2424 © 1989 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 62, 2424—2426 (1989) [Vol. 62, No. 7

Electroorganic Synthesis Using Organometals. 2. Reductive Dehalogenation of Halides with Carbonylferrates Derived from Pentacarbonyliron(0) and Cathodically-Generated Methoxide Ion

Shigeto HASHIBA, Toshio FUCHIGAMI,* and Tsutomu NONAKA*
Department of Electronic Chemistry, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

(Received March 9, 1989)

Synopsis. A stoichiometry for the reductive dehalogenation of an organic halide with carbonylferrates was established: One mol of the halide was quantitatively reduced with the carbonylferrates derived from 0.2 mol of pentacarbonyliron(0) and 2 mol of cathodically-generated tetramethylammonium methoxide. The dehalogenation was also examined using a variety of halides under the stoichiometric reaction conditions.

Organic synthetic chemistry using transition metal carbonyls has been extensively developed.[1] Particularly, pentacarbonyliron(0) [$Fe(CO)_5$] has been favorably used because of its relatively low toxicity and price.[2] Pentacarbonyliron(0) itself has a reducing power and can be used as a unique reducing reagent. For instance, it reduces selectively vinyl chlorides, enol acetates and α,β-unsaturated aldehydes to the corresponding olefins, but the reduction requires undesirable reaction conditions such as high temperature, long reaction time and the use of large excess amounts of $Fe(CO)_5$, and product yields are not high.[3] On the other hand, alkali metal tetracarbonylferrates [$M_2Fe(CO)_4$ and $MHFe(CO)_4$; M=K, Na], which can be conveniently prepared, mostly in situ, from $Fe(CO)_5$ and alkali metal hydroxides (NaOH, KOH), have stronger reducing powers and can be used for the selective hydrogenation of α,β-unsaturated compounds[1–6] and for the selective dehalogenation of α-halo ketones at room temperature.[7] However, in all the reactions, more than one mol of $Fe(CO)_5$ (or the tetracarbonylferrates) to one mol of the substrates must be used to obtain reasonable or high product yields. Exceptionally, Takegami et al.[8] reported that one mol of allyl chloride could be reductively dechlorinated with 0.33 mol of $K_2Fe(CO)_4$ to give 0.63 mol of propylene and 0.06 mol of 1,5-hexadiene. If the reaction were completed, this fact would suggest that 0.5 mol of $K_2Fe(CO)_4$ is stoichiometrically consumed to dechlorinate 1 mol of the chloride. However, there was no evidence for the completion of the reaction. Collman et al.[9] made a kinetic and mechanistic study on oxidative addition of alkyl halides to $Na_2Fe(CO)_4$ and proposed a two-electron S_N2-type mechanism with no detectable competing one-electron halogen atom abstraction and/or radical chain mechanism,[10] but did not mention stoichiometry of the reductive dehalogenation reaction which occurs successively to the oxidative addition. Moreover, although the stoichiometry of formation reaction of the ferrates has been established,[11–13] in the in situ preparation of the ferrates used actually as reducing reagents, 0.5 mol of NaOH to 1 mol of $Fe(CO)_5$ was used in a case[4] while 3 mol of KOH in another one.[7]

In this work, an overall stoichiometry for the reductive debromination of an organic bromide was established, and then the dehalogenation of a variety of halides was examined under the stoichiometric reaction conditions.

Results and Discussion

Establishment of Stoichiometry. For a stoichiometric study it is desired that a reaction completes under given reaction conditions within an experimental time scale used. However, the reductive dehalogenation with sodium and potassium ferrates does not seem to proceed at reaction rates enoughly high to perform successfully the stoichiometric study because of low product yields and/or long reaction times.[7,8] For instance, 1 mol of 2-bromocamphor,[7] which was selected as a substrate in this work, reacted with $KHFe(CO)_4$ prepared from 1 mol of $Fe(CO)_5$ and 3 mol of KOH, in a 1,2-dimethoxyethane–ethanol mixture for a few days at room temperature to give camphor in only 59%. Generally, the reactivity of anion reagents is enhanced by weakening interaction with their counter cations. In fact, the oxidative addition of alkyl halides to $Na_2Fe(CO)_4$ is accelerated by using crown ethers, cryptands and highly nucleophilic solvents, or by replacing the counter cation (Na^+) by quaternary ammonium cations.[9] Ferrates and their analogues can be also prepared using alkali metal alkoxides instead of NaOH and KOH.[14,15] In this work, a quanternary ammonium alkoxide was used.

