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ORGANOMETALLIC COMPOUNDS
VII*. DECOMPOSITION OF ALKYL HALIDES BY THE COBALTOUS CHLORIDE/METHYLMAGNESIUM IODIDE SYSTEM; THE MECHANISM OF THE KHARASCH REACTION

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SUMMARY

The action of a large excess of methylmagnesium iodide on cobaltous chloride results in formation of a colloidal suspension. This colloid decomposes iodomethane and the 1-halooctanes to give hydrocarbons derived from the Grignard reagent and hydrocarbons derived from the alkyl halide. From studies of product distributions and of the kinetics of decomposition of 1-bromooctane, it is concluded that these decompositions are heterogeneous and proceed at the surface of the catalyst to give an intermediate complex; this complex can break down to yield free alkyl radicals, and can also break down by a series of hydrogen abstraction reactions that possibly involve a cobalt hydride. The observed products of reaction have been accounted for both qualitatively and quantitatively by these free-radical and non-free-radical processes.

INTRODUCTION

In Part VI of this series[1], we described experiments in which a large excess of methylmagnesium iodide** was allowed to react with cobaltous chloride. The resulting product is an extremely active reagent for the decomposition of alkyl halides, and, in this second paper on the Kharasch reaction, we seek to determine the course and mechanism of these catalysed decompositions.

There have been many theories put forward as to the mechanism of Kharasch reactions, especially those in which cobalt compounds were employed as catalysts. Kharasch himself suggested[2,3] that cobaltous subhalide was the actual catalytic species, and that equimolar quantities of the Grignard reagent and the organic halide decomposed to give free-radicals [eqn. (1), X = halogen]. Norman and Walters[4]

$$\begin{aligned}&RMgX + CoX_2 \rightarrow RCoX + MgX_2\\&RCoX \rightarrow R^{\cdot} + {}^{\cdot}CoX \qquad (1)\\&R'X + {}^{\cdot}CoX \rightarrow R'^{\cdot} + CoX_2\end{aligned}$$

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* For Part VI, see ref. 1.

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

later provided support for this mechanism by showing that when methylmagnesium iodide was allowed to react with iodomethane in the presence of added cobaltous chloride and anthracene, there was formed a derivative of anthracene resulting from attack by the radical $CH_3\dot{C}HOC_2H_5$. This observation was interpreted[4] by means of Kharasch's mechanism [eqn. (1), $R=R'=CH_3$], followed by hydrogen abstraction by methyl radicals [eqn. (2)]. However, Kharasch and Urry[5] had already had doubts

$$CH_3^{\cdot}+C_2H_5OC_2H_5 \rightarrow CH_4+CH_3\dot{C}HOC_2H_5 \qquad (2)$$

on the application of the simple scheme [eqn. (1)]. They had observed that whereas free propyl radicals in solvent ether mainly abstracted hydrogen from the solvent to give propane, Kharasch reactions of propylmagnesium chloride with various alkyl halides yielded almost equal amounts of propane and propene. Kharasch and Urry therefore suggested[5] that the propane and propene arose from a free-radical/Grignard reagent/ether complex, and that the free-radicals in the complex could disproportionate more readily than could radicals free in solution.

Two further reaction schemes were based on the supposition that cobalt metal, rather than cobaltous subhalide, was the active catalyst. Wilds and McCormack suggested[6] that the cobalt metal attacked the organic halide [eqn. (3), $R'X$ = anethole hydrobromide] but Frey[7] put forward a more reasonable scheme (4) in which both

$$\left.\begin{array}{l} 2\,RMgX+CoX_2 \rightarrow R_2Co+2\,MgX_2 \\ R_2Co \rightarrow [RH+RH_{-1}]+Co \\ 2\,R'X+Co \rightarrow 2\,R'^{\cdot}+CoX_2 \end{array}\right. \qquad (3)$$

the Grignard reagent and the organic halide were necessary for the cobalt metal to react.

$$\left.\begin{array}{l} 2\,RMgX+CoX_2 \rightarrow R_2Co+2\,MgX_2 \\ R_2Co \rightarrow [2\,R^{\cdot}]+Co \\ RMgX+Co+R'X \rightarrow RCoR'+MgX_2 \\ RCoR' \rightarrow R^{\cdot}+R'^{\cdot}+Co \end{array}\right. \qquad (4)$$

An entirely new hypothesis was advanced by Tsutsui, in 1961, in order to account for the formation of diphenyl in Kharasch reactions of phenylmagnesium halides. Tsutsui[8] supposed that a diphenylcobalt intermediate decomposed to diphenyl in a "π-radical hybridisation step" that did not involve free-radicals at all. Parker and Noller[9]*, in a study of Kharasch reactions catalysed by metal halides such as cuprous bromide and cobaltous bromide, concluded that only part of the products were derived from free-radicals (which abstracted hydrogen from the solvent to give the corresponding alkanes) and that the remaining products were formed by a non-free-radical mechanism. In the purely aliphatic systems studied by Parker and Noller, Tsutsui's mechanism is not applicable and Parker and Noller suggested[9] that a catalyst complex, involving both alkyl halide and Grignard reagent, was formed and subsequently decomposed to give alkane from the alkyl halide and alkene from the Grignard reagent. At the same time as Parker and Noller, Costa and his co-wor-

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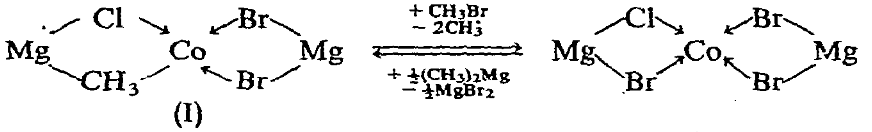
* Di-n-butyl ether was used as solvent in the experiments of Parker and Noller.

kers[10] also suggested that a catalyst complex (I) was formed and that the complex reacted with alkyl halide, liberating free-radicals [eqn. (5)].



(5)

Although two free-radicals per molecule of alkyl halide are produced in this scheme [*cf.* eqns. (1), (3) and (4)], Costa and his co-workers did not discuss the reactions of these radicals, but suggested[10] that this aspect of the Kharasch reaction merited further study.

It is evident, therefore, that there is no general agreement as to the course and mechanism of the Kharasch reaction, although it appears probable, from the work of Kharasch and Urry[5] and of Parker and Noller[9], that only part of the total overall reaction proceeds through formation of true free-radicals that are liberated into the bulk of the solvent. In the preceding paper of this series, we concluded[1] that the action of a large excess of methylmagnesium iodide on cobaltous chloride yielded a colloidal suspension of cobalt-containing particles in a supporting medium of the excess of Grignard reagent. The particles, of diameter 20 Å to 1000 Å, were considered[1] to consist of a core of material of composition Co[CH_3MgI]$_2$, containing zero-valent, but non-ferromagnetic cobalt, surrounded by a sheath of solvating ether molecules. The total system (in the present work that is an 0.75 *M* ethereal solution of methylmagnesium iodide with 0.0076 *M* suspended cobalt) is a very active reagent for the decomposition of alkyl halides, and we have investigated a number of such decompositions in an attempt to deduce the course and mechanism of the Kharasch reaction.

