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# ORGANOMETALLIC COMPOUNDS
# VI*. THE ACTION OF METHYLMAGNESIUM IODIDE ON COBALTOUS CHLORIDE

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## SUMMARY

The action of an ethereal solution of methylmagnesium iodide on cobaltous chloride, in a molar ratio of 2 : 1, results in reduction of the cobaltous chloride to zero-valent cobalt complexed with magnesium halide. When a large excess of methylmagnesium halide is used, the product is a colloidal suspension of particles, suggested to have the composition $Co[CH_3MgI]_2$, containing zero-valent but non-ferromagnetic cobalt and heavily solvated with molecules of ether. A complex mixture of hydrocarbons is evolved on formation of the colloidal suspension, and, on the assumption that two methyl radicals are liberated per molecule of cobaltous chloride, the observed hydrocarbons can be accounted for both qualitatively and quantitatively by means of a series of free-radical reactions.

## INTRODUCTION

In general, solutions of Grignard reagents** react very slowly, or not at all, with alkyl halides whereas in the presence of certain transition metal halides a catalysed reaction takes place[2-4] readily. Kharasch and his co-workers investigated numerous such reactions, especially those in which cobaltous chloride was used as a catalyst, and the term "Kharasch reactions" has been used[5] to describe these catalysed reactions between Grignard reagents and organic halides. The procedure mostly adopted in carrying out a Kharasch reaction has been to add cobaltous chloride to the Grignard reagent, followed by addition of the organic halide and a subsequent working-up of the mixture to isolate the various products. However, in order to determine the course of these complicated reactions it seems essential to carry out the Kharasch reaction in two stages and to investigate each stage separately. In the present paper we deal with the action of a solution of methylmagnesium iodide in diethyl ether on cobaltous chloride, and in Part VII of this series[6] we shall describe an investigation of the action of the catalytic system so produced on various alkyl halides.

If Grignard reagents and cobaltous halides are allowed to react in equivalent quantities or thereabouts (usually a mole ratio of Grignard reagent to cobaltous

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* For Part V see ref. 1.

** Unless stated otherwise, all Grignard reagents are as solutions in diethyl ether.

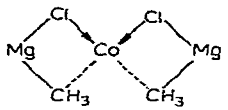
halide of 2 : 1 or 3 : 1), a black cobalt-containing solid is precipitated. Knowledge of the constitution of these solids should aid any investigation into the constitution of the catalytic species in the Kharasch reaction; in Table 1 are outlined the main theories of the nature of these cobalt-containing solids. There appears to be only one investigation in which these solids were analysed; Costa and his co-workers reporting[9] that action of methylmagnesium bromide on cobaltous chloride or bromide (ratio 6 : 1)* gave a black solid of empirical formula $(CH_3)_{0.7}ClBrMg_2Co$, which they suggested was composed of structures such as (I) and (II). The deficiency of methyl groups in the analysed sample was attributed to difficulties in handling such a reactive solid. Costa and his co-workers[9] also suggested (II) as a possible structure for the solid obtained with a ratio of 3 : 1, and they reported that whereas the solids themselves were not ferromagnetic, the Grignard component was removed on washing them with ether to leave cobalt in a ferromagnetic state; the cobalt in (I) and (II) was considered to be in a zero-valent state, but non-ferromagnetic.

TABLE 1

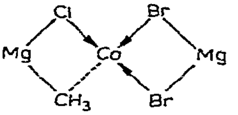
THE NATURE OF THE SOLID COBALT-CONTAINING PRODUCTS OBTAINED BY THE ACTION OF GRIGNARD REAGENTS ON COBALTOUS HALIDES

| Grignard reagent | Cobaltous halide | Ratio[a] | Product | Ref. |
|---|---|---|---|---|
| $C_6H_5CH_2CH_2MgBr$ | $CoBr_2$ | 1 : 1.22 | Co[b] | Lee and Thornhill[7] |
| $CH_3MgBr$ | $CoBr_2$ | 3 : 1 | Co[c] | Smith[8] |
| $C_2H_5MgBr$ | $CoBr_2$ | 2 : 1 | Co | Smith[8] |
| $C_4H_9MgBr$ | $CoBr_2$ | 2 : 1 | Co | Smith[8] |
| $C_6H_5MgBr$ | $CoBr_2$ | 2 : 1 & 1 : 1 | Co | Smith[8] |
| $CH_3MgBr$ | $CoBr_2$ & $CoCl_2$ | 6 : 1 | (I) and (II)[d] | Costa *et al.*[9] |
| $CH_3MgBr$ | $CoBr_2$ & $CoCl_2$ | 3 : 1 | (II) | Costa *et al.*[9] |

