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## THESIS

A KINETIC STUDY OF THE KHARASCH REACTION

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by

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Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

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IN
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ABSTRACT

A kinetic study of the reaction between organometallics and organic halides under cobaltous halide catalysis. Possible mechanisms of the reaction are discussed using experimental data. Rate expressions are derived from previously postulated mechanisms and compared to the experimentally derived rate expression.

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## INTRODUCTION

The coupling reaction between Grignard reagents and organic halides under cobaltous halide catalysis has been known since 1944. This reaction has been studied by several people, the foremost being Kharasch at the University of Chicago. He studied the reaction rather extensively, and used it frequently as a synthetic tool.[1] Even though Kharasch studied many aspects of the reaction and postulated a possible mechanism, he made no effort to prove his mechanism experimentally.

The kinetic study of the Kharasch reaction between amyl Grignard and cobaltous halides was undertaken hoping that some information could be gained on the nature of the reaction. The data are used to calculate a rate equation. Possible partial mechanisms of the reaction are discussed in light of these results.

[1] M. S. Kharasch and O. Reinmuth, Grignard Reaction of Non-Metallic Substance, Prentice Hall, 1954.

## HISTORICAL

Any attempt at a comprehensive review of the reactions of Grignard reagent with metallic halides would extend far beyond the scope of this work. There has been, and continues to be, a great deal of discussion and conflict in the literature concerning the mechanisms of such reactions, since, present knowledge of the reactions of Grignard reagents with metallic halides is by no means extensive or exact. Kharasch made many studies of the Grignard reagent and its reactions with metallic halides[2] and, in fact, studied one reaction so extensively that it is now commonly referred to as "The Kharasch Reaction".[3] This Kharasch reaction is the reaction between Grignard reagent and an organic halide that is catalyzed by halides of Group VIII metals, notably cobaltous halides.

$$RMgX + RX \xrightarrow{CoX_2} R\text{-}R + MgX_2$$

or

$$RMgX + RX \xrightarrow{CoX_2} R_{(H+)} + R_{(H-)} + MgX_2$$

Kharasch postulated the following equations to explain the observed products.

$$RMgX + CoX_2 \rightarrow RCoX + MgX_2$$

$$2RCoX \rightarrow R\text{-}R + 2CoX\cdot$$

$$2RCoX \rightarrow R_{(H+)} + R_{(H-)} + 2CoX\cdot$$

$$RCoX \rightarrow R\cdot + CoX\cdot$$

[2] cf. Kharasch and Reinmuth, loc. cit., page 119-129

[3] Some leading references to synthetic use
M. S. Kharasch, et. al., J. Org. Chem., 18 575 (1953)
J. T. Gragson, et. al., ibid., 20 129, (1955)
M. S. Kharasch, et. al., ibid., 21 129, (1956)
W. B. Smith, ibid., 23 509 (1958)

$$R'X + CoX\cdot \rightarrow R'\cdot + CoX_2$$

$$*2R\cdot \rightarrow R\text{-}R$$

$$2R\cdot \rightarrow R_{(H+)} + R_{(H-)}$$

These equations are followed by the statement, "The principal argument in favor of the transitory existence of organocobalt compounds of cobaltous subhalides is the utility of the working hypothesis based thereupon".[4]

Even though Kharasch seemed unsure of the existence of the cobaltous subhalide in the reaction sequence, he was very definite about the existence of a free radical during the reaction.[5,6,7]

Wilds and McCormack proposed an alternative reaction scheme,[8] postulating an unstable diorganocobalt compound as an intermediate and a highly reactive (colloidal) form of metallic cobalt as the active reducing agent. This proposal may be expressed as follows:

$$2RMgBr + CoCl_2 \rightarrow MgBr_2 + MgCl_2 + \{R_2Co\}$$

$$\{R_2Co\} \rightarrow R_{(+H)} + R_{(-H)} + Co$$

$$2Co + 2RX \rightarrow CoX_2 + \{R_2Co\}$$

Kharasch felt that elemental cobalt, in any physical state, was not sufficiently active to participate in the reaction as the reducing agent.[9]

*Kharasch did not include these steps, however it is apparent that they are required.

[4] cf. Kharasch and Reinmuth, loc. cit., page 125

[5] W. H. Urrey and M. S. Kharasch, J. Am. Chem. Soc., 66 1438 (1944)

[6] M. S. Kharasch and W. H. Urrey, J. Org. Chem., 13 101 (1948)

[7] M. S. Kharasch, et. al., J. Org. Chem., 24 303 (1959)

[8] A. L. Wilds and W. B. McCormack, J. Org. Chem., 14 45-55 (1949)

[9] cf. Kharasch and Reinmuth, loc. cit., page 128

He found that in a reaction involving phenylmagnesium bromide and bromobenzene, a few mole percent of cobaltous chloride was very effective in catalyzing the reaction and pyrophoric metallic cobalt, even in equivalent quantities, had no effect whatever.[10] Kharasch went on to say, however, that this observation was completly irrelevant if the colloidal metallic cobalt of Wilds and McCormack was significantly more active than pyrophoric cobalt.