DISCUSSION

The action of the above colloidal material on iodomethane and on 1-halooctanes results in evolution of gas, and complete decomposition of the alkyl halides*. Results of analysis of this evolved gas, and of the ethereal solution obtained on subsequent hydrolysis of the reaction mixture are given in Table 1 for the three alkyl halides thus used. We did not concentrate the ethereal solution obtained on hydrolysis,

TABLE 1

PRODUCTS OF THE CATALYSED DECOMPOSITION OF ALKYL HALIDES

Halide	Gaseous products[a,b]						Liquid products[a,c]			
	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	Total	C_8H_{18}	1-C_8H_{16}	2-C_8H_{16}	$C_{16}H_{34}$
CH_3I	1.542	0.084	0.308	0.002	0.084	2.020				
n-$C_8H_{17}I$	0.742	0.027	0.152	0.002	0.037	0.960	0.34	0.31	0.00	0.175
n-$C_8H_{17}Cl$	0.775	0.027	0.181	0.006	0.080	1.069	0.61	0.34	0.03	0.01
$CH_3I/2$	0.771	0.042	0.154	0.001	0.042	1.010				

[a] Mole per mole of alkyl halide. [b] Only traces of C_4 hydrocarbons found. [c] No C_9 hydrocarbons found.

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* We have shown (see experimental section) that in the absence of added cobaltous chloride, methylmagnesium iodide reacts extremely slowly with iodomethane and with 1-iodooctane.

as this can lead[11] to loss of even quite high-boiling constituents, but examined the ethereal solution as such. Little comparison can be made with previous work, but Kharasch and Urry[5] found for the $CH_3Br/CH_3MgBr/CoCl_2$ (overall) reaction at 35°, the following products (mole per mole of alkyl halide): CH_4 (1.09), C_2H_6 (0.22), and C_2H_4 (0.25). They also noticed formation of dicumyl when cumene was present in the reaction mixture; presumably free methyl radicals are formed at some stage and abstract hydrogen from cumene. Kharasch, Hambling and Rudy[12] have investigated the 1-$C_8H_{17}Br/CH_3MgBr/CoCl_2$ reaction and have found products and yields to be: CH_4 (1.07), C_2H_6 (0.06), C_2H_4 (0.06), n-C_8H_{18} (0.17), 1-C_8H_{16} (0.42), 2-C_8H_{16} (0.10), n-$C_{16}H_{34}$ (0.12), and $C_{16}H_{32}$ (0.03). The quantity of n-hexadecane is in line with the results shown in Table 1, but those of the other hydrocarbons are considerably different to the quantities that would be expected from our results.

It is noteworthy that no C_9 products were observed in the 1-halooctane decompositions, although our analytical technique would have shown up any, if produced. We did observe, in the 1-halooctane experiments, small quantities of a compound that had the retention characteristics, on gas chromatography, of an ether of b.p. 201–207° and possessing twelve or thirteen carbon atoms. It is possible that this minor product is either $C_8H_{17}{-}CH(CH_3){-}O{-}C_2H_5$ or $C_8H_{17}{-}CH_2{-}CH_2{-}O{-}C_2H_5$.

The iodomethane decomposition

As an initial hypothesis, we could consider this decomposition to take place via purely free-radical reactions, with an initial stoichiometry as in eqn. (6) [compare mechanisms (1), (4) and (5)].

$$CH_3MgI + CH_3I \xrightarrow{\text{catalyst}} MgI_2 + 2\,CH_3^{\bullet} \qquad (6)$$

The methyl radicals would then abstract hydrogen to give methane and ether radicals [eqns. (7) and (8)], and the latter could then break down to yield methane, ethane,

$$CH_3^{\bullet} + C_2H_5OC_2H_5 \rightarrow CH_4 + CH_3\dot{C}HIC_2H_5 \qquad (7)$$

$$CH_3^{\bullet} + C_2H_5OC_2H_5 \rightarrow CH_4 + \dot{C}H_2CH_2OC_2H_5 \qquad (8)$$

and ethylene (together with a little propane and propene) by the processes postulated in part VI of this series[1]. This free-radical decomposition cannot be the only path available, however, for if two free methyl radicals are produced per molecule of iodomethane and react by hydrogen abstraction there should be formed not less than 2.0 mole methane per mole of iodomethane, whereas the observed figure (Table 1) is only 1.542. Furthermore, from the two free methyl radicals should be produced[1] the following amounts of hydrocarbons: CH_4 (2.19), C_2H_6 (0.23), C_2H_4 (0.20), C_3H_8 (0.02), and C_3H_6 (0.02). These quantities are again different to those found (Table 1). As the reaction mixture in the present work contains also iodomethane and methylmagnesium iodide, it could be suggested that some of the observed products arise from interaction of methyl radicals with these two entities. It seems more probable, however, that such interaction would lead to no net chemical conversion [eqns. (9) and (10)].

$$CH_3^{\bullet} + CH_3^{0}I \rightarrow CH_3I + CH_3^{0\bullet} \qquad (9)$$

$$CH_3^{\bullet} + CH_3^{0}MgI \rightarrow CH_3MgI + CH_3^{0\bullet} \qquad (10)$$

We are forced to conclude that another reaction path, apart from the formation of free methyl radicals in solution, must be available, and that one of the main effects of this reaction path is the loss of methyl groups and a marked increase in the proportion of ethylene produced.

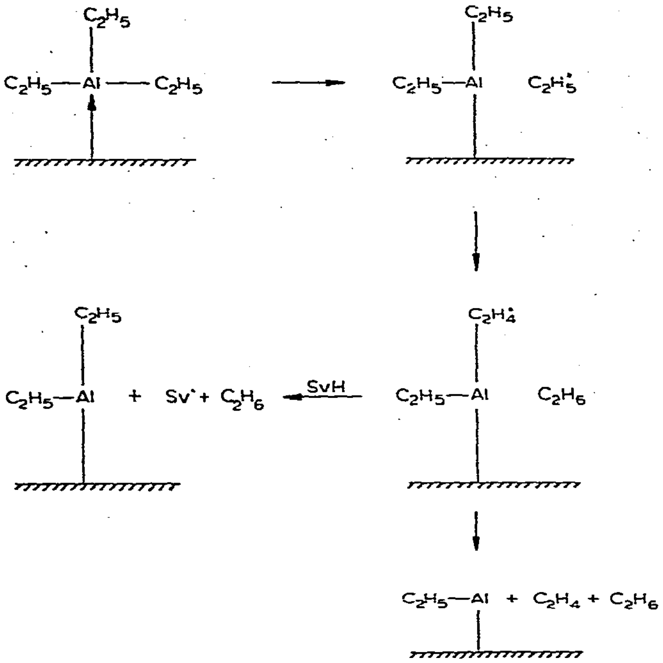


Fig. 1. The Prince and Weiss mechanism (SvH = solvent).

