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THE CATALYZED REACTION OF ALKYL BROMIDES WITH ALKYLMAGNESIUM BROMIDES

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When cuprous bromide reacts with an excess of ethylmagnesium bromide in ethyl or _n_-butyl ether, a copper-containing red solution is formed that markedly catalyzes the reaction of ethyl bromide with ethylmagnesium bromide to give a mixture of ethane and ethylene,[2] usually in the ratio of 1.3 or less. This red solution, the nature of which is uncertain, is hereafter simply called the catalyst.

The results of an extensive investigation of the catalyzed reaction using gas chromatographic techniques, to be reported in detail later, show that a small amount of butane also is formed. The ratio of ethane to ethylene to butane is approximately 1.3:1:0.25. In the past, reactions of this type have been explained as proceeding by way of free radicals that disproportionate and combine. Recent work[3] has shown,

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[1] American Chemical Society Fellow, 1961-1963.

[2] C. B. Linn and C. R. Noller, _J. Am. Chem. Soc._, _58_, 816 (1936).

[3] (a) H. Cerfontani and K. O. Kutsche, _Can. J. Res._, _36_, 344 (1958); (b) J. C. J. Thyme, _Trans. Far. Soc._, _58_, 676 (1962).

however, that the ratio of disproportionation to combination of ethyl radicals in the gas phase is only 0.12 to 0.14, and that in a solvent cage the ratio is around 0.14 in "isooctane" and 0.18 in 2-propanol.[4] Accordingly, the low yield of butane in the catalyzed reaction of ethylmagnesium bromide with ethyl bromide indicates that the amount of ethylene and ethane resulting from disproportionation of free radicals is negligible and may be disregarded. The excess of ethane over ethylene represents the amount of ethane formed from ethyl radicals by hydrogen abstraction from the solvent, while practically all of the ethylene, along with an equivalent amount of ethane, must result from a process that does not involve free radicals, although it may or may not involve homolysis of bonds. The products of the reaction of several alkylmagnesium bromides with several alkyl bromides, using catalysts prepared from the alkylmagnesium bromide with various metallic halides, have led us to suggest that the nonradical portion of the reaction results from the decomposition of a solvated molecular complex of Grignard reagent, alkyl bromide, and catalyst, in such a way that the alkene arises from the Grignard reagent and the alkane from the alkyl halide.

To test this hypothesis, the catalyzed reactions of *i*-propylmagnesium bromide with 1-C^{14}-*i*-propyl bromide and of 1-C^{14}-*i*-propylmagnesium bromide with *i*-propyl bromide were investigated. We have found that the catalyst also promotes the exchange of alkyl groups between alkylmagnesium bromide and alkyl bromide. Since the catalyst is necessary for all reactions, they must go through intermediate

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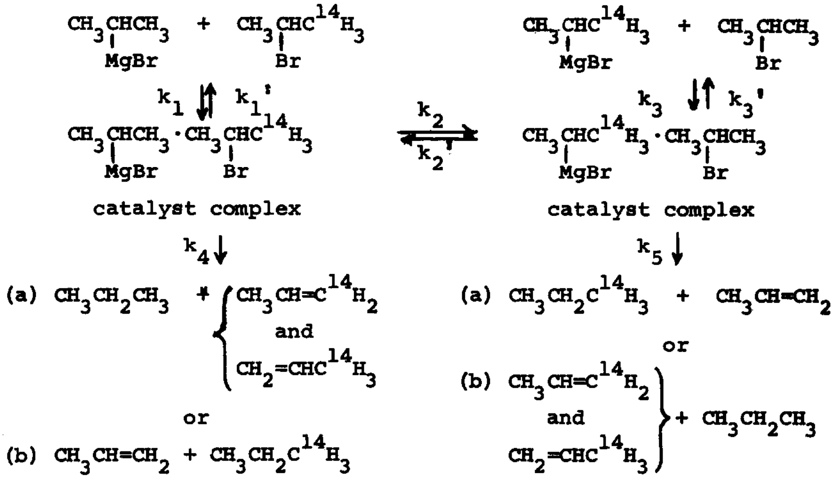
[4] M. Matsuoka, P. S. Dixon, A. P. Stefani, and M. Swarc, *Proc. Chem. Soc.*, 304 (1962).

