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Article

# $\beta$-Elimination in the Reactions of $\cdot CR^1R^2CR^3R^4X$ Radicals with Metal Powders Immersed in Aqueous Solutions

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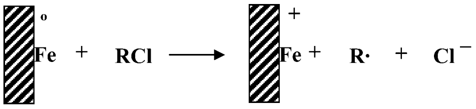
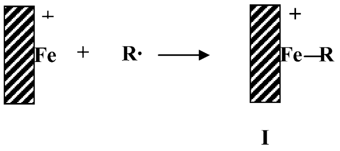
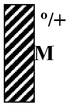
The reactions of several radicals of the type $\cdot CR^1R^2CR^3R^4X$ (where X = OH or $NH_3^+$) with metal powders that have been immersed in aqueous solutions were studied. The radicals were formed by radiation chemical techniques. One of the products in all these reactions is the corresponding alkene, $R^1R^2C{=}CR^3R^4$. The results are in accord with a mechanism in which the radicals react with the metals that are forming transients with metal–carbon $\sigma$ bonds. The latter transients decompose via two competing reactions: (a) heterolysis of the metal–carbon $\sigma$ bond and (b) $\beta$-elimination of $X^-$. Moreover, the dehalogenation of $BrCH_2CH_2NH_3^+$ and $ClCH_2(CH_3)_2COH$ by metal powders was studied. Also in these reactions, the corresponding alkene is one of the products. This result is consistent with the suggestion that, in the dehalogenation reaction, an alkyl radical is formed in the first step. This radical then reacts with the metal. Alternatively, the transients with metal–carbon $\sigma$ bonds in the dehalogenation processes might be formed via a concerted mechanism.

## Introduction

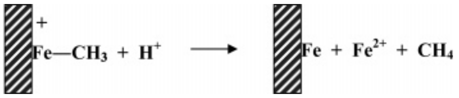
The use of Fe° in the batch and in situ remediation of groundwater contaminated with halogenated organic compounds recently has received considerable attention.[1−9] Despite significant progress in understanding the dehalogenation mechanism[5,10,11] many questions remain unanswered. It seems reasonable to assume that the first steps in the dehalogenation process are

(1) 

(2) 

(*The  represent a metal particle with the corresponding charge.)

and that the nature of the final products depends in the mechanisms of decompositions of the transients I. Recently, it was shown that methyl radicals indeed react with Fe°, and with Cr°, Mn°, Co°, Ni°, and Zn°, to form methane.[12] Thus, it was proposed that, in these processes, transients I are formed and decompose via

(3) 

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(1) Gillham, R. W.; O'Hannesin, S. F. *Groundwater* **1994**, *32*, 958.
(2) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, *28*, 2045.
(3) Boronina, T.; Klabunde, K. J.; Sergeev, G. *Environ. Sci. Technol.* **1995**, *29*, 1511.
(4) Chuang, F. W.; Larson, R. A.; Wessman, M. S. *Environ. Sci. Technol.* **1995**, 29, 2460.
(5) Helland, B. R.; Alvarez, P. J. J.; Schnoor, J. L. *Hazard. Mater*. **1995**, *41*, 205.
(6) Muftikian, R.; Fernando, Q.; Korte, N. *Water Res.* **1995**, *29*, 2434.
(7) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654.
(8) Campbell, T. J.; Burris, D. R.; Roberts, A. L.; Wells, J. R. *Environ. Toxicol. Chem*. **1997**, *16*, 625.
(9) Fennelly, J. P.; Roberts, A. L. *Environ. Sci. Technol.* **1998**, *32*, 1980.
(10) Warren, K. D.; Arnold, R. G.; Bishop, L. C.; Lindholm, E. A.; Betterton, J. *Hazard. Mater.* **1995**, *41*, 217.
(11) Totten, L. A.; Jans, U.; Roberts, A. L. *Environ. Sci. Technol.* **2001**, *35*, 2268.