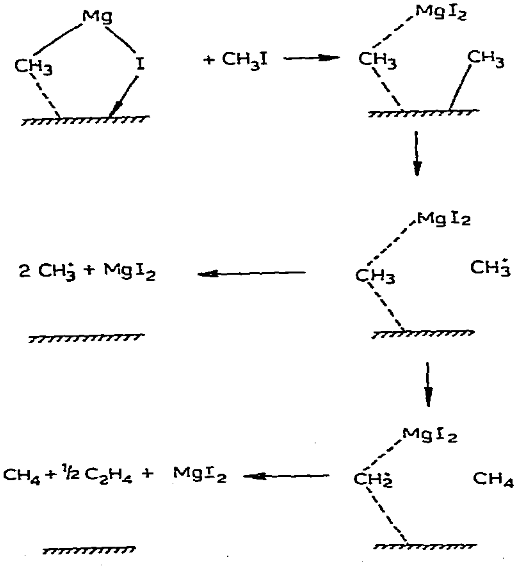
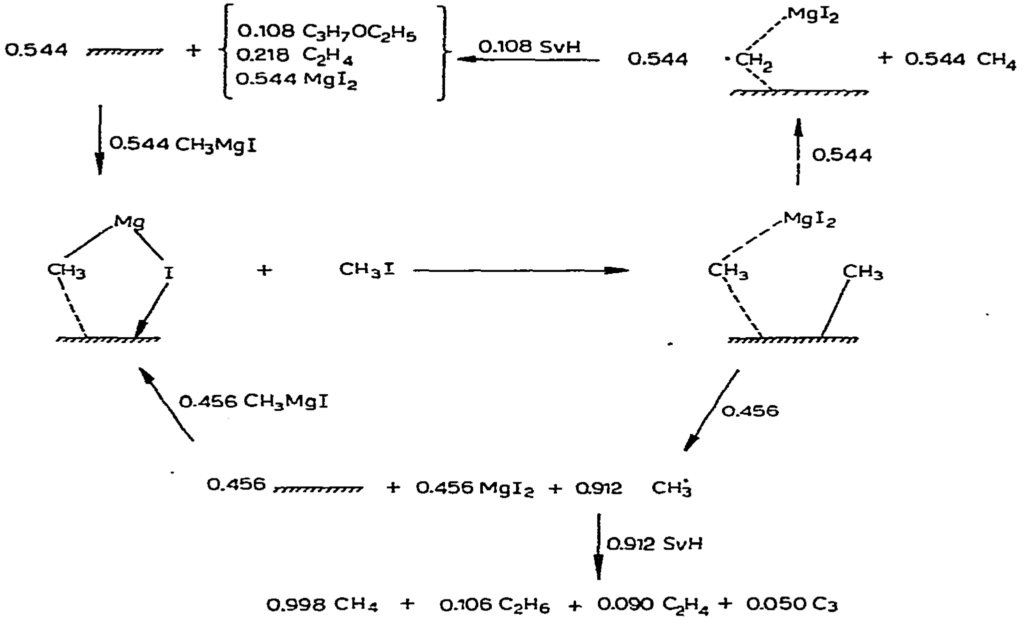


Fig. 2. Possible routes in the decomposition of iodomethane.

Now recently, Prince and Weiss[13], in an investigation of the degradation of triethylaluminium by cobaltous chloride, have suggested that an ethyl radical formed at the surface of a catalyst could abstract hydrogen from a σ-bonded ethyl group (Fig. 1). Zeiss and Sneeden[14] have also suggested that in the decomposition of the tribenzylchromium–diethylether complex, a benzyl radical is formed and remains within the complex; the radical can then abstract hydrogen from a solvating ether molecule or can react with a σ-bonded benzyl group by coupling or hydrogen transfer (the latter possibly via a chromium hydride[14]). The alkyl-to-alkyl hydrogen transfer (mechanism of Prince and Weiss (Fig. 1) is only applicable to methylmetal compounds if the σ-bonded methyl group is converted into a methylene derivative. If this is the case, it provides an explanation for the loss of methyl groups and the formation of much ethylene (by combination of the methylene derivatives) in the present work. Such a mechanism, together with the possibility that part of the process proceeds via the free-radical steps of eqns. (6), (7) and (8), results in the sequences shown in Fig. 2; the formation of ethylene could well involve two $^{\bullet}CH_2$–Co groups on the catalyst surface*. In addition, a fraction of the $^{\bullet}CH_2$–Co groups could collapse to methylene and escape into the solvent, there to react[15] by insertion [eqn. (11)]. If we assume that any free methyl radicals liberated into the solvent abstract hydrogen [eqns. (7) and (8)] and

$$:CH_2 + C_2H_5OC_2H_5 \rightarrow C_3H_7OC_2H_5 \qquad (11)$$

that the ether radicals so formed decompose to yield the same products as postulated[1]



Calculated overall stoichiometry:

$$CH_3MgI + CH_3I \rightarrow 1.542\ CH_4 + 0.106\ C_2H_6 + 0.308\ C_2H_4 + 0.050\ C_3 + MgI_2$$

Fig. 3. Decomposition of iodomethane by the free-radical route and the alkyl-to-alkyl hydrogen transfer route.

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* We shall discuss later our reasons for suggesting that the hydrogen transfers take place at a surface, rather than in solution.

previously, then such methyl radicals will yield the product quantities of eqn. 12. Incorporation of eqns. (11) and (12) into the basic sequence of Fig. 2 allows a quantitative treatment to be made (Fig. 3).

$$CH_3^{\cdot}+C_2H_5OC_2H_5 \rightarrow 1.094\ CH_4+0.116\ C_2H_6+0.099\ C_2H_4 +0.055\ C_3 \text{ compounds} \quad (12)$$

The Prince and Weiss mechanism is not the sole possibility for the non-free-radical process, and a sequence which involves the catalyst as an hydrogen abstractor [as in the OXO reaction[16], *cf.* eqn. (13)] is an attractive alternative.

$$Co\text{–}CH_2CH_2R \rightleftarrows Co\text{–}H+CH_2{=}CHR \quad (13)$$

This alkyl-to-cobalt hydrogen transfer mechanism is shown in Fig. 4, and it is evident that exactly the same numerical values for the quantities of the products will be obtained as in the alkyl-to-alkyl mechanism; there appears to be no way of deciding between the two schemes in the present work.

The 1-*chloro- and* 1-*iodo-octane decompositions*

Inspection of Table 1 shows that the composition of the gas from the halooctane reactions is quite similar to that from the iodomethane reaction. We may reasonably assume, therefore, that in the halooctane reactions, part of the methyl group (from the Grignard reagent) is liberated as methyl radicals, and that part suffers removal of hydrogen to give the methylene-catalyst intermediate. In order to deduce whether or not analagous reactions involving the n-octyl group take place, it is necessary to know the possible reactions of n-octyl free-radicals in solution. Tomilov and Fioshin[17] have suggested that n-butyl and n-hexyl free-radicals, when produced in high concentration in ether, dimerise quantitatively. This is in marked contrast to reactions of free-radicals in the gas phase, as it has been reported[18] that the ratio of disproportionation to combination (dimerisation) for n-pentyl radicals in the gas phase is $k_d/k_c=0.7$*, but is in accord with the suggestion of Wagner[20] that alkyl radicals do not disproportionate in the liquid phase, that is when they are formed singly in solution and not as a pair of radicals in a solvent cage.

Sargent and his co-workers[21] have examined the products obtained from free-radicals produced from alkyl halides in solvent 1,2-dimethoxyethane. They found the following percentage yields from the 1-halopentanes:

	n-Pentane	1-Pentene	n-Decane
1-Chloropentane:	43.9	0	0
1-Bromopentane:	29.2	0	5.0
1-Iodopentane:	17.3	3.7	55.7

Clearly the two major reactions of n-pentyl radicals are hydrogen abstraction and combination; the small yields of 1-pentene would indicate that disproportionation is of little consequence (*cf.* Wagner[20]). It was thought[21] that the increase in yield of n-decane along the series Cl < Br < I reflected the reactivity of the alkyl halides and consequently the actual concentrations of free-radicals.