[a] Ratio of Grignard reagent to cobaltous halide. [b] A black finely-divided solid, magnetic and pyrophoric; no analyses given. [c] A black metallic sludge; not analysed. [d] A black, non-ferromagnetic solid.



(I)



(II)

In contrast to the black solids obtained with low ratios of Grignard reagent: cobaltous halide, when a large excess of Grignard reagent is used no precipitate is formed, and the product appears to be a black liquid**. These black liquids are active catalysts in Kharasch reactions; the nature of the actual catalytic species has been the subject of much controversy and in Table 2 we give the main theories that have been advanced on the nature of the catalyst and its mode of formation. It is interesting

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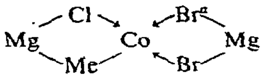
* Ratios will always be given as the ratio of magnesium to cobalt.

** We refer to this product as a "black liquid" to avoid any preconception as to whether it is a colloidal suspension or a true solution.

TABLE 2

SUGGESTED SCHEMES FOR THE ACTION OF AN EXCESS OF GRIGNARD REAGENT ON COBALTOUS HALIDES

| Reaction sequence | Catalytic species produced | Ref. |
|---|---|---|
| $RMgX+CoX_2 \rightarrow RCoX+MgX_2$<br>$RCoX \rightarrow R^{\cdot}+{}^{\cdot}CoX$ | Cobaltous subhalide, $^{\cdot}CoX$ | Kharasch *et al.*[2,4] |
| $2RMgX+CoX_2 \rightarrow R_2Co+2MgX_2$<br>$R_2Co \rightarrow 2R^{\cdot}+Co$ | Colloidal cobalt metal | Wilds and McCormack[10], Frey[11] |
| $2RMgX+CoX_2 \rightarrow R_2Co+2MgX_2$<br>$R_2Co \rightarrow R\text{-}R+Co$ | Finely divided "atomic" cobalt | Tsutsui[12] |
| $2RMgX+CoX_2 \rightarrow R_2Co+2MgX_2$<br>$R_2Co \rightarrow 2\,R^{\cdot}+Co$ | Highly reactive "atomic" cobalt, not colloidal | Zeiss[13] |
|  | Solvated complex of Grignard reagent with an organometallic compound | Noller *et al.*[14] |
| $3\,MeMgBr+CoCl_2 \rightarrow$  $+MgBrCl+(2\,Me^{\cdot})$ | Zerovalent cobalt complexed with $MgX_2$ and MeMgX | Costa *et al.*[9] |

[a] A series of reactions was postulated[9] to lead to this complex; we have given the overall stoichiometry.

to note that the two most recent theories have both postulated a catalyst complex, Noller and his co-workers[14]* suggesting that a complex was formed between an alkylmagnesium halide and an organometallic compound, and Costa and his co-workers[9] giving a detailed sequence leading to (II), which they regarded as one possible catalyst.

Finally, the physical nature of the black liquids is still obscure. Ultracentrifugation has failed[9,14] to precipitate the cobalt-containing species, and it is still not known whether the black liquids are true solutions or colloidal suspensions.

## DISCUSSION

### *The nature of methylmagnesium iodide*

Ashby and Smith[15] have indicated that ethereal solutions of methylmagnesium iodide at concentrations between 0.5 and 1.0 *M* (in $CH_3MgI$) contain essentially dimeric species. It was suggested[15] that a complex dynamic equilibrium (1) obtained, with the equilibrium lying (at the above concentrations) in favour of the species $(CH_3MgI)_2$. However any one of the four organometallic species in (1) could be the actual reactive entity in a given chemical reaction, and in view of this difficulty we shall use the formula $CH_3MgI$ to represent methylmagnesium iodide even though we acknowledge that under our concentration conditions the predominant species in the undisturbed equilibrium (1) is dimeric.