Another aspect has been discussed by Slaugh,[11] who believes that many reactions between Grignard reagents and organic halides apparently involve radical formations; <u>however</u>, care must be taken when interpreting these reactions since the interchange reaction between Grignard reagent and organic halide are important side reactions and may in some cases entirely determine the reaction products. Slaugh concludes from the data obtained from preparing cyclopropane from 3-phenoxypropyl bromide and several other reactions that the mechanism is probably;

$$C_6H_5\text{-O-}C_3H_6\text{-Br} + C_2H_5MgBr \xrightarrow{CoBr_2}$$

$$C_6H_5\text{-O-}C_3H_6\text{-MgBr} + C_2H_5Br$$

$$C_6H_5\text{-O-}C_3H_6\text{-MgBr} \rightarrow C_6H_5\text{-O-MgBr} + C_3H_6$$

$$C_2H_5Br + C_2H_5MgBr \xrightarrow{CoBr_2} C_2H_4 + C_2H_6 + MgBr_2$$

The mechanism remains unsettled and is perhaps best summed up by Kharasch himself who wrote concerning the difference in his proposed mechanism and that of Wilds and McCormack. "So far as existing <u>direct</u> evidence is concerned the reader need feel no compulsion to reject one proposed scheme in favor of the other."

[10] M. S. Kharasch and J. Fields, J. Am. Chem. Soc., <u>63</u> 2316 (1941)

[11] L. Slaugh, J. Am. Chem. Soc., <u>83</u> 2734 (1961)

## EXPERIMENTAL

Reagents. 1-Bromopentane was fractionally distilled through a 75x2 cm column packed with glass helices. Only the middle fraction (b.p 128-128.5 at 760 mm., $n_D^{20}$ 1.4439; lit. 129.5, 1.4443 (12) ) was used. The 1-chloropentane ($n_D^{20}$ 1.4120; lit. 1.4128 (13) ) was found by gas chromatography to be over 98% pure and no further purification was attempted. Cobaltous bromide was prepared from cobaltous hydroxide and hydrobromic acid, then dried at 115°C for 2 days. Cobaltous chloride (Baker and Adamson) was also dried at 115°C for 2 days. Both were used without further treatment. The Grignard reagent was prepared in the usual manner[14] and concentrations determined by the acidimetric method.[15]

Procedure. The reactions were carried out under slight nitrogen pressure in a 150 cc jacketed vessel that was thoroughly dried and purged with dry nitrogen gas before use. Stirring was accomplished with a magnetic stirrer. Water from a constant temperature bath was pumped through the jacket and the temperature was maintained constant ±0.05 degrees throughout. A freshly prepared solution of the Grignard reagent in ether or tetrahydrofuran (THF) was placed in the vessel, followed by a solution of cobaltous halide in the same solvent. This latter solution was added in one portion. Samples were drawn by a 5 cc automatic pipette during the reaction and added to water, then the concentration of

[12] H. Gilman and R. H. Kirby, Org. Syn. Coll. Vol. I, Wiley, 361-363, (1932)

[13] H. Gilman, et. al., J. Am. Chem. Soc. 45, 150-158 (1923)

[14] B. Mair, Journal of Research of the National Bureau of Standards Washington D.C. 9, (1932) (Beilstein II 95)

[15] F. Whitmore, et. al., J. Am. Chem. Soc. 60, 2541 (1938) (Beilstein II 96)

Grignard reagent remaining was determined by adding excess HCl and back titrating with NaOH. The reaction mixture was analyzed by gas chromatography through a 2 meter polypropylene glycol column at 150°C and a flow rate of 60 ml/min of helium as carrier gas. Two peaks were detected, one 30 sec after the air peak, the other 18 sec later. Addition of n-pentane to the mixture caused the relative area under the initial peak to increase. Addition of THF caused the relative area under the final peak to increase. A solution of THF and n-decane was analyzed under the above conditions. The THF came off at 48 sec, the n-decane at 5.3 minutes. On the runs with ether as the solvent the pentane peak was obscured by the ether and no decane peak was observed. Bromine in carbon tetrachloride was used to titrate the pentene.[16] Samples were drawn from the reaction vessel and then excess bromine in carbon tetrachloride was added. The mixture was acidified, KI was added and then titrated with $Na_2S_2O_3$.