In the present work we observed that 1-iodooctane decomposes much more rapidly than does 1-chlorooctane. Judging from the behaviour of n-pentyl radicals, we

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* Another value[19] for k_d/k_c for n-pentyl radicals in the gas phase is ≈0.2.

would therefore expect that if n-octyl free-radicals were liberated at some stage, there should be formed n-octane and n-hexadecane from the 1-iodooctane decomposition, and n-octane with much less n-hexadecane from the 1-chlorooctane reaction. This is indeed found to be so (see Table 1) and suggests that part of the decompositions must involve free n-octyl radicals. Once again, however, we must invoke another reaction path in order to account for the considerable quantities of octene produced in both decompositions, and it is of some interest to determine whether or not the hydrogen transfer mechanisms we have postulated above could lead to the observed yields of octene.

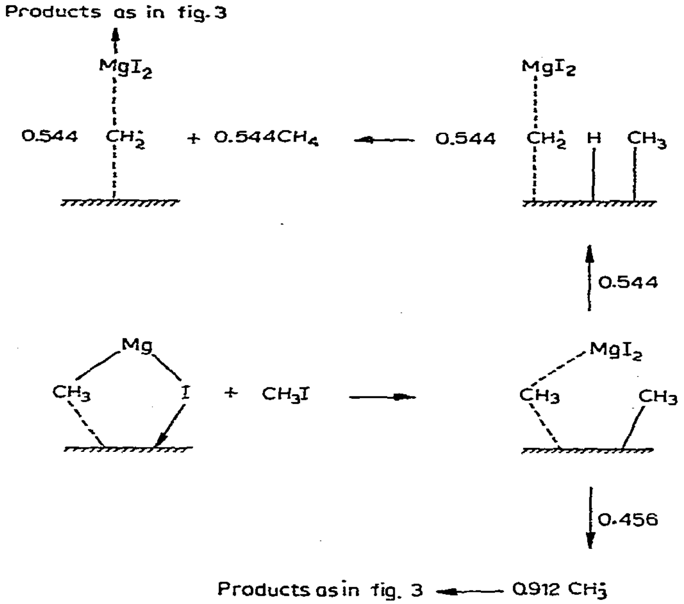


Fig. 4. Decomposition of iodomethane by the free-radical route and the alkyl-to-cobalt hydrogen transfer route.

Before attempting to apply the reaction schemes shown in Fig. 3 and Fig. 4 to the halooctane decompositions, we have to consider a number of other possible free-radical reactions that may involve methylmagnesium iodide and halooctane as substrates. The Grignard exchange reaction [eqn. (14)], judging from known[22] alkyl–metal bond energies, will be endothermic by some 5 kcal per mole; the reverse

$$\text{n-C}_8\text{H}_{17}^{\cdot}+\text{CH}_3\text{MgI} \rightarrow \text{n-C}_8\text{H}_{17}\text{MgI}+\text{CH}_3^{\cdot} \qquad (14)$$

reaction is more likely to take place as this would lead to the more stable free-radical ($\text{n-C}_8\text{H}_{17}^{\cdot}$). As we have also been unable to detect the presence of n-octylmagnesium iodide in the reaction products (that is before the final hydrolysis), reaction (14) can be eliminated. Both methyl and n-octyl free-radicals could attack any halooctane present. In the latter case, no net chemical conversion would take place [*cf.* eqn. (9)] but the former case would lead to the exchanges (15) and (16) in competition with the abstraction reaction (7 plus 8). Now Fox, Evans and Szwarc[23] have shown that

$$CH_3^{\cdot}+n\text{-}C_8H_{17}Cl \rightarrow CH_3Cl+n\text{-}C_8H_{17}^{\cdot} \tag{15}$$

$$CH_3^{\cdot}+n\text{-}C_8H_{17}I \rightarrow CH_3I+n\text{-}C_8H_{17}^{\cdot} \tag{16}$$

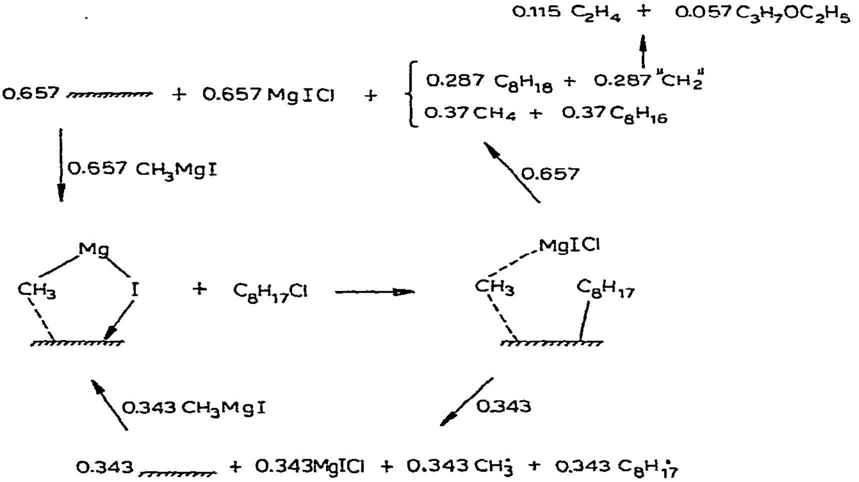
$k_{18}/k_{17}=180$ in solvent toluene at 65°, and from data compiled by Trotman-Dickenson[24] we estimate that $(k_7+k_8)/k_{17} \approx 1.9$. Hence $k_{18}/(k_7+k_8) \approx 95$. As 1-iodooctane

$$CH_3^{\cdot}+C_6H_5CH_3 \rightarrow C_6H_5CH_2^{\cdot}+CH_4 \tag{17}$$

$$CH_3^{\cdot}+C_2H_5I \rightarrow CH_3I+C_2H_5^{\cdot} \tag{18}$$

will probably be rather more reactive than iodoethane, we can say that $k_{16}/(k_7+k_8)$ will be of the order of 100, and taking into account the average concentrations of 1-iodooctane and ether present in the reaction mixture (about 0.003 to 1), the relative rates of (16) to [(7) plus (8)] could be about 0.3 to 1. Hence a significant proportion of the liberated methyl radicals could react by eqn. (16) rather than by hydrogen abstraction from the solvent. Fox, Evans and Szwarc[23] also showed that alkyl bromides reacted some 10^{-4} times as rapidly as alkyl iodides in corresponding reactions to eqn. (18), and thus eqn. (15) may surely be disregarded.