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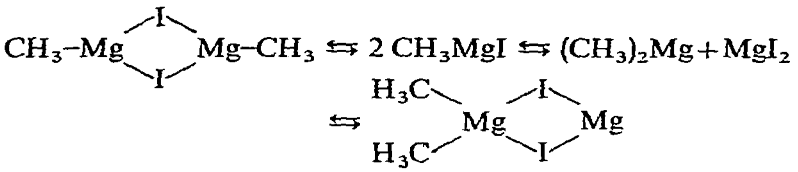
* Di-n-butyl ether was used as solvent in the experiments of Noller and his co-workers.



(1)

*The action of methylmagnesium iodide on cobaltous chloride (ratio 2 : 1)*

Addition of cobaltous chloride to two equivalents of methylmagnesium iodide ($CH_3MgI$) at 35° brought about a rapid reaction in which the ethereal medium became black and gas was evolved. When gas evolution had ceased, there remained a clear, colourless ethereal solution together with a black powder (when the initial solution of Grignard reagent was 0.01 *M*) or a black tar-like material (when the initial solution of Grignard reagent was 0.77 *M*). The black tar could be converted into a black powder by repeated washing with ether; during this washing process, magnesium halide was removed from the tar as an ethereal solution. Neither the black powders, nor any of the ethereal supernatant liquids or washings gave methane (or indeed any gaseous hydrocarbons at all) on treatment with water or acid and hence no methyl–metal bonds remained after reaction. The black powder, however, did evolve hydrogen on contact with water or acid; for example a sample whose composition we had deduced to be $Co[MgX_2]_{0.926}$ evolved 0.25 mole hydrogen per atom of cobalt, even though the powder had been previously warmed under reduced pressure.

Analysis of the black powders presented some difficulty as they were completely soluble only in hot perchloric acid. By analysing the entire ethereal washings and supernatant solution obtained from a black tar that had been converted to a powder by the minimum of washing, we obtained a composition of $CoMg_{0.893}I_{0.768}Cl$ by a mass balance, as compared to one of $CoMg_{0.926}I_{0.685}Cl_{1.167}$ by an analysis of the bulk of the solid powder. The black powders, however, are not homogeneous; analysis of two portions of one particular black solid product gave ratios of 1.13 : 1 and 0.91 : 1 for magnesium/cobalt.

On further washing of the black powders with ether, magnesium halide is gradually removed, but even after treatment with boiling water for five hours some magnesium halide still remains. Table 3 gives details of various treatments and em-

TABLE 3

COMPOSITIONS OF THE BLACK SOLIDS OBTAINED BY THE ACTION OF METHYLMAGNESIUM IODIDE ON COBALTOUS CHLORIDE (RATIO 2 : 1)

| Original form of solid | Treatment | Final composition[a] |
|---|---|---|
| Black tar | Washed with ether until converted into a powder | $Co[MgX_2]_{1.14}$<br>$CoMg_{0.93}I_{0.69}Cl_{1.17}$<br>$CoMg_{0.89}I_{0.77}Cl$ |
| Black tar | Washed with ether as above, then washed with ether a further 20 times | $Co[MgX_2]_{0.388}$ |
| Black powder | Washed well with ether | $Co[MgX_2]_{0.265}$ |
| Black tar | Washed with ether until a powder, then boiled with water for 5 h | $Co[MgX_2]_{0.156}$ |

[a] Excluding hydrogen.