Preparation of anion reagents with onium counter cations from the corresponding alkali metal salts is mostly troublesome and not practical, since the use of expensive crown ethers and onium fluorides is required in an ordinary method. Phase-transfer catalysts also are not always applicable owing to the impossibility of realizing anhydrous reaction conditions. On the other hand, cathodic reduction of a certain kind of organic compounds can easily generate anionic species with onium counter cations, when onium salts are used as supporting electrolytes. Previously,[16–19] it was confirmed that anionic species generated cathodically from alcohols, carboxylic acids, carbon acids and amides in nonaqueous cathodic solutions containing quaternary ammonium salt supporting electrolytes are much more reactive bases than those generated using alkali metal salt electrolytes. In this work, methanol solutions of tetramethylammonium methoxide ($Me_4N^{+}\cdot{}^{-}OMe$) in various concentrations could be prepared by electrolyzing a methanol solution of Me_4NCl at various amounts of charge passed in a divided cell. One mol of the methoxide is formed by passing 1 F (1 F=96484.56 C) of charge, according to the following equation:

Table 1. Reductive Dehalogenation of Halides under the Stoichiometric Conditions[a)]

Run	Halide	Yield[b)]/%	By-product (Yield/%)
1	Octyl iodide	68	
2	Cyclohexyl iodide	58	
3	1-Bromo-2-phenylethane	5	Styrene (90)
4	1-Bromo-1-phenylethane	30	2,3-Diphenylbutane (15)
5	*meso*-1,2-Dibromo-1,2-diphenylethane	0	*trans*-Stilbene (86)
6	Tripenylmethyl bromide	50	Methyl triphenylmethyl ether (33)
7	Phenacyl bromide	82	Methyl phenacyl ether (trace)
8	*p*-Bromophenacyl bromide	78	
9	3-Bromocamphor	91	

a) See the text. b) For the corresponding normal dehalogenation products.

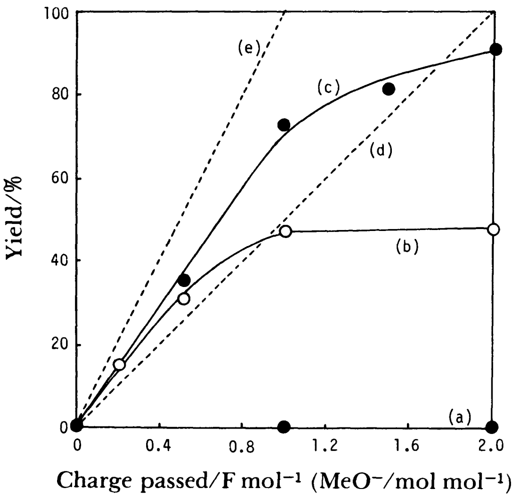

Fig. 1. Relationship between camphor yield and amount of charge passed (methoxide) in the reductive debromination of 3-bromocamphor. (a) 0, (b) 0.1, and (c) 0.2 mol of Fe(CO)$_5$ to 1 mol of 3-bromocamphor, and theoretical lines for (d) two-electron and (e) one-electron reduction.

$$\mathrm{MeOH} + \mathrm{e} \xrightarrow{\mathrm{Me_4NCl}} \mathrm{Me_4N^{+}\cdot{}^{-}OMe} + \frac{1}{2}\mathrm{H_2}$$

To the cathodic solution electrolyzed at a prescribed amount of charge between 0 to 2.0 F mol^{-1} of 3-bromocamphor, which correspond to 0 to 2.0 mol of methoxide/mol of 3-bromocamphor, was added a prescribed amount of Fe(CO)$_5$ (0 to 0.2 mol/mol of 3-bromocamphor) and then α-bromocamphor itself. The reaction mixture was stirred for 3 h at room temperature. A longer reaction time did not result in any detectable increase in the yield of camphor.