For the decomposition of 1-chlorooctane, we are thus restricted to the types of reaction postulated for the iodomethane decomposition, with the liberated n-octyl radicals abstracting hydrogen from the solvent to yield n-octane. All of the octene



$0.343\ CH_3^{\cdot}+0.343\ SvH \rightarrow 0.343\ CH_4+0.343\ Sv^{\cdot}$

$0.02\ C_8H_{17}^{\cdot} \rightarrow 0.01\ C_{16}H_{34}$

$0.323\ C_8H_{17}^{\cdot}+0.323\ SvH \rightarrow 0.323\ C_8H_{18}+0.323\ Sv^{\cdot}$

$0.666\ Sv^{\cdot} \rightarrow 0.062\ CH_4+0.077\ C_2H_6+0.066\ C_2H_4+0.037\ C_3$

Calculated overall stoichiometry:

$$CH_3MgI+C_8H_{17}Cl \rightarrow 0.61\ C_8H_{18}+0.37\ C_8H_{16}+0.01\ C_{16}H_{34} +0.775\ CH_4+0.077\ C_2H_6+0.181\ C_2H_4+0.037\ C_3+MgICl$$

Fig. 5. Decomposition of 1-chlorooctane.

formed must be produced on the catalyst surface by either octyl-to-alkyl or octyl-to-cobalt hydrogen abstraction, and in Fig. 5 we present a quantitative scheme of decomposition*. We have not specified the origin of the 2-octene produced, but in view

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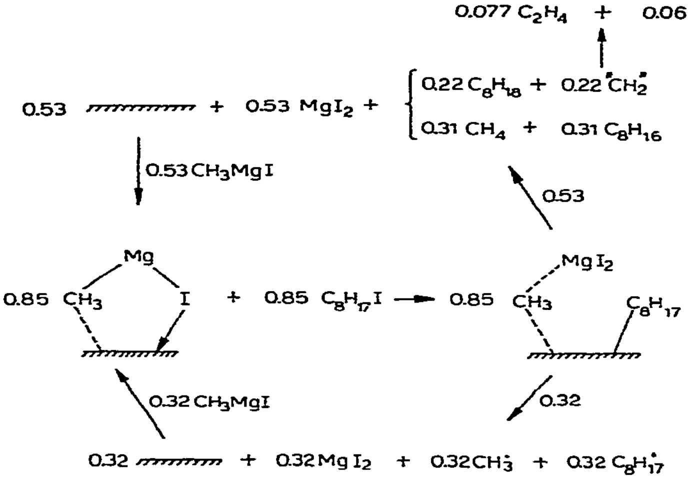
* This scheme applies to both hydrogen abstraction mechanisms.

of the slow rate of reaction of 1-chlorooctane, it is possible that the 2-octene arises by isomerisation of the initially produced 1-octene.

The decomposition of 1-iodooctane is considerably more complicated; only part of the 1-iodooctane reacts with the catalyst complex, and the remainder is converted into n-octyl radicals and iodomethane [eqn. (16)]. This iodomethane can then itself react with the catalyst complex, according to the scheme shown in Fig. 4, to yield products in accordance with the results given in Table 1. Octyl radicals, formed in higher concentration than in the 1-chlorooctane system, may combine (to give n-hexadecane). The final total set of reactions is given in Fig. 6, with the ratio of methyl radicals reacting by reaction (16) to reactions (7) plus (8) being 0.15 to 0.17, as compared with our rough estimate of 0.3 to 1. In neither Fig. 5 nor Fig. 6 have we suggested any process leading to the minor product tentatively identified as $C_8H_{17}CH(CH_3)$-OC_2H_5 or $C_8H_{17}CH_2CH_2OC_2H_5$, but combination of n-octyl radicals with the ether radicals produced by reactions (7) and (8) would lead to such a product.



$0.15\ CH_3^{\cdot}+0.15\ C_8H_{17}I \rightarrow 0.15\ CH_3I+0.15\ C_8H_{17}^{\cdot}$
$0.17\ CH_3^{\cdot}+0.17\ SvH \rightarrow 0.17\ CH_4+0.17\ Sv^{\cdot}$
$0.35\ C_8H_{17}^{\cdot} \rightarrow 0.175\ C_{16}H_{34}$
$0.12\ C_8H_{17}^{\cdot}+0.12\ SvH \rightarrow 0.12\ C_8H_{18}+0.12\ Sv^{\cdot}$
$0.29\ Sv^{\cdot} \rightarrow 0.027\ CH_4+0.034\ C_2H_6+0.029\ C_2H_4+0.016\ C_3$
$0.15\ CH_3I+0.15\ CH_3MgI/\text{Catalyst} \rightarrow 0.231\ CH_4+0.013\ C_2H_6+0.046\ C_2H_4+0.013\ C_3$

Calculated overall stoichiometry:

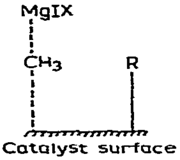
$$CH_3MgI+C_8H_{17}I \rightarrow 0.34\ C_8H_{18}+0.31\ C_8H_{16}+0.175\ C_{16}H_{34}+0.738\ CH_4+0.047\ C_2H_6 +0.152\ C_2H_4+0.029\ C_3$$

Fig. 6. Decomposition of 1-iodooctane.

Comparison of the alkyl halide decompositions

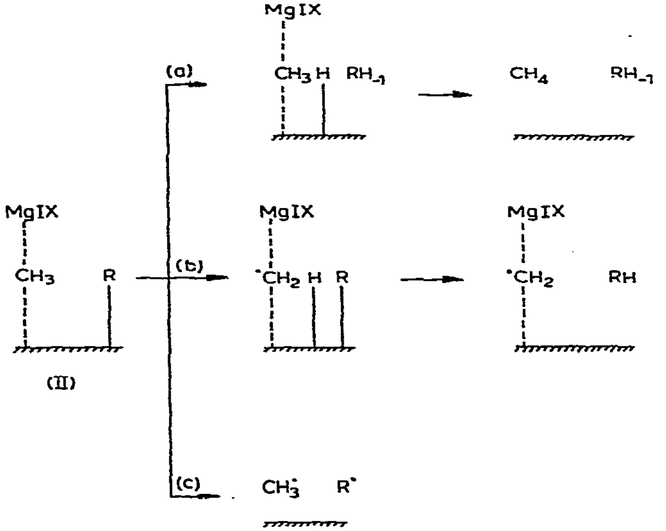
The reaction sequences shown in Figs. 3 to 6 all lead to an overall stoichiometry in which one mole of alkyl halide and one mole of Grignard reagent (as CH_3-MgI) are consumed; this is in accord with the theories referred to in the Introduction. An essential feature of these above sequences is an intermediate complex [(II), R = alkyl, X = halogen)] in which both the alkyl group of the Grignard reagent (CH_3)

and the alkyl group of the alkyl halide (R) are bonded to a catalyst surface, no doubt by alkyl-to-cobalt bonds. The complex (II) may decompose in three ways, (a) hydrogen



(II)

abstraction from the group R, (b) hydrogen abstraction from the methyl group, and (c) collapse to $CH_3^\bullet$ and $R^\bullet$ free-radicals. The proportion of (II) decomposing by these three routes has a major effect on the eventual product distribution, and these proportions are given in Fig. 7, for the alkyl halides investigated, in terms of the alkyl-to-cobalt hydrogen abstraction theory (the proportions are the same on the alkyl-to-alkyl theory). Most noticeable in Fig. 7 is that route (a) is much more favoured when R = n-octyl than with R = methyl. This is as expected, for elimination to give octene (R = n-octyl) should indeed be preferred to elimination to give a methylene compound (R = methyl). As a result of this restriction on route (a), route (c) becomes the predominant path when R = methyl.