[16] F. Wild, Estimation of Organic Compounds, Cambridge Press 1953; 13-16

TABLE I

$$\text{rate} = k[\text{Grignard}]^a\ [CoX_2]^b \qquad k = \frac{\text{liters}^{(a+b-1)}}{\text{moles}^{(a+b-1)}\ \text{Min}}$$

| Run # | Solvent | Halide | Temp. (°C) | (RMgX) | ($CoX_2$) | k | a | b |
|---|---|---|---|---|---|---|---|---|
| 1 | THF | Br | 20.5 | .078M | $2.08\times10^{-3}$M | 346 | 2.46 | .56 |
| 2 | THF | Br | 20.5 | .078 | $1.04\times10^{-3}$ | 346 | 2.46 | .56 |
| 3 | THF | Br | 20.5 | .039 | $2.08\times10^{-3}$ | 355 | 2.46 | .56 |
| 4 | THF | Br | 20.5 | .069 | $2.08\times10^{-3}$ | 355 | 2.46 | .56 |
| 5 | THF | Br | 20.5 | .080 | $1.04\times10^{-3}$ | 339 | 2.46 | .56 |
| 6 | THF | Br | 20.5 | .083 | $1.04\times10^{-3}$ | 287 | 2.46 | .56 |
| 7 | THF | Br | 20.5 | .082 | $2.08\times10^{-3}$ | 258 | 2.46 | .56 |
| 8 | THF | Br | 1.0 | .078 | $2.08\times10^{-3}$ | 155 | 2.46 | .56 |
| 9 | THF | Br | 1.0 | .067 | $1.04\times10^{-3}$ | 126 | 2.46 | .56 |
| 10 | THF | Cl | 20.5 | .086 | $1.83\times10^{-3}$ | 198 | 2.46 | .56 |
| 11 | THF | Cl | 20.5 | .041 | $1.83\times10^{-3}$ | 254 | 2.46 | .56 |
| 12 | THF | Cl | 1.0 | .072 | $1.83\times10^{-3}$ | 36 | 2.46 | .56 |
| 13 | THF | Cl | 1.0 | .080 | $1.83\times10^{-3}$ | 57 | 2.46 | .56 |
| 14 | Ether | Br | 20.5 | .082 | $2.08\times10^{-3}$ | 163 | 2.14 | .65 |
| 15 | Ether | Br | 20.5 | .040 | $2.08\times10^{-3}$ | 166 | 2.14 | .65 |
| 16 | Ether | Br | 20.5 | .108 | $1.04\times10^{-3}$ | 166 | 2.14 | .65 |
| 17 | Ether | Br | 1.0 | .083 | $2.08\times10^{-3}$ | 36 | 2.14 | .65 |

Precision

THF - Br 9/100 at 20° 10/100 at 1°

THF - Cl 12/100 at 20° 30/100 at 1°

Ether - Br .6/100 at 20°

TABLE II

| Solvent | Halide | Δ H* Kcal/mole |
|---|---|---|
| THF | Br | 6.8 |
| THF | Cl | 13.8 |
| ETHER | Br | 14.2 |

Run #1

$[RMgBr]_{init.}$ = 0.078M $[CoBr_2]$ = 0.00208M In THF @ 20.5°C

Initial rate (slope) = 0.022 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 5 cc 0.3925M HCl added |
|---|---|
| 0 | 29.95 |
| 0.5 | 30.30 |
| 1.0 | 30.99 |
| 1.5 | 30.50 |
| 2.0 | 31.50 |
| 2.5 | 32.15 |
| 3.0 | 31.60 |
| 3.5 | 31.40 |
| 4.0 | 33.00 |
| 4.5 | 33.05 |
| 5.0 | 33.05 |
| 7.0 | 32.95 |
| 9.0 | 33.00 |
| 11.0 | 33.16 |
| 13.0 | 33.27 |
| 15.0 | 33.45 |
| 20.0 | 33.45 |
| 30.0 | 33.40 |
| 45.0 | ----- |
| 60.0 | 33.43 |

Run #2

$[RMgBr]_{init.}$ = 0.078M  $[CoBr_2]$ = 0.00104M  In THF @ 20.5°C

Initial rate (slope) = 0.015 $\frac{moles}{min}$

| Time (min) | cc of 0.05736M NaOH added after 5cc 0.3925M HCl added |
|---|---|
| 0 | 26.58 |
| 0.5 | 27.72 |
| 1.0 | 27.88 |
| 3.0 | 27.90 |
| 5.0 | 27.70 |
| 10.0 | 28.00 |
| 15.0 | 28.07 |
| 20.0 | 27.97 |
| 25.0 | 27.99 |
| 30.0 | 28.02 |
| 35.0 | 27.95 |
| 40.0 | 27.95 |
| 50.0 | 27.80 |
| 60.0 | 27.99 |
| 70.0 | 27.97 |
| 80.0 | 28.10 |
| 90.0 | 27.90 |
| 100.0 | 28.15 |
| 110.0 | 27.97 |
| 120.0 | 27.95 |

Run #3

$[RMgBr]_{init.}$ = 0.039M  $[CoBr_2]$ = 0.00208M  In THF @ 26.5°C

Initial rate (slope) = 0.004 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 16.67 |
| 0.5 | 16.82 |
| 1.0 | 16.99 |
| 1.5 | 16.81 |
| 2.0 | 17.00 |
| 2.5 | 17.10 |
| 3.0 | 17.10 |
| 3.5 | 17.07 |
| 4.0 | 17.10 |
| 4.5 | 17.17 |
| 5.0 | 17.12 |
| 7.0 | 17.10 |
| 9.0 | ----- |
| 11.0 | 17.12 |
| 13.0 | 17.12 |
| 15.0 | 17.00 |
| 20.0 | 17.05 |
| 30.0 | 17.07 |
| 45.0 | 17.01 |
| 60.0 | 17.10 |