As shown in Fig. 1, the debromination of 3-bromocamphor did not occur with neither Fe(CO)$_5$ nor methoxide [see (a)]. When 0.1 mol of Fe(CO)$_5$ to 1 mol of 3-bromocamphor was used, the yield of camphor reached to ca. 50% at 1.0 F of charge (corresponding to 1.0 mol of cathodically-generated methoxide) per 1 mol of 3-bromocamphor and no increase was observed at a larger amount (2.0 F) of charge [see (b)]. On the other hand, the yield approximated to 100% at 2.0 F using 0.2 mol of Fe(CO)$_5$ [see (c)]. These facts suggest that 3-bromocamphor is debrominated to camphor by overall two-electron reduction which consumes stoichiometrically 0.2 mol of Fe(CO)$_5$ and 2 mol of methoxide, and consequently a stoichiometry for the reactants and camphor formed can be formulated as follows:

$$\mathrm{R{-}Br} + \frac{1}{5}\mathrm{Fe(CO)_5} + 2\,\mathrm{MeO^-} \xrightarrow{\mathrm{H^+}} \mathrm{R{-}H} + [\mathrm{X}]$$

R–Br and R–H: 3-bromocamphor and camphor, respectively
H$^+$: Proton from water added in work-up procedure
[X]: A mixture of unknown products

Composition of [X], which should consist of iron and bromine compounds and probably CO$_2$,[20)] has remained unknown, because products other than camphor were not analyzed. Therefore, at present it is difficult to discuss reaction mechanism in detail.

It is interesting that curves (b) and (c) at amounts of charge smaller than 1.0 and 2.0 F, respectively, lie in an area between straight lines (d) and (e) which indicate theoretical yields in the two- and one-electron reductions, respectively (see Fig. 1), though the overall reaction is the two-electron reduction as descrived above. This fact suggests that the one-electron reduction occurs concurrently with the two-electron reduction under conditions where amounts smaller than 10 mol of methoxide to 1 mol of Fe(CO)$_5$, or that an iron complex with more reducing capacity is formed under such conditions. Concerning the latter, it should be noted that contribution of the reduction with the zero-valent iron of Fe(CO)$_5$ is negligibly small to explain reasonably increases in the capacity.

Reductive Dehalogenation of a Variety of Halides under the Stoichiometric Conditions. The establishment of stoichiometry for the starting compounds is practically useful for performing efficiently the reductive dehalogenation from a synthetic aspect, though the reaction mechamism has not been clarified. Table 1 shows results of the dehalogenation of a variety of halides under the stoichiometric conditions where 1 mol of halides, 0.2 mol of Fe(CO)$_5$ and 2 mol of methoxide were used.

As shown in Table 1, most of iodides and bromides used could be dehalogenated using a much smaller amount of Fe(CO)$_5$ than that reported in previous papers[4–8)] to give the corresponding products in good or high yields. Alkyl chlorides were hardly dechlorinated.[9)] Bromobenzene also could not be debrominated.

Some types of side reactions occurred. The normal debromination of 1-bromo-2-phenylethane was almost completely suppressed due to predominant occurrence of hydrogen bromide elimination with base, and consequently the main product was styrene (Run 3). The side reaction of a benzyl bromide seems to proceed mainly by a one-electron reduction process via the corresponding benzyl radical intermediate (Run 4). Although *meso*-1,2-dibromo-1,2-diphenylethane has two bromine atoms at the benzyl position and also gave exclusively *trans*-stilbene which is apparently a one-electron reduction product, the reaction mechanism is not necessarily rationalized by the one electron-transfer process (Run 5).[21] The formation of methyl ethers as by-products may be owing to direct nucleophilic reaction of methoxide with bromides (Runs 6, 7).