pirical formulae (excluding hydrogen) of the resulting solid products. The black powders were ferromagnetic, but not sufficiently so as to suggest that all of the cobalt present is in the form of cobalt metal in its usual state. Interestingly, Costa and his co-workers found[9] that black powders having a magnesium/cobalt ratio of 2 : 1 were not ferromagnetic. It therefore seems to us possible that the initial products of reaction have a ratio 2 : 1 and are not ferromagnetic, washing with ether converts them to materials with a ratio 1 : 1 and weakly ferromagnetic, and ultimately (although we have not achieved this) washing could convert them to the strongly ferromagnetic cobalt metal itself. We suggest that the black powders contain zero-valent cobalt bound chemically to magnesium halide, and that the initially formed black tars are similarly constituted but with a magnesium/cobalt ratio of 2 : 1. Washing the tar with ether removes magnesium halide to give the first-analysed product, a black powder, of composition nearly $CoMgX_2$. The action of methylmagnesium iodide on cobaltous chloride, in the ratio of 2 : 1, could thus be represented by eqn. (2), where the production of two methyl radicals is necessary to account for the entire loss of all methyl–metal bonds. In the black powders there is a marked excess of chloride over

$$2\,CH_3MgI + CoCl_2 \rightarrow Co[MgICl]_2 + 2\,CH_3^{\cdot} \qquad (2)$$

iodide; this is compatible with the observation of Costa and his co-workers[9] that bromide was removed from the solids they had isolated much easier than was chloride. In the present work, removal of iodide (as magnesium iodide), from $Co[MgICl]_2$, preferentially to chloride leads to compositions such as $Co[MgI_{0.74}\,Cl_{1.26}]_{0.926}$. The comparative ease of removal of iodide might also account for the fact that the solids we were able to isolate contain less magnesium halide than do those isolated by Costa and his co-workers[9].

As noted above, we observed evolution of hydrogen when the black powders were added to water or dilute acid. It is a matter for speculation as to the origin of this hydrogen, but three possibilities occur to us, *viz.*: (1) part of the cobalt metal in the powder is sufficiently active to displace hydrogen from water, (2) the hydrogen is present as a cobalt hydride and the composition of the powder is better described by formulae such as $[Co]_{0.75}[CoH_2]_{0.25}\,[MgX_2]_{0.926}$ rather than by $Co[MgX_2]_{0.926}$ (recent work[16] on the action of Grignard reagents on cobaltous stearate would lend support to such a theory), and (3) the hydrogen is present as adsorbed hydrogen, *e.g.* $Co[MgX_2]_{0.926}\,[H_2]_{0.25}$ (finely divided cobalt is known[17] to occlude hydrogen readily). If either possibility (2) or (3) were correct, then equation (2) should be modified so as to include the small quantity of hydrogen in the composition of the initially-formed material.

### *The action of an excess of methylmagnesium iodide on cobaltous chloride*

(*i*) *Liquid products.* Addition of catalytic quantities of cobaltous chloride to methylmagnesium iodide (ratio of methylmagnesium iodide to cobaltous chloride from 5 : 1 to 20,000 to 1) at 35° produced an immediate evolution of gas and a black ethereal liquid. These black liquids are stable and show no tendency to precipitate out cobalt-containing solids; furthermore, as shown in Part VII of this series[6], they are highly active catalysts for the decomposition of alkyl halides.

The liquid obtained from an experiment using a 20,000 : 1 ratio appeared black under normal lighting conditions, but in an intense beam of white light the transmitted light was orange-brown. No particles were revealed on examination of the liquid under a microscope at an angle of 90° to the beam of transmitted light, and the Tyndall effect was not observed. If the system is indeed particulate in nature we can therefore say that the particles must be very small[18,19] (less than about 100 Å)[19] and/or that the particles are so heavily solvated by ether molecules that the refractive index of the particles is close to that of the supporting liquid medium[18].

Ultracentrifugation of a black liquid (from an experiment using an 83:1 ratio) at 50,000 rev. per minute for several hours resulted in a partial sedimentation of the black species to leave a small depth of an entirely clear ethereal liquid. Observations over a period of ten hours gave a value of $0.4 \times 10^{13}$ sec for the sedimentation coefficient, $s$, at 2°. The Svedberg eqn. (3) may then be used[20] to calculate the molecular