Proportion decomposing by route:	(a)	(b)	(c)
$R=CH_3, X=I$	0.272[a]	0.272[a]	0.456
$R=C_8H_{17}, X=I$	0.365	0.259	0.376
$R=C_8H_{17}, X=Cl$	0.370	0.290	0.340

[a] These proportions here assumed equal, although not necessarily so.

Fig. 7. Decomposition routes of the complex (II).

Finally, it is of interest to calculate the products arising from decomposition of the methylene-complex system [route (b) when R = n-octyl, and routes (a) plus (b) when R=methyl] in the three cases. The proportion of the methylene-complex yielding ethylene is 0.80 (R=methyl, X=iodine), 0.70 (R=n-octyl, X=iodine), and 0.80 (R=octyl, X=chlorine); as decomposition of the methylene-complex system does not formally involve the alkyl groups n-octyl and methyl, the above proportions might be expected to be approximately constant, as indeed found.

It is evident that the reaction schemes we have advanced above can account qualitatively and quantitatively for the major products found in the Kharasch reactions of iodomethane and 1-iodo- and 1-chloro-octane with methylmagnesium iodide. We conclude, as did Parker and Noller[9], that only part of the reaction products arise from free-radicals liberated into the bulk of the solvent. On our hypothesis, a large fraction of the products are formed as a result of a series of hydrogen abstraction reactions on the catalyst surface, possibly involving a cobalt hydride. In the case of the 1-halooctane reactions, both n-octyl groups and methyl groups become attached to the catalyst surface where the n-octyl group preferably loses a hydrogen atom (to give 1-octene and, eventually methane) rather than gains a hydrogen atom (to give n-octane and a methylene-catalyst compound). This contrasts with the finding of Parker and Noller[9], on the 2-bromopropane/isopropylmagnesium bromide/cobaltous bromide reaction, that the alkyl group of the alkyl halide gained a hydrogen atom rather than lost one. The two sets of results are not incompatible, at least on the theories put forward in the present work, if we regard hydrogen abstraction from the alkyl group of the halide and the Grignard reagent to be in direct competition with each other. Even if the alkyl group of the halide has a tendency to gain a hydrogen atom (*i.e.*, when the two alkyl groups concerned are the same), the reluctance of the methyl group to lose a hydrogen atom would lead to the situation found in the present work*.

Kinetic and mechanistic studies

We have shown previously[1] that the catalyst system used in the present work is heterogeneous, with the cobalt contained in particles, about 20 Å to 1000 Å diameter, as a colloidal suspension in the ethereal solution of an excess of methylmagnesium iodide. Addition of alkyl halide to the catalyst system does not alter the heterogeneous nature, the catalyst system remains as a colloidal suspension both during and after the alkyl halide decomposition. It does not seem possible that the cobalt in the particles is removed into solution during the decomposition, then to revert back into particulate form, and we feel that it is much more reasonable to assume that the cobalt remains contained in the particles throughout the decomposition.

The particles are very small, their total surface area is large, and encounters between the particle surface and species in solution are thus highly probable. We have earlier suggested[1] that the particles in colloidal suspension contain not only zero-valent cobalt, but also the Grignard reagent (complexed to the cobalt). Hence an encounter between the particle surface and a molecule of alkyl halide will suffice to bring together the three fundamental species: alkyl halide, Grignard reagent, and cobalt.

In order to obtain more information on these mechanistic details we have briefly studied the kinetics of alkyl halide decomposition. The rates of decomposition

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* In other words, formation of a methylene derivative from an attached methyl group is a much less favoured process than formation of 1-octene from an attached n-octyl group.

of alkyl halides by our catalytic system were in the order 1-iodooctane > 1-bromooctane ≈ iodomethane > 1-chlorooctane (compare the sequence bromoethane > chloroethane found by Parker and Noller[9] for the ethyl halide/ethylmagnesium bromide/cuprous chloride system). For kinetic studies, 1-bromooctane was the most convenient halide to use, and we have measured the rate of evolution of gas on decomposition of this halide. In any kinetic experiment the concentration of catalyst remains constant, and as the methylmagnesium halide is always in large excess its concentration may be taken as constant throughout a given kinetic run. Each experiment was thus treated as a first-order reaction and results are given in Table 2. If we assume that the rate of evolution of gas is equal to the rate of decomposition of 1-bromooctane, then in any run the order with respect to 1-bromooctane is unity*. Results in Table 2 (*A*) show that over a $2\frac{1}{2}$-fold increase in the initial concentration of 1-bromooctane, the first order constant in fact decreases somewhat. The order with respect to catalyst can be deduced from Table 2 (*B*) and is 1.3; in view of the heterogeneous nature of the system it is not surprising that this order deviates from unity (although Parker and Noller[9] found first-order in catalyst). Results in Table 2 (*C*) are more difficult to interpret, even taking into account a dimer ⇄ monomer equilibrium for the Grignard reagent, *e.g.*:

TABLE 2

KINETICS OF THE CATALYSED DECOMPOSITION OF 1-BROMOOCTANE BY METHYLMAGNESIUM IODIDE AT 36°

Run	Initial concentrations (mole·l^{-1})			k_1	
	CH_3MgI	$CoCl_2$	$1\text{-}C_8H_{17}Br$	(min^{-1})	
(*A*)					
33	0.760[a]	6.94×10^{-3}	0.0207	0.75	
32	0.760	6.94×10^{-3}	0.0311	0.71	
30	0.760	6.95×10^{-3}	0.0414	0.68	
39	0.760	6.90×10^{-3}	0.0518	0.51	
(*B*)					$k_1/[CoCl_2]_0^{1.3}$
27	0.760	2.33×10^{-3}	0.0414	0.175	460
28	0.760	3.86×10^{-3}	0.0414	0.31	425
29	0.760	5.36×10^{-3}	0.0414	0.49	440
30	0.760	6.95×10^{-3}	0.0414	0.68	430
31	0.760	8.50×10^{-3}	0.0414	0.97	480
(*C*)					$k_1/[CH_3MgI]_0^{0.5}$
37	0.142	6.90×10^{-3}	0.0414	0.28	0.74
36	0.219	6.90×10^{-3}	0.0414	0.38	0.81
35	0.296	6.94×10^{-3}	0.0414	0.44	0.81
34	0.373	6.90×10^{-3}	0.0414	0.52	0.85
30	0.760	6.95×10^{-3}	0.0414	0.68	0.78

[a] All figures in this column are corrected for the amount consumed in the initial reaction with cobaltous chloride.

$$(CH_3)_2Mg\cdot MgI_2 \rightleftharpoons 2\,CH_3MgI$$

$$CH_3MgI + \text{Reactant} \rightarrow \text{Products}$$

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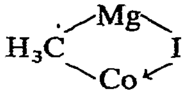
* The overall order is complex, and the rate of decomposition of the alkyl halide may be represented by $-d[1\text{-}C_8H_{17}Br]/dt \approx 500\ l^{1.8}\cdot mole^{-1.8}\cdot min^{-1}\cdot[1\text{-}C_8H_{17}Br]\cdot[Catalyst]^{1.3}\cdot[CH_3MgI]^{0.5}$.