Run #4

$[RMgBr]_{init.} = 0.069M$ $[CoBr_2] = 0.00208M$ in THF @ 20.5°C

Initial rate (slope) = 0.016 $\frac{moles}{min}$

| Time (min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 14.12 |
| 0.5 | 14.76 |
| 1.0 | 14.80 |
| 1.5 | 14.90 |
| 2.0 | 14.78 |
| 2.5 | 14.72 |
| 3.0 | 14.80 |
| 3.5 | 14.82 |
| 4.0 | 14.70 |
| 4.5 | 14.82 |
| 5.0 | 14.85 |
| 10.0 | 14.83 |
| 30.0 | 14.86 |

Run #5

$[PhMgBr]_{init.} = 0.080M$ $[CoBr_2] = 0.00104M$ In THF @ 20.5°C

Initial rate (slope) = 0.014 $\frac{moles}{min}$

| Time (min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 13.05 |
| 0.5 | 13.75 |
| 1.0 | 13.85 |
| 1.5 | 14.00 |
| 2.0 | 14.00 |
| 2.5 | 13.87 |
| 3.0 | 13.71 |
| 3.5 | 13.89 |
| 4.0 | 13.92 |
| 4.5 | 13.90 |
| 5.0 | 13.95 |
| 10.0 | 13.98 |

Run #6

$[RMgBr]_{init.} = 0.083M$ $[CoBr_2] = 0.00104M$ In THF @ 20.5°C

Initial rate (slope) = 0.013 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 12.92 |
| 0.5 | 13.60 |
| 1.0 | 13.70 |
| 1.5 | 13.42 |
| 2.0 | 13.28 |
| 2.5 | 13.12 |
| 3.0 | 13.50 |
| 3.5 | ----- |
| 4.0 | 13.47 |
| 4.5 | 13.52 |
| 5.0 | 13.55 |
| 10.00 | 13.48 |

Run #7

$[RMgBr]_{init.}$ = 0.082M $[CoBr_2]$ = 0.00208M In THF @ 20.5°C

Initial rate (slope) = 0.017 $\frac{moles}{min}$

| Time (min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 13.00 |
| 0.5 | 13.75 |
| 1.0 | 13.80 |
| 1.5 | 13.85 |
| 2.0 | 13.77 |
| 2.5 | 13.88 |
| 3.0 | 13.85 |
| 3.5 | 13.88 |
| 4.0 | 13.87 |
| 4.5 | 13.90 |
| 5.0 | 13.94 |
| 10.0 | 13.90 |
| 30.0 | 13.87 |

Run # 8

$[RMgBr]_{init.}$ = 0.078M $[CoBr_2]$ = 0.00208M In THF @ 1.0°C

Initial rate (slope) = 0.009 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 13.30 |
| 0.5 | 14.00 |
| 1.0 | 14.10 |
| 1.5 | 14.12 |
| 2.0 | 14.20 |
| 2.5 | 14.11 |
| 3.0 | 14.00 |
| 3.5 | 14.20 |
| 4.0 | 14.27 |
| 4.5 | 14.33 |
| 5.0 | 14.28 |
| 7.0 | 14.39 |
| 9.0 | 14.37 |
| 11.0 | 14.30 |
| 13.0 | 14.30 |
| 15.0 | 14.37 |
| 20.0 | 14.35 |
| 30.0 | 14.30 |
| 40.0 | 14.33 |
| 60.0 | 14.37 |

Run #9

$[RMgBr]_{init.} = 0.067M$ $[CoBr_2] = 0.00104M$ In THF @ $1.0^oC$

Initial rate (slope) = 0.004 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 14.30 |
| 0.5 | 14.50 |
| 1.0 | 14.60 |
| 1.5 | 14.57 |
| 2.0 | 14.53 |
| 2.5 | 14.50 |
| 3.0 | 14.62 |
| 3.5 | 14.59 |
| 4.0 | 14.65 |
| 4.5 | 14.71 |
| 5.0 | 14.76 |
| 7.0 | ----- |
| 9.0 | 14.80 |
| 11.0 | ----- |
| 13.0 | 14.82 |
| 15.0 | ----- |
| 20.0 | 14.75 |
| 30.0 | ----- |
| 45.0 | 14.90 |
| 60.0 | ----- |

Run #10

$[RMgCl]_{init.} = 0.086M$ $[CoCl_2] = 0.00183M$ In THF @ 20.5°C

Initial rate (slope) = 0.013 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 12.60 |
| 0.5 | 13.35 |
| 1.0 | 13.66 |
| 1.5 | 13.61 |
| 2.0 | 13.49 |
| 2.5 | 13.68 |
| 3.0 | 14.00 |
| 3.5 | 13.92 |
| 4.0 | 13.97 |
| 4.5 | 13.95 |
| 5.0 | 13.92 |
| 7.0 | 13.96 |
| 9.0 | 14.00 |
| 11.0 | 13.99 |
| 13.0 | 13.97 |
| 15.0 | 14.02 |
| 20.0 | 13.99 |
| 30.0 | 14.00 |
| 45.0 | 14.00 |
| 60.0 | 13.98 |