molecular complexes. Hence the reactions involved may be represented as follows:



$$\underset{MgBr}{CH_3CHCH_3} + \underset{Br}{CH_3CHC^{14}H_3} \qquad\qquad \underset{MgBr}{CH_3CHC^{14}H_3} + \underset{Br}{CH_3CHCH_3}$$

$$k_1 \downarrow\uparrow k_1' \qquad\qquad\qquad\qquad k_3 \downarrow\uparrow k_3'$$

$$\underset{\text{catalyst complex}}{\underset{MgBr}{CH_3CHCH_3}\cdot\underset{Br}{CH_3CHC^{14}H_3}} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \underset{\text{catalyst complex}}{\underset{MgBr}{CH_3CHC^{14}H_3}\cdot\underset{Br}{CH_3CHCH_3}}$$

$$k_4 \downarrow \qquad\qquad\qquad\qquad k_5 \downarrow$$

(a) $CH_3CH_2CH_3 + \left\{ \begin{matrix} CH_3CH{=}C^{14}H_2 \\ \text{and} \\ CH_2{=}CHC^{14}H_3 \end{matrix} \right.$

or

(b) $CH_3CH{=}CH_2 + CH_3CH_2C^{14}H_3$

(a) $CH_3CH_2C^{14}H_3 + CH_3CH{=}CH_2$

or

(b) $\left. \begin{matrix} CH_3CH{=}C^{14}H_2 \\ \text{and} \\ CH_2{=}CHC^{14}H_3 \end{matrix} \right\} + CH_3CH_2CH_3$

Processes (a) and (b) are alternative possibilities. In process (a) the alkene comes from the alkyl halide, whereas in process (b) it comes from the Grignard reagent. The rate constants k_1, k_2, k_3, k_4(b), and k_5(a) should not be subject to primary isotope effects because the labeled carbon is not involved. Hence $k_1 = k_3$, $k_1' = k_3'$, and $k_2 = k_2'$. The maximum isotope effect expected for $k_{C^{12}H}/k_{C^{14}H}$ is approximately 1.04[5]. For k_4(a) and k_5(b) the maximum effect should be approximately 1.02 because hydrogen may be removed from either methyl group. If exchange is so much more rapid than disproportionation that equilibrium essentially is established before reaction

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[5] J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, 1962, p. 72.

takes place, the activity of the propane should exceed that of the propylene regardless of which reagent is labeled but should be at most only 1.02 times greater. The same conclusions hold if the alkene and alkane arise solely from the formation of free radicals followed by disproportionation and hydrogen abstraction.

If the rate of exchange is slower or not much faster than the rate of decomposition of the complex and process (a) takes place, the activity of the propane should be less than that of the propylene starting with labeled bromide and greater than that of propylene starting with labeled Grignard. If process (b) takes place the reverse is expected. The results obtained are listed in Table 1. Runs using catalyst solutions prepared from cobaltous bromide, nickel bromide, and ferric chloride also are included.

Table 1

Relative Activities of Products from the Catalyzed Reaction of Isopropylmagnesium Bromide with Isopropyl Bromide Using C^{14}-Labeled Reagents

Run	Metal in catalyst	Labeled reagent	Relative Activity Propane	Relative Activity Propylene
1	Copper	Halide	57	43
2	Copper	Halide	55	45
3	Copper	Halide	56	44
4	Copper	Halide	53	47
5	Copper	Grignard	41	59
6	Copper	Grignard	44	56
7	Cobalt	Halide	56	44
8	Cobalt	Halide	55	45
9	Nickel	Halide	55	45
10	Nickel	Halide	56	44
11	Iron	Halide	61	39
12	Iron	Halide	60	40

Triplicate analyses on the gas obtained in run 1 and duplicate analyses on the gas from run 6 gave perfect checks indicating excellent reproducibility of the analyses. The variation between runs is larger than desired, but the deviation from the average is a maximum of 4 per cent in runs 1 to 4 and one per cent or less in the other pairs of runs. Moreover none of the runs crossed from one side of a 1:1 ratio to the other.

The excess of propane over propylene indicates that about 23 per cent of the propane arises from free radicals that abstract hydrogen. Since only half of this propane arises from active reagents, it has a leveling effect on the difference between the activity of the propane compared to that of the propylene. Thus in process (b) it decreases the activity of the propane starting with labeled bromide and increases the activity starting with labeled Grignard.

From all of these considerations we believe that the observed differences are real and that process (b) rather than process (a) is involved. The portion of the reaction that does not go by way of free radicals results from the decomposition of a molecular complex in such a way that the alkene arises from the Grignard reagent and the alkane from the alkyl halide. Moreover the rate of decomposition appears to be of the same order of magnitude as the rate of exchange.

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