As the actual association factor for CH_3MgI could vary[25] from about 1.4 in run 37 (0.14 *M* in Grignard) to 2.0 in run 30 (0.76 *M* in Grignard), it is clear that there is little we can say as to the kinetic role of the Grignard reagent. We can conclude, though, that the rate of alkyl halide decomposition is influenced by the nature and the concentration of the alkyl halide, and by the concentration of the catalyst; a rate-determining encounter between the catalyst particle surface and the alkyl halide is therefore indicated. The surface of the catalyst (composition $Co[CH_3MgI]_2$) will contain



(III)

groups such as (III) and reaction of such a group with a molecule of alkyl halide could lead to destruction of the elements of the Grignard reagent and formation of methyl-to-catalyst and alkyl-to-catalyst bonds*. The intermediate complex (II) breaks down by a series of rapid reactions, partly free-radical and partly non-free-radical, to leave an inactive site on the surface of the catalyst. Finally an active catalytic site is regenerated by the Grignard reagent. Whether the inactive site is a "hole" at the surface

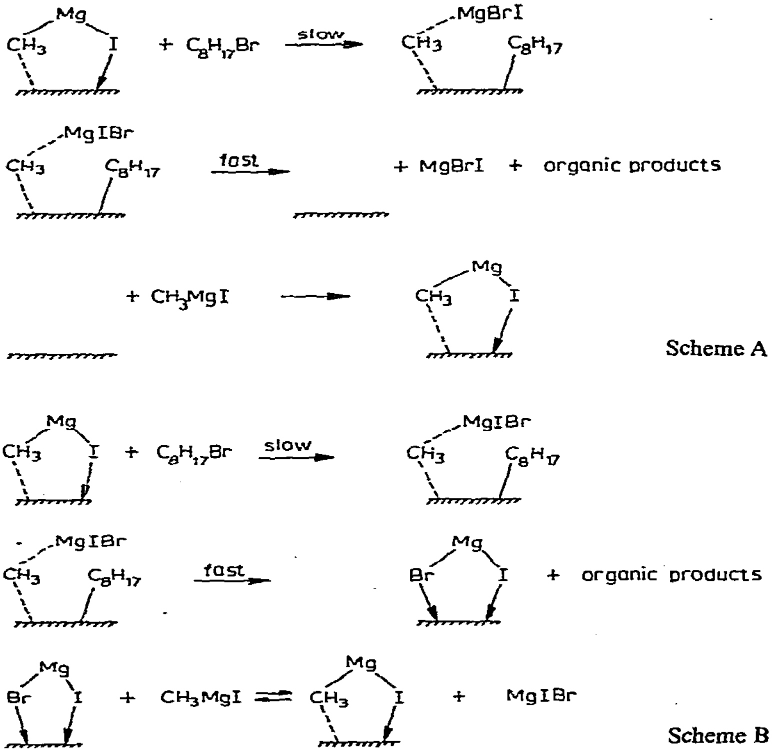


Fig. 8. Mechanistic scheme for the Kharasch reaction; illustrated for the decomposition of 1-bromooctane by methylmagnesium iodide.

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* Probably methyl-to-cobalt and alkyl-to-cobalt bonds, but these bonds need not necessarily involve the same cobalt atom.

[Fig. 8(A)] or a site at which inactive magnesium halide has replaced the active Grignard reagent [Fig. 8(B)] cannot be determined with certainty, although from further experiments (see below) we favour sequence (B) shown in Fig. 8; the resemblance of this scheme to that suggested[10] by Costa and his co-workers [eqn. (5)] is noteworthy.

Support for scheme (B) shown in Fig. 8 comes from a final set of experiments starting with a black solid of composition[1] $Co[MgX_2]_{0.27}$. A suspension* of this solid in ether reacts neither with 1-iodooctane nor with methylmagnesium iodide, but in the presence of both of these reagents (equal molar quantities) the solid is converted into a black colloidal suspension [(IV), Fig. 9]. Unlike the colloids used in the previous experiments, the particles in this colloidal suspension are not surrounded by an excess of Grignard reagent and are likely to have the composition $Co[MgX_2]_2$. 1-Iodooctane is not decomposed by this colloid [(IV), Fig. 9], but when methylmagnesium iodide is then added the characteristic evolution of gas is observed. Our interpretation follows scheme (B) of Fig. 8. The particles in the colloid [(IV), Fig. 9] have magnesium halide groups bound to the surface; these groups are inactive towards alkyl halides, but on addition of methylmagnesium iodide some magnesium halide groups are replaced by CH_3MgI groups at the surface. The latter are active catalytic sites and thus readily react with alkyl halides.

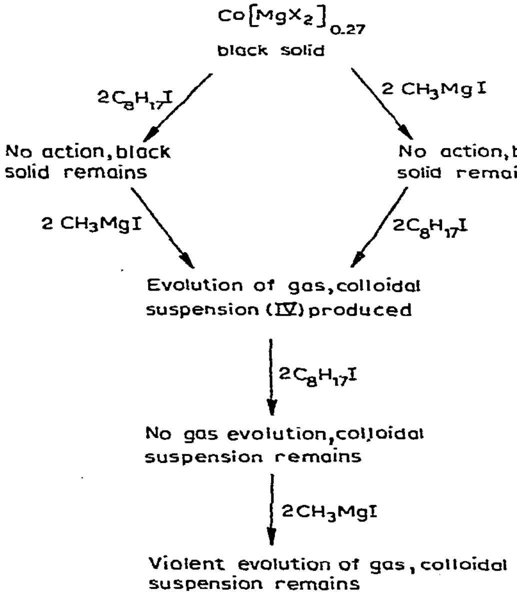

Fig. 9. The action of 1-iodooctane and methylmagnesium iodide on the solid, $Co[MgX_2]_{0.27}$.

Scheme (B) shown in Fig. 8, together with the sequences shown in Figs. 2 to 7**, thus serves to correlate all of our observations on the course and mechanism of the Kharasch reaction.

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* Not a colloidal suspension, note.

** For clarity, Figs. 2 to 7 have actually been written in terms of mechanism (8A); the application of mechanism (8B) to the schemes shown in Figs. 2 to 7 is straightforward.

EXPERIMENTAL

Anhydrous cobaltous chloride was prepared as described[1] previously. Ether was sodium dried and freshly distilled. The alkyl halides were commercial samples; gas chromatography showed no detectable impurities. Nitrogen was purified as before[1].

Gaseous hydrocarbon analyses were carried out using a Shandon flame thermocouple gas chromatograph as outlined[1] previously. Analyses of ethereal solutions were performed using a Pye Argon gas chromatograph in which the glass columns had been adapted for the injection of samples from a hypodermic syringe. Columns of 3 % squalane and of 10 % tritolyl phosphate were used for qualitative analysis of the C_8 hydrocarbons at 25°, and columns of 2 % Apiezon L and of 10 % silicone oil were used for qualitative analysis of C_{16} hydrocarbons at 125°. For quantitative analysis of these hydrocarbons (obtained as dilute solutions in ether) internal standards were used and the relative molar responses of the various components and standards were obtained under the conditions of the actual analyses. The C_8 analyses were performed at 25° using a column of 15% tritolyl phosphate on 100–125 mesh celite, an argon flow rate of 25 ml/min, and a detector voltage of 2000; under these conditions the relative molar responses were n-octane (0.84), 1-octene (1.05), and 2-octene (1.00). A known quantity of 2-octene was added as an internal standard. For samples which already contained 2-octene, the appropriate calculation was made. Analyses for n-hexadecane were carried out at 200° using a column of 18 % Apiezon L on 100–125 mesh celite, an argon flow rate of 35 ml/min, and a detector voltage of 1500; the internal standard was n-tetradecane and the relative molar responses were n-hexadecane (1.04) and n-tetradecane (1.00).