$$M = \frac{R \cdot T \cdot s}{D(1 - V \cdot \rho_0)} \tag{3}$$

weight ($M$) of the smallest particles, provided that the densities of the smallest particles ($\rho$) and of the surrounding medium ($\rho_0$) are known, and that the diffusion coefficient ($D$) is known or can be estimated [the partial specific volume of the smallest particles ($V$) is taken as the reciprocal of the particle density]. If the core of the particles is composed of equal molecular proportions of cobalt ($\rho = 8.9$ g·cm$^{-3}$)[21], magnesium iodide ($\rho = 4.24$ g·cm$^{-3}$)[22], and dimethylmagnesium ($\rho = 0.96$ g·cm$^{-3}$)[23] it will have a density of 3.0 g·cm$^{-3}$. Now if this core is solvated by ether molecules to the extent of a sheath about two molecules thick, the resulting density of the entire particle will be reduced* to about 0.8 g·cm$^{-3}$. For an ethereal solution at 2° we may take[24] $\rho_0$ to be 0.73 g·cm$^{-3}$. It is not easy to estimate the diffusion coefficient, but a reasonable value for $D$ would be around $50 \times 10^{-7}$ cm$^2$·sec$^{-1}$, and substitution of these above values in eqn. (3) yields a value for $M$ of 2000 and, from this, a diameter for the smallest particles of $2 \times 10^{-7}$ cm (20 Å).

It is of interest that application of the simple eqn. (4), using the above figures for $s$, $\rho$, and $\rho_0$, together with a value[25] of $3 \times 10^{-3}$ poise for the viscosity of the ethereal medium at 2°, results in a value of $1.8 \times 10^{-7}$ cm (18 Å) for $d$, the diameter of the smallest particles.

$$d^2 = 18\,\eta \cdot s(\rho - \rho_0) \tag{4}$$

The above calculations only provide estimates of the size of the smallest particles, and it is somewhat difficult to put an upper limit to the particle size range. In view of the optical properties of the black liquids, and their great stability, it does not seem possible that particles of diameter greater than $10^{-5}$ cm (1000 Å) are present. A particle range of 20 to 1000 Å would account for the repeated failure of previous workers to obtain noticeable sedimentation of the black liquid, as the smallest particles would remain dispersed under most experimental conditions.

Magnetic susceptibility measurements on 0.7 $M$ methylmagnesium iodide containing no added cobaltous chloride, $4.7 \times 10^{-3}$ $M$ cobaltous chloride, and $4.6 \times 10^{-2}$ $M$ cobaltous chloride, showed that in all three cases the material was diamagnetic, and that the gram susceptibility remained constant for fields of up to 7000 oer-

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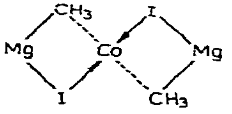
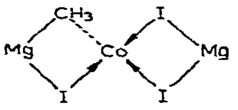
* This only applies to the smallest particles; as the size of the core increases, the effect of the sheath becomes progressively less and the density of the total particle will gradually increase from the value of 0.8 g·cm$^{-3}$.

steds. In the light of our conclusions on the nature of the black powders (above), these results indicate that the cobalt-containing species in the black liquids have magnesium to cobalt ratios of not less than 2 : 1. Either (III) or (IV) would be a possible structural unit, and in view of the large excess of methylmagnesium iodide in the supporting medium, we regard (III) as the main structural unit of the cobalt-containing particles. From the particle size range of these particles, it is evident that the unit (III) must be extensively polymerised, possibly by metal–metal bonds, and it is clear also that the surface of the particles will accommodate layers of strongly held solvent molecules [*e.g.* (V), Sv = Ether]. We have not dealt with the possibility of the particles containing hydrogen in some form, as we have no evidence one way or the other on this point, but we feel that this should not be overlooked.



(III)



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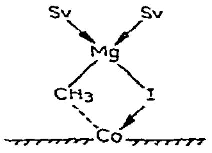

(V)

Our final conclusion as to the nature of the cobalt-containing species in the black liquids is that the cobalt is contained in particles between 20 Å and 1000 Å diameter. These particles consist of zero-valent cobalt bound to molecules of methylmagnesium iodide, the whole being extensively solvated by ether molecules and being non-ferromagnetic. Our views on the state of the cobalt in the black liquids are thus in close agreement with those of Costa, Mestroni, and Boscarato[9], although in the present work the particulate, heterogeneous nature of the black liquids has in addition been demonstrated.