Run #11

$[RMgCl]_{init.}$ = 0.041M $[CoCl_2]$ = 0.00183M In THF @ 20.5°C

Initial rate (slope) = 0.003 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 16.48 |
| 0.5 | 16.92 |
| 1.0 | 17.00 |
| 1.5 | 16.82 |
| 2.0 | 17.01 |
| 2.5 | 17.00 |
| 3.0 | 17.02 |
| 3.5 | 16.97 |
| 4.0 | 17.10 |
| 4.5 | 17.07 |
| 5.0 | 17.17 |
| 7.0 | 17.05 |
| 9.0 | 17.12 |
| 11.0 | 17.10 |
| 13.0 | 17.10 |
| 15.0 | 17.13 |
| 31.5 | 17.12 |
| 45.0 | ----- |
| 60.0 | ----- |

Run #12

$[RMgCl]_{init.} = 0.072M$ $[CoCl_2] = 0.00183M$ In THF @ $1.0^oC$

Initial rate (slope) = 0.0015 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 13.87 |
| 0.5 | 14.00 |
| 1.0 | 14.00 |
| 1.5 | 14.12 |
| 2.0 | 14.12 |
| 2.5 | 14.15 |
| 3.0 | 14.21 |
| 3.5 | 14.23 |
| 4.0 | 14.25 |
| 4.5 | 14.20 |
| 5.0 | 14.30 |
| 7.0 | 14.37 |
| 9.0 | 14.40 |
| 11.0 | 14.40 |
| 13.0 | 14.48 |
| 15.0 | 14.62 |
| 20.0 | 14.50 |
| 30.0 | 14.30 |
| 45.0 | 14.32 |
| 60.0 | 14.10 |

Run #13

$[RMgCl]_{init.}$ = 0.080M $[CoCl_2]$ = 0.00183M In THF@ 1.0°C

Initial rate (slope) = 0.005 $\frac{moles}{min}$

| Time(min) | cc of 0.5736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 13.15 |
| 0.5 | 13.30 |
| 1.0 | 13.56 |
| 1.5 | 13.83 |
| 2.0 | 14.04 |
| 2.5 | 14.38 |
| 3.0 | 14.45 |
| 3.5 | 14.40 |
| 4.0 | 14.28 |
| 4.5 | 14.13 |
| 5.0 | 14.00 |
| 10.0 | 14.37 |
| 20.0 | 14.45 |
| 40.0 | 14.50 |

Run #14

$[RMgBr]_{init.}$ = 0.082M $[CoBr_2]$ = 0.00208M In ether @ 20.5°C

Initial rate (slope) = 0.014 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 5cc 0.3925M HCl added |
|---|---|
| 0 | 26.25 |
| 0.5 | 26.80 |
| 1.0 | 26.52 |
| 1.5 | 26.75 |
| 2.0 | 26.80 |
| 2.5 | 26.78 |
| 3.0 | 26.85 |
| 3.5 | 26.82 |
| 4.0 | 26.80 |
| 4.5 | 26.90 |
| 5.0 | 26.98 |
| 7.0 | 27.11 |
| 9.0 | 27.15 |
| 11.0 | 27.10 |
| 13.0 | 27.12 |
| 15.0 | 27.15 |
| 20.0 | 27.00 |
| 30.0 | 27.10 |
| 45.0 | 27.10 |
| 60.0 | 27.12 |

Run #15

$[RMgBr]_{init.}$ = 0.040M $[CoBr_2]$ = 0.00208M In ether @ 20.5°C

Initial rate (slope) = 0.003 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 5cc 0.3925M HCl added |
|---|---|
| 0 | 29.87 |
| 0.5 | 30.00 |
| 1.0 | 30.07 |
| 1.5 | 30.20 |
| 2.0 | 30.05 |
| 2.5 | 29.70 |
| 3.0 | 30.10 |
| 3.5 | 30.27 |
| 4.0 | 30.47 |
| 4.5 | 30.50 |
| 5.0 | 30.47 |
| 7.0 | ----- |
| 9.0 | 30.52 |
| 11.0 | 30.82 |
| 13.0 | 30.77 |
| 15.0 | 30.80 |
| 20.0 | 30.60 |
| 30.0 | 30.77 |
| 45.0 | 30.82 |
| 60.0 | 30.90 |