Methylmagnesium iodide was prepared and analysed by the methods described[1] previously. The catalytic colloidal suspension was obtained by the addition of anhydrous cobaltous chloride (0.1 g, 7.6×10^{-4} mole) to a refluxing solution of 0.77 *M* methylmagnesium iodide (100 ml, 7.7×10^{-2} mole). Hydrocarbon gases were removed either by (*a*) refluxing the resulting colloidal suspension for several hours under a slow stream of nitrogen, or (*b*) cooling the colloidal suspension by a solid carbon dioxide/acetone mixture, and degassing the colloid under a high vacuum.

Action of the colloidal suspension on alkyl halides

The alkyl halide (5×10^{-3} mole) was allowed to fall into the stirred colloidal suspension (100 ml; prepared as above) whilst the latter was gently refluxing. Evolution of gas began immediately, and after evolution had ceased the volume of the evolved gas was measured and the entire gaseous products then swept out from the apparatus in a stream of nitrogen, collected, and analysed. To the remaining ethereal liquid (which was still a black colloidal suspension) was carefully added dilute sulphuric acid, and the ethereal layer separated, washed with water, and analysed. Apart from the C_8 and C_{16} hydrocarbons already mentioned, there was one other high-boiling substance present (as a minor constituent); from the behaviour of this constituent on gas chromatography on several stationary phases, it was identified as an ether, of b.p. 201–207°, containing twelve or thirteen carbon atoms. There were also present a number of low-boiling minor constituents, with gas chromatographic retention times slightly greater than that of diethylether. Analytical results are presented in

Table 1, and are averages of triplicate experiments for each alkyl halide. The material balance of C_8 and C_{16} compounds was 110% in the 1-chlorooctane reaction and 90% in the 1-iodooctane reaction. We feel that these figures reflect some systematic errors in the analyses, and the figures given in Table 1 have been corrected to a mass balance of 100% in both cases.

Search for n-octylmagnesium halide

1-Iodooctane (5×10^{-3} mole) was allowed to react with the colloidal suspension (100 ml) as described in the previous section. After evolution of gas had ceased, the resulting product was not hydrolysed, but an excess of mercuric iodide, in solvent dimethoxyethane, was added in order to convert alkylmagnesium groups into alkylmercury groups. After the mixture had been refluxed, an excess of iodine was then added to convert the alkylmercury groups into the corresponding alkyl iodides. Examination of the ethereal mixture by gas chromatography revealed the presence of iodomethane, but showed no 1-iodooctane. Even after concentration to small bulk, no more than a mere trace of component with the same retention time as 1-iodooctane was found.

Action of methylmagnesium iodide on alkyl halides

An ethereal solution of 0.83 *M* methylmagnesium iodide (100 ml) was boiled under reflux for three h, during which time no gas was evolved. To the refluxing solution was added iodomethane (8.25×10^{-4} mole) and after a further ten h reflux there was collected 2.7×10^{-4} mole of gaseous products, with a % molar composition CH_4 (67.2), C_2H_6 (12.2), C_2H_4 (12.8), C_3H_8 (6.7), and C_3H_6 (0.9). Hydrolysis of the ethereal solution followed by gas chromatography revealed iodomethane (77% of the starting material).

In a similar experiment using 1-iodooctane (4.5×10^{-3} mole) as the halide, there was collected 6.7×10^{-4} mole of gaseous products, after nine h reflux, of % molar composition CH_4 (11.4), C_2H_6 (3.4), C_2H_4 (5.2), C_3H_8 (76.2), and C_3H_6 (3.8). Gas chromatography of the liquid products showed only 1-iodooctane; no trace of C_8 or C_{16} hydrocarbons was found.

Kinetic experiments

Anhydrous cobaltous chloride was added to the refluxing solution of methylmagnesium iodide (100 ml) and, after conditions had stabilised, the apparatus was connected to a gas burette. An ampoule of the 1-bromooctane was caused to fall into the refluxing colloidal suspension and the evolution of gas measured at intervals of time. If V_t is the volume of gas evolved after time t, and V_∞ the total volume evolved, then a plot of $\log_e[V_\infty/(V_\infty - V_t)]$ *vs.* t should give a straight line of slope k_1. This was found to be the case, and the results of experiment 32 are given below as a typical kinetic run. Time in min (V_t in ml): 0 (0); 0.5 (13.3); 1.0 (28.5); 1.5 (42.5); 2.0 (52.9); 2.5 (61.0); 3.0 (66.2); 3.5 (68.4); 4.0 (71.1); 4.5 (72.0); 5.0 (72.8); 5.5 (72.8); 6.0 (73.4); ∞ (74.7).

Table 2 gives the results of various experiments in which the initial concentration of 1-bromooctane and of the added cobaltous chloride were varied [Table 2 (*A*) and Table 2 (*B*), respectively]. All of these runs are at a temperature of 36°, that of boiling 0.76 *M* methylmagnesium iodide. For runs in which the Grignard reagent concentration was varied [Table 2 (C)], the reaction temperature was less than 36° (runs 34 to 37). We have corrected for this on the rough basis that a drop of 1° in reaction temperature would lead to a 10% reduction in the rate of reaction. The observed values of k_1, together with the "corrected" values are shown below; in Table 2 (C) the corrected values are given. Run No. (observed k_1, corrected k_1): 37 (0.25, 0.28); 36 (0.35, 0.38); 35 (0.41, 0.44); 34 (0.49, 0.52); 30 (0.68, 0.68). There is little difference between the observed and corrected figures, and the corrections do not affect the results to any marked extent.

Action of 1-*iodooctane and of methylmagnesium iodide on* $Co[MgX_2]_{0.27}$

Addition of anhydrous cobaltous chloride to an 0.05 M solution of methylmagnesium iodide (ratio CH_3MgI to Co 2:1) yielded a black powder after two h reflux. The powder was separated, washed with dry, oxygen-free ether and dried by warming under a high vacuum. Analysis gave a composition $Co[MgX_2]_{0.27}$. To the solid was added 0.77 M methylmagnesium iodide (ratio CH_3MgI to Co 2:1), and the mixture stirred and then refluxed for two h. The solid remained undispersed and only slight evolution of gas was noticed. On addition of 1-iodooctane (ratio alkyl halide to Co 2:1) to the cooled mixture, fine streams of bubbles were observed to rise from the solid at the vessel bottom; after half-an-hour the solid was completely dispersed as a black colloidal suspension, with a small evolution of gas. A further addition of 1-iodooctane (ratio alkyl halide to Co 2:1) led to no apparent change, but on addition of methylmagnesium iodide (ratio CH_3MgI to Co 2:1) the 1-iodooctane was decomposed with evolution of heat and much gas. A further addition of Grignard reagent produced but little gas.

When 1-iodooctane (ratio alkyl halide to Co 2:1) was added to the solid, $Co[MgX_2]_{0.27}$, suspended in ether, there was no reaction, but addition of Grignard reagent (ratio CH_3MgI to Co 2:1) resulted in a brief evolution of gas and formation of a black colloidal suspension.

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