(*ii*) *Gaseous products.* The composition of the evolved gas produced by the action of an excess of methylmagnesium iodide on cobaltous chloride (ratio 100 : 1) at 35° was found to be $CH_4$ (2.188), $C_2H_6$ (0.232), $C_2H_4$ (0.197), $C_3H_8$ (0.087), and $C_3H_6$ (0.023), all in moles per mole of cobaltous chloride. Only very small traces of $C_4$ hydrocarbons were found. The above quantities of hydrocarbons are not too dissimilar to those found by Smith[8] from the action of methylmagnesium bromide on cobaltous bromide (ratio 3 : 1), *viz.* $CH_4$ (2.95), $C_2H_6$ (0.103), and $C_2H_4$ (0.085). In both the present work and that of Smith, the total quantity of hydrocarbons produced seems to be much larger than that found by Costa[9] and his co-workers. The latter give a figure of not greater than 2.20 for the ratio $[CH_4+2(C_2H_6+C_2H_4)]/CoCl_2$ whereas our figure is 3.05 and that of Smith[8] is 3.33. Unfortunately, Costa gives no analytical figures for the individual hydrocarbons.

The varied hydrocarbons obtained in our experiments suggests the possibility of free-radical reactions taking place. It is an attractive hypothesis that methylmagnesium iodide initially alkylates the cobaltous chloride to give a methylcobalt compound which then rapidly decomposes to yield methyl radicals and cobalt in a lower valence state. Properties of methyl radicals in solution are not too well documented, but there is general agreement[26] that when generated in solution, methyl radicals preferentially react by hydrogen abstraction from the solvent. Only when formed as a pair of radicals in a solvent cage do methyl radicals in solution combine to give ethane[26]. Thus two primary reactions of methyl radicals liberated singly in diethyl ether are reactions (5) and (6)[27–31], of which (5) is rather more facile than

$$CH_3^{\cdot}+C_2H_5OC_2H_5 \rightarrow CH_4+CH_3{\cdot}CHOC_2H_5 \tag{5}$$

$$CH_3^{\cdot}+C_2H_5OC_2H_5 \rightarrow CH_4+{}^{\cdot}CH_2CH_2OC_2H_5 \tag{6}$$

is (6)[29]. Following these two primary reactions, a number of secondary reactions of the ether radicals can take place; these include radical combination to give ether dimers[29], and radical breakdown to yield smaller free-radicals[27,30,32] as in reactions (7) to (9). The fate of the ethyl radical [from reaction (7)] is again a matter of some

$$CH_3{\cdot}CHOC_2H_5 \rightarrow CH_3CHO+C_2H_5^{\cdot} \tag{7}$$

$${}^{\cdot}CH_2CH_2OC_2H_5 \rightarrow C_2H_4+C_2H_5O^{\cdot} \tag{8}$$

$$C_2H_5O^{\cdot} \rightarrow CH_3^{\cdot}+HCHO \tag{9}$$

controversy; electrolysis of ethylmagnesium halides in diethyl ether affords[30,31] ethane and ethylene, suggested to arise[30] by quantitative disproportionation of ethyl radicals. Other work, however, indicates[33,34] again that hydrogen abstraction from the solvent (to give ethane) is the preferred mode of reaction unless the ethyl radicals are stabilised by the presence of transition metal compounds, when butane is produced[34] as well as ethane. It is of interest to see if reactions (5) to (9) can be used to account quantitatively for the observed $C_1$ and $C_2$ hydrocarbons [reactions (8) and (9) are particularly noteworthy as they provide an explanation for the quantity of methane in excess of 2.00 moles per mole of cobaltous chloride]. The small amounts of $C_3$ hydrocarbons could arise from reactions such as (10), and in Table 4 we give a complete set of postulated reactions.