Run #16

$[RMgBr]_{init.}$ = 0.108M $[CoBr_2]$ = 0.00104M In ether @ 20.5°C

Initial rate (slope) = 0.016 $\frac{moles}{min}$

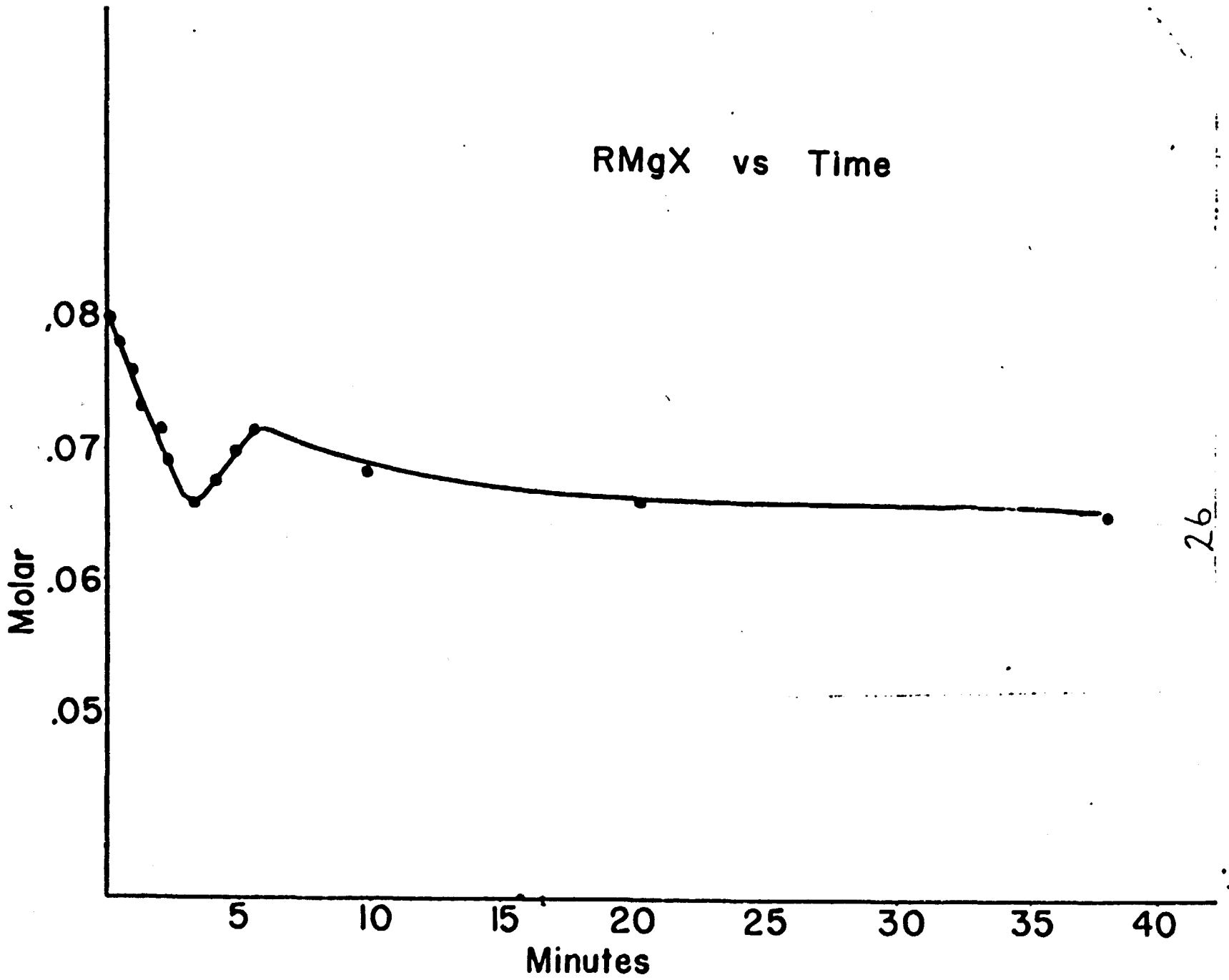
| Time(min) | cc of 0.05736M NaOH added after 5cc 0.3925M HCl added |
|---|---|
| 0 | 24.20 |
| 0.5 | 24.72 |
| 1.0 | 24.82 |
| 3.0 | 24.30 |
| 5.0 | 24.40 |
| 10.0 | 24.50 |
| 15.0 | 24.55 |
| 20.0 | 24.47 |
| 25.0 | 24.45 |
| 30.0 | 24.50 |
| 35.0 | 24.45 |
| 40.0 | 24.52 |
| 50.0 | 24.55 |
| 60.0 | 24.50 |
| 70.0 | 24.57 |
| 80.0 | 24.55 |
| 90.0 | 24.60 |
| 120.0 | 24.62 |

Run #17

$[RMgBr]_{init.}$ = 0.083M $[CoBr_2]$ = 0.00208M In ether @ 1.0°C

Initial rate (slope) = 0.0015 $\frac{moles}{min}$

| Time(min) | cc of 0.05736M NaOH added after 2cc 0.5822M HCl added |
|---|---|
| 0 | 13.00 |
| 0.5 | 13.20 |
| 1.0 | 13.25 |
| 1.5 | 13.30 |
| 2.0 | 13.37 |
| 2.5 | 13.42 |
| 3.0 | 13.50 |
| 3.5 | 13.77 |
| 4.0 | 13.68 |
| 4.5 | 13.80 |
| 5.0 | 13.97 |
| 7.0 | 13.78 |
| 9.0 | 13.88 |
| 11.0 | 13.90 |
| 13.0 | 13.85 |
| 15.0 | 14.00 |
| 20.0 | 13.90 |
| 30.0 | 13.92 |
| 45.0 | 13.95 |
| 60.0 | 13.88 |


