling dibutyl ether, cobalt chloride was reduced very slowly by magnesium. After 2 d all the $CoCl_2$ had disappeared; no black solution had formed, but a dark grey precipitate. After additional 5 d of refluxing followed by aqueous work-up a small quantity of butanol was detected (eq. 4). In the corresponding reaction of *N,N*-dimethylaniline a trace of monomethylaniline was produced, which indicates an alkyl–anilide cleavage of the amine (eq. 5).

Concluding remarks

Reagents consisting of combinations of Main Group and transition metal compounds are becoming increasingly used for reductions and other preparative purposes, especially in organic chemistry; examples are the McMurry reduction [8] and reductions with alkali hydrides catalyzed by transition metals [23]. The investigations described above demonstrate that these reagents can attack not only the intended substrate, but sometimes also the solvents commonly used for such reactions (especially THF). This observation suggests that it may be possible to use the cleavage of substrates often considered as inert, such as ethers and amines, in preparative chemistry. Compounds might be synthesized which are accessible only with difficulty by other methods; for example, the organomagnesium derivative **2**, which provides an interesting synthetic building block [13], is more difficult to prepare by other methods [24] than by THF ring opening.

Experimental

All experiments were carried out under argon using Schlenk flask techniques. Water- and oxygen-free solvents were used.

Materials

Activated magnesium was either obtained (in halide-free form [13]) from B. Spliethoff (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr) or prepared in situ by Rieke's procedure [25] from anhydrous magnesium chloride (Aldrich) and potassium. (There is no essential difference in the reactivities of the two types of activated magnesium [13].)

Metal halides were dried either by heating in vacuo (KF, NaI, $MnCl_2$, $CoCl_2$, Cu_2Cl_2) or by treatment with thionyl chloride [26] ($NiCl_2$, $CrCl_3$). All other metal halides were used as purchased. Titanium alkoxides were obtained from Dynamit Nobel AG, iron and nickel ethoxide from W. Eisenbach [27] (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr); cobalt alkoxides were prepared in situ by metathesis reaction of cobalt chloride with sodium ethoxide (Dynamit Nobel AG) or potassium t-butoxide (Merck-Schuchardt) respectively.

Cleavage of THF

(a) n-Butanol as final product. In a typical experiment, 10 mmol of the anhydrous transition metal chloride or alkoxide and the additive if any (for molar amounts see Table 1) were dissolved or suspended in 50 ml THF and 100 mmol of magnesium were added. (If the latter was obtained by the Rieke procedure (see above) the transition metal chloride had to be added after the completion of that procedure.) In experiments with $TiCl_4$, VCl_4, $NbCl_5$, $TaCl_5$, $MoCl_5$, $FeCl_3$, or activated magnesium, respectively, mixing was carried out at $-70°C$. The mixture was refluxed for the required time (see Table 1), then cooled to room temperature and filtered through a frit. The residue in the frit was washed with few ml of THF. The residue and the filtrate (after evaporation in vacuo) were hydrolyzed separately with diluted hydrochloric acid (at $-10°C$), and the hydrolysates were extracted carefully several times with diethyl ether or chloroform. The content of butanol in the extracts was determined by GLC analysis (with n-octane or toluene as internal standard).

(b) δ-Valerolactone as final product. Mixing and refluxing of the components were carried out as described above. After filtration the filtrate was cooled to $-78°C$, and an excess of dry ice was added. After cautious warming to room temperature the mixture was treated with dilute hydrochloric acid then extracted with several portions of ether. The extracts were evaporated in vacuo at r.t. and the residue was distilled under reduced pressure (14–16 mbar, 110–115°C; yields are given in Table 1). The distillate tends to polymerize [28].

Experiments with other substrates

Reactions were carried out as for those involving THF. In the case of anisole, 100 mmol of this ether were added to the mixture before the refluxing. In the case of dibutyl ether and *N,N*-dimethylaniline, these reagents were used as solvents (50 ml each) without any THF (for reaction conditions see data in eqs. 3–5). At the end of the reaction the solvents were evaporated or distilled off in vacuo, and the residue was carefully hydrolyzed with diluted hydrochloric acid. Extraction of the hydrolyzate and GLC analysis were carried out as usual.

Acknowledgements

The initial experiments in this work were carried out at the Max Planck-Institut für Kohlenforschung, Mülheim/Ruhr, West Germany; I thank Prof. Dr. B. Bogdanovic and the Director of the institute, Prof. Dr. G. Wilke, for making that possible.

The practical help of Astrid Fichte during the major part of the work is acknowledged.

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