Instead of methanol, ethanol, ethanethiol, 2-propanol, phenol, and acetic acid were also used as sources of cathodically-generated bases, but they did not give any satisfactory results except for ethanol.

Experimental

Chemicals used were commercially available.

A typical experimental procedure was as follows: A methanol solution (10 cm^3 as either a catholyte or an anolyte) containing Me_4NCl (0.4 $mol\ dm^{-3}$) as a supporting electrolyte was galvanostatically electrolyzed at 1 $A\ dm^{-2}$ of cathodic current density under a nitrogen atmosphere at room temperature in a divided cell. The cathode and anode were platinum plates. After a prescribed amount of charge was passed, a prescribed amount of $Fe(CO)_5$ was added to the catholyte. After allowed to stand for 15 min, a halide (1 mmol) was added. The reaction mixture was stirred for 3 h at room temperature under a nitrogen atmosphere, and then poured into a 1% hydrochloric acid solution. The resulting mixture was repeatedly extracted with ether and the combined ethereal extract was washed with a 1% sodium hydrogencarbonate solution and water, and then was dried over anhydrous sodium sulfate. The ethereal solution obtained thus was subjected to gas chromatography (PEG 20M column, 60—170 °C) for product analysis. The products were also separated by thin layer chromatography (Silica gel, hexane).

References

1) For a review: R. Noyori, "Kagaku Sosetsu, No. 19," ed by T. Shiba, Gakkai Shuppan Center, Tokyo (1978), Chap. 6.

2) For a review: H. Takaya and R. Noyori, *Yuki Gosei Kagaku Kyokai Shi,* **35**, 615 (1977).

3) S. J. Nelson, G. Detre, and M. Tanabe, *Tetrahedron Lett.,* **1973**, 447.

4) R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.,* **37**, 1542 (1972).

5) M. Yamashita, Y. Watanabe, T. Mitsudo, and Y. Takegami, *Tetrahedron Lett.,* **1975**, 1867.

6) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, and J. I. Brauman, *J. Am. Chem. Soc.,* **98**, 4685 (1976).

7) H. Alper, *Tetrahedron Lett.,* **1975**, 2257.

8) Y. Takegami, Y. Watanabe, T. Mitsudo, and T. Okajima, *Bull. Chem. Soc. Jpn.,* **42**, 1992 (1969).

9) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.,* **99**, 2515 (1977).

10) The two-electron S_N2 mechanism can be also supported from a stereochemical result of the reductive debromination of 3-bromocamphor with $KDFe(CO)_4$.[7]

11) W. Hieber and G. Brendel, *Z. Anorg. Allgem. Chem.,* **289**, 338 (1957).

12) H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.,* **78**, 5704 (1956).

13) H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.,* **79**, 6116 (1957).

14) H. Hock and H. Stuhlman, *Chem. Z.,* **55**, 874 (1931); *Chem. Abstr.,* **25**, 935 (1932).

15) E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.,* **91**, 1233 (1969).

16) T. Fuchigami, T. Awata, T. Nonaka, and M. M. Baizer, *Bull. Chem. Soc. Jpn.,* **59**, 2873 (1986).

17) T. Komori, T. Nonaka, T. Fuchigami, and K. Zhang, *Bull. Chem. Soc. Jpn.,* **60**, 2315 (1987).

18) M. Minato, T. Nonaka, and T. Fuchigami, *Chem. Lett.,* **1986**, 1071.

19) S. Hashiba, T. Fuchigami, and T. Nonaka, *J. Org. Chem.,* **54**, 2475 (1989).

20) Considerable amounts of CO_2 were evolved in the dechlorination of allyl chloride.[8]

21) J. Casanova and H. R. Rogers, *J. Org. Chem.,* **39**, 2408 (1974)