RMgX vs Time
.08
.07
.06
.05
Molar
5
10
15
20
25
30
35
40
Minutes

## DISCUSSION

The data from the several kinetic runs (Table I) was used along with the initial rate technique to formulate the following rate expression for the Kharasch reaction.

$$\text{Rate} = k[RMgX]^2 [CoX_2]^{0.5}$$

The second order dependence of the rate on the concentration of Grignard reagent can be reduced to first order when the structure $R_2Mg + MgX_2$ (in THF) or $R_2Mg \cdot MgX_2$ (in ether) is used.[17] Then, rate = k[Grignard] $[CoX_2]^{0.5}$.

The mechanism as proposed by Kharasch[18] can be represented by the following equations.

$$(1) \quad RMgX + CoX_2 \xrightarrow{k_1} RCoX + MgX_2$$

$$(2) \quad 2RCoX \xrightarrow{k_2} R\text{-}R \quad 2CoX\cdot$$

$$(3) \quad 2RCoX \xrightarrow{k_3} R_{(H+)} + R_{(H-)} + 2CoX\cdot$$

$$(4) \quad RCoX \xrightarrow{k_4} R\cdot + CoX\cdot$$

$$(5) \quad RX + CoX\cdot \xrightarrow{k_5} R\cdot + CoX_2$$

$$(5A) \quad 2R\cdot \rightarrow R_{(H+)} + R_{(H-)}$$

If (1) is the rate controlling step then, rate = $k_2$ [RMgX][$CoX_2$] which is in disagreement with the data. Equation (2) will be disregarded because no coupling products were found for the amyl system. If the slow step is the disproportionation of RCoX (3), then rate = $k_3$ $[RCoX]^2$. If

[17] For leading references see A. Kinman, R. Hamelin and S. Hayes, Bull. Soc. Chim. France, 1395-1403 (1963)

[18] cf. Kharasch and Reinmuth loc. cit., page 124

a steady state for [RCoX] is assumed ie) d[RCoX]/dt = 0, then

$$0 = -k_1 [RMgX][CoX_2] + k_3 [RCoX]^2 + k_4[RCoX]$$

and

$$[RCoX] = \frac{-k_4 \pm \sqrt{k_4^2 + 4k_3k_1 [RMgX][CoX_2]}}{2k_3}$$

and rate = $1/4k_3(k_4^2 \pm 2k_4 \sqrt{k_4^2 + 4k_3k_1 [RMgX] [CoX_2]} + k_4^2 + 4k_3k_1 [RMgX] [CoX_2] )$

which is not consistant with the data. Using the same rate step (3) but assuming that $k_3 \cong k_1 \cong k_4$ then rate = $K + K_1 [RMgX] [CoX_2]$, where K is greater than $K_1$, and we have disagreement in both RMgX and $CoX_2$ dependence. If we assume that the rate controlling step is (4) and make the steady state approximation for [RCoX] the same form and dependence on [RMgX] and $[CoX_2]$ will be obtained as when (3) was considered. If (5) is rate controlling, rate = $k_5 [RX] [CoX\cdot]$. The steady state approximation gives, rate = $k_3 [RCoX]^2 + k_4 [RCoX]$. Now if we make the assumption that d[RCoX]/dt = 0, a form similar to those already mentioned is obtained.

If the more recent structure of the Grignard reagent is used ie) $R_2Mg\cdot MgX_2$,[19] then Kharasch's first equation may be rewritten;

$$1A)\ R_2Mg\cdot MgX_2 + 2CoX_2 \xrightarrow{k_1} 2RCoX + 2MgX_2 .$$

Assuming that this is the rate controlling step in the sequence we then have rate = $k_1 [R_2Mg\cdot MgX_2][CoX_2]^2$, still in disagreement with the experimental data. If the other equations are used as rate controlling the same approximations are made, the form of the rate expression still differs from the form obtained experimentally.

[19]Kinman, et. al., loc. cit., page 1395-1403

The Mechanism of Wilds and McCormack[20] can be expressed

$$(6)\quad R_2Mg\cdot MgX_2 + CoX_2 \xrightarrow{k_1} 2MgX_2 + \{R_2Co\}$$

$$(7)\quad \{R_2Co\} \xrightarrow{k_2} R_{(H+)} + R_{(H-)} + Co$$

$$(8)\quad 2Co + 2RX \xrightarrow{k_3} CoX_2 + \{R_2Co\}$$

If (6) is considered as rate controlling, then rate = $[R_2Mg\cdot MgX_2]\,[CoX_2]$, again disagreement with experimental evidence is found. It would seem very unlikely that (7) is rate controlling, since $R_2Co$ was postulated as an unstable intermediate, however, even if (7) is used as the slow step we find; rate = $k_2[R_2Co]$ and making the steady state approximations, rate = $K\,[R_2Mg\cdot MgX_2]\,[CoX_2] + K^1\,[Co]^2\,[RX]^2$, still in disagreement with the data. If (8) is rate controlling and the steady state approximation for Co is used then the rate expression will show a dependence on RX which was not found experimentally.