TABLE 4

PROPOSED REACTION SCHEME FOR THE ACTION OF AN EXCESS OF METHYLMAGNESIUM IODIDE ON COBALTOUS CHLORIDE

| | |
|---|---|
| Initiation | Excess of $CH_3MgI+CoCl_2 \rightarrow Co(CH_3MgX)_2+MgX_2+2\ CH_3^{\cdot}$ |
| Primary radical reactions | $1.747\ CH_3^{\cdot}+1.747\ C_2H_5OC_2H_5 \rightarrow 1.747\ CH_4+1.747\ CH_3{\cdot}CHOC_2H_5$ |
| | $0.253\ CH_3^{\cdot}+0.253\ C_2H_5OC_2H_5 \rightarrow 0.253\ CH_4+0.253\ {}^{\cdot}CH_2CH_2OC_2H_5$ |
| Secondary radical reactions | $1.550\ CH_3{\cdot}CHOC_2H_5 \rightarrow$ dimer |
| | $0.197\ CH_3{\cdot}CHOC_2H_5 \rightarrow 0.197\ C_2H_5^{\cdot}+0.197\ CH_3CHO$ |
| | $0.197\ C_2H_5^{\cdot}+0.197\ C_2H_5OC_2H_5 \rightarrow 0.197\ C_2H_6+0.197$ tert. products |
| | $0.253\ {}^{\cdot}CH_2CH_2OC_2H_5 \rightarrow 0.253\ C_2H_4+0.253\ C_2H_5O^{\cdot}$ |
| | $0.253\ C_2H_5O^{\cdot} \rightarrow 0.253\ CH_3^{\cdot}+0.253\ HCHO$ |
| | $0.160\ CH_3^{\cdot}+0.160\ C_2H_5OC_2H_5 \rightarrow 0.160\ CH_4+0.160$ tert. products |
| | $0.093\ CH_3^{\cdot}+0.093\ C_2H_4 \rightarrow 0.093\ C_3H_7^{\cdot}$ |
| Tertiary reactions | 0.357 tert. products $\rightarrow \frac{0.357}{2.000} \times$ secondary products |
| Products: Primary | $2.000\ CH_4$ |
| Secondary | $0.160\ CH_4+0.197\ C_2H_6+0.160\ C_2H_4+0.093\ C_3$ |
| Tertiary | $0.028\ CH_4+0.035\ C_2H_6+0.028\ C_2H_4+0.017\ C_3$ |
| Calculated totals | $2.188\ CH_4+0.232\ C_2H_6+0.188\ C_2H_4+0.110\ C_3$ |
| Observed totals | $2.188\ CH_4+0.232\ C_2H_6+0.197\ C_2H_4+0.110\ C_3$ |

$$CH_3^{\cdot}+C_2H_4 \rightarrow C_3H_7^{\cdot} \tag{10}$$

We have not invoked participation of the cobalt-containing material in the scheme shown in Table 4, as the main effect of such participation seems to be[6] to reduce drastically the yield of methane, whereas in the present work there is an excess of methane to be accounted for. It can be seen from Table 4 that the production of the observed hydrocarbons can qualitatively and quantitatively be understood in terms of already known reactions, starting from the liberation of two methyl radicals per cobalt atom. Thus our above suggestion that cobaltous chloride suffers reduction to cobalt in a lower valence state, nominally $Co^0$, receives support from the proposed reaction sequence shown in Table 4.

## EXPERIMENTAL

Magnesium raspings were a kind gift from Magnesium Elecktron Ltd.; an independent analysis of the raspings themselves showed the following impurities (in parts per million): Fe (30), Zn (20), Ca (10), K (10), Mn (10), Al (5), Cu (5), Pb (4), Si (3), Ni (2) Na (1), Cr (< 1), and Li (< 1). In addition the following elements were sought but were not detected: Ag, As, Au, B, Ba, Be, Bi, Cd, Co, Cs, Ga, Ge, H, Hf, Hg, In, Ir, Mo, Nb, Os, P, Pb, Pt, Rb, Re, Rh, Ru, S, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, and Zr.

Anhydrous cobaltous chloride was prepared[35] by maintaining the laboratory reagent "anhydrous cobaltous chloride" at 170° in a current of dry hydrogen chloride for one hour. The product was allowed to cool in a stream of dry hydrogen chloride and traces of the latter removed by flushing the product with a stream of dry nitrogen for two hours. Ether was sodium dried and freshly distilled, iodomethane was the best available commercial sample used as such, and nitrogen was freed from traces of oxygen by passage through chromous chloride solution and then dried.

Gaseous hydrocarbon analyses were carried out, using a Shandon flame thermocouple gas chromatograph, on a column of 100–125 mesh alumina with a 2% w/w loading of squalane. The molar composition of the gas samples were calculated using the known[36] relationship between the peak area and the molar heat of combustion for any hydrocarbon. We checked the validity of this procedure for our particular instrument by analysis of a hydrocarbon mixture kindly supplied by the Shell Refining Co. Ltd., who had previously analysed the mixture on a katharometer chromatograph standardised against a mass spectrometer. Results of the two sets of analyses were in good agreement:

| Hydrocarbon component: | ethane | ethylene | propane |
|---|---|---|---|
| Molar ratios, this work: | 0.141 | 0.014 | 0.361 |
| Molar ratios, "Shell" analysis: | 0.168 | | 0.358 |

| Hydrocarbon component: | propene | isobutane | n-butane |
|---|---|---|---|
| Molar ratios, this work: | 0.308 | 0.082 | 0.093 |
| Molar ratios, "Shell" analysis: | 0.307 | 0.076 | 0.091 |

In the analysis of any given gaseous mixture, five separate analyses were performed and the results averaged.

Magnesium alone, and magnesium and cobalt in the presence of each other, were determined by standard EDTA methods[36,37]. Chloride and iodide, both alone and in the presence of each other, were determined by Volhard's method, in conjunction with the potassium iodate method[37].

Methylmagnesium iodide was prepared, under nitrogen, in the usual way using a slight excess of the magnesium raspings in order to consume all of the iodomethane. The resulting product was boiled under reflux for several hours in order to remove traces of volatile hydrocarbons and then filtered through a fine sinter to give a clear colourless solution. A representative analysis was: basic magnesium 0.740 *M*, total magnesium 0.764 *M*, and iodide 0.766 *M*, and the nominal concentration thus taken as 0.740 *M*. All operations involving methylmagnesium iodide were carried out in an atmosphere of dry, oxygen-free, nitrogen.

### *Action of methylmagnesium iodide on cobaltous chloride in a ratio 2:1*

Cobaltous chloride was added to a magnetically stirred solution of the Grignard reagent (0.77 *M*). The mixture became black immediately and a vigorous reaction ensued, with evolution of gas and heat. After subsidence there was left a clear colourless supernatant solution over a tar-like black product. The supernatant solution was drawn off, replaced by a similar volume of ether, and the mixture stirred and boiled under reflux for 20 min. Repeated several times, such treatment converted the tar into a black powder which could be manipulated, under nitrogen, into various specimen tubes. Traces of ether were removed by warming under vacuum and the specimen tubes then sealed off under vacuum.

Alternatively, methylmagnesium iodide was added to a stirred mixture of cobaltous chloride (0.50 g) in ether (400 ml). The mixture became black immediately, and after boiling under reflux for 2 h there was obtained a black powder together with a clear, colourless supernatant solution.

Magnetic susceptibility measurements on the black powders were made on a Gouy balance with fields from 1615 oersteds up to 4880 oersteds; measurements were not practicable at higher field strengths as the specimens then adhered to the poles of the magnet.

### *Action of a large excess of methylmagnesium iodide on cobaltous chloride*

The cobaltous chloride was added to a refluxing, well stirred (magnetically) solution of the Grignard reagent in a closed apparatus connected to a gas-collection device through a short tube containing phosphorous pentoxide and calcium chloride. The ethereal mixture immediately became black, and a short, vigorous evolution of gas followed. The gas was collected over brine, well scrubbed to remove ether vapour, and its volume and composition ascertained. The black ethereal liquid showed no tendency to deposit any solid products, and was manipulated into various pieces of apparatus for examination under a microscope, for magnetic susceptibility measurements, and for ultracentrifugation.

Magnetic susceptibility measurements were again made by the Gouy method, with fields strengths of up to 7000 oersteds. Ultracentrifugation was carried out in an MSE Automatic "Superspeed 50" Refrigerator Centrifuge using 10 × 10 ml tube rotors closed to the atmosphere. Measurements were made at 2° on specimens centrifuged at 50,000 rpm for up to 10 h.

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