It would seem that neither Kharasch or Wilds and McCormack had the complete or exact mechanism.

The data obtained leads to the following possible <u>partial</u> mechanism.

$$(9)\quad CoX_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co + 2X\cdot$$

$$(10)\quad R_2Mg + X\cdot \xrightarrow{k_3} \text{Products}$$

If (10) is the rate controlling step then rate = $k_3[R_2Mg][X\cdot]$ . Using the steady state approximation that $d[X\cdot]/dt = 0$, then

$$0 = k_1[CoX_2] - k_2[Co][X\cdot]^2 - k_3[R_2Mg][X\cdot]$$

and

$$[X\cdot] = \frac{k_3[R_2Mg] \pm \sqrt{k_3^2[R_2Mg]^2 + 4k_1k_2[Co][CoX_2]}}{2k_2[Co]}$$

[20] cf. Kharasch and Reinmuth, loc. cit., page 125

now if $k_1$ is very much larger than $k_3$ ($k_3$ is rate controlling) and if $k_2$ is less than $k_2$, $[X\cdot] \cong \frac{K[CoX_2]^{0.5}}{[Co]^{0.5}}$

and rate $= \frac{Kk_3[R_2Mg][CoX_2]^{0.5}}{[Co]^{0.5}}$

the presence of Co in the rate expression seems to contradict the data however, it can be shown using the steady state method that [Co] = constant or alternatively that $\frac{[CoX_2]}{[Co]}$ = constant. Even though the first two steps of this mechanism fit the data it is still far too simple to represent the entire reaction. The data show that the Grignard is still present even after several hours and that the addition of more RX at this time does not cause the reaction to resume. These observations force the conclusion that the Co is somehow deactivated. This deactivation of the Co is probably what caused the "growing in" of some basic, titrable species during the reaction. This species while unknown was present during every kinetic run and caused the apparent anomaly in the plot of [RMgX] vs time (fig. 1). The inflection point on the plot was found in every run and the minimum was found to vary from one to five minutes. The persistance of the inflection point did little to clarify the mechanism but it did point out that the later reaction is probably too complex to be represented by a simple mechanism.

Even though the reaction mechanism is not understood completely the data give strong support to two steps similar to those postulated in equations (9) and (10). The amount of Grignard used corresponds to approximately six times the amount of $CoX_2$ added, meaning that there is

some sort of regeneration and probably a parallel reaction that stops the regeneration. The rate of the reaction was found to be about three times faster with RMgBr and $CoBr_2$ that with RMgCl and $CoCl_2$. This can be accounted for by the fact that Br· is considerably more stable in solution than is Cl· . A basic fault with this radical mechanism is the lack of coupling products such as $X_2$, R-R and higher molecular weight products. Further, estimation from heat of formation data suggest an equilibrium constant of about $10^{-66}$ for equation (9).

Another mechanism that fits the data equally as well can be formalized as follows;

$$(11)\ CoX_2 \overset{K}{\rightleftharpoons} CoX^+ + X^-$$

$$(12)\ X^- + R_2Mg \overset{k}{\rightarrow} \text{Products}$$

where $K = \frac{[CoX^+]\,[X^-]}{[CoX_2]}$

If we assume that all the $X^-$ comes from the $CoX_2$ and none from the Grignard reagent then,

$$\text{rate} = kK^{0.5}[R_2Mg]\,[CoX_2]^{0.5}$$

If we consider this ionic form, then the lack of coupling products is to be expected. The rate dependence on solvent can be explained because THF is a better ionizing solvent than ether and we would therefore expect more ionization of $CoX_2$ in THF. Also $Br^-$ probably requires less solvation than $Cl^-$, thus explaining the rate difference between halides.

Using the rate constants from Table I an average value of the energy of activation was found for each of the 3 conditions. These values are tabulated in Table II. The values found for $\Delta H^*$ seem reasonable.

The amount of pentene formed varied between 30 and 90% of the amount of Grignard used. No value was placed on this data because the method used to determine the amount of olefin may not have been reliable for the system being analyzed and not enough work was done with it to provide criteria of meaning.

An ultraviolet analysis was attempted on the THF, RMgBr, $CoBr_2$ system using solid $CoBr_2$. This analysis was tried when the reaction was thought to be relatively slow. The negative results were probably due to the fact that the reaction was over before the proper region could be scanned.

It is apparent that many parts of the problem remain unanswered questions. Other systems, both symmetric and unsymmetric need to be studied. The intermediate that causes the inflection in the plot of Grignard concentration vs time should be studied and identified if possible. The mechanism for the Kharasch reaction cannot be completely understood until the latter is accomplished.

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