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**Table 1.** Metal Powders Used in This Study

| metal powder | supplier | assay | size |
|---|---|---|---|
| Fe | Merck | 99% | ≤10 μm |
| Co | Alfa Aesar | 99.5% | 325 mesh |
| Zn | Aldrich | 98% | <10 μm |
| Mn | Aldrich | 99% | 325 mesh |
| Ni | Merck | 99.5% | <10 μm |

In principle, one could suggest that reaction 2 proceeds via the outer sphere mechanism, i.e., that $R^-$ carbanions are formed. However, alkyl radicals are rarely involved in redox processes, at least in aqueous solutions. This is due to the low self-exchange rates of the $R^\bullet/R^-$ couple, in analogy to those of the $H^\bullet/H^-$ couple. Furthermore, the formation of $R^-$ is highly endothermic, because the redox potential of the $(R^\bullet + H^+)/RH$ couple takes into account the formation of the R−H bond.

It is well-known that the reactions of a variety of radicals of the type $^\bullet CR^1R^2CR^3R^4X$, where X is a good leaving group (e.g., X = OH, OR, $NH_3^+$, Cl, Br) with low-valency transition-metal complexes in homogeneous aqueous solutions proceed via[13−16]

$$M^nL_m + {}^\bullet CR^1R^2CR^3R^4X \xrightarrow{-L} L_{m-1}M^{n+1}{-}CR^1R^2CR^3R^4X \qquad (4)$$

$$L_{m-1}M^{n+1}{-}CR^1R^2CR^3R^4X + L \rightarrow M^{n+1}L_m + R^1R^2C{=}CR^3R^4 + X^- \qquad (5)$$

Therefore, it seemed reasonable to suggest that analogous reactions also occur when the $^\bullet CR^1R^2CR^3R^4X$ radicals react with metal powders. Therefore, it was decided to perform this study in two consecutive steps:

(1) To investigate the reaction of a variety of radicals of the type $^\bullet CR^1R^2CR^3R^4X$ (where X is a good leaving group in this study (OH or $NH_3^+$)) with metal powders. The desired radicals can be formed in situ via radiation chemical techniques.

(2) If the $R^1R^2C{=}CR^3R^4$ indeed are formed in the latter reactions, then it would be of interest to investigate the reaction of $YCR^1R^2CR^3R^4X$ (Y = Cl or Br) with metal powders. If the product is again $R^1R^2C{=}CR^3R^4$ this will be consistent with the suggestion that the dehalogenation process indeed involves reaction 1 followed by reaction 2 as has recently been proposed.[12]

The results of this study indeed support this hypothesis.

## Experimental Section

The sources and properties of metal powders used in this study are summarized in Table 1. All other chemicals were of analytical reagent (AR) grade and were used without further purification. The water used was deionized water that was further purified by a Millipore Milli-Q setup with a final resistivity of >10 MΩ. The solutions were deaerated by bubbling $N_2O$ or helium through them for 15 min, using the syringe technique. Then, 2.5 mL of the solution were added to a glass bulb (15 mL) sealed with a rubber septum containing 10 g of the metal powder, which, for M = Fe°, Co°, and Ni°, was previously activated by $H_2SO_4$ (0.1 M) for 2 min and then was washed 7−8 times by 8-mL portions of water. The activation process dissolves, at least partially, the hydroxides/oxides present on the surface of the metal powders. The activation clearly increases the rate of dissolution of the metal powders and the rates of reaction of the radicals with them (see Table 2 and ref 12). This effect is attributed to the increase in "clean" surface area of the powders. This bulb was also deaerated by $N_2O$ or helium prior to the injection of the solution. ***Caution:*** *For metals that are powerful reducing agents or for reactions with easily reducible halo-organic compounds, care should be taken, because the gases that are formed might cause an explosion (see Table 5 presented later in this paper).*

The given pH values are always initial pH values. Because of the slow dissolution of the metals,[12] some $H_2$ and some $OH^-$ ions are formed. Also, the heterolytic decomposition of the transients I forms $OH^-$ ions. These ions induce the precipitation of $M(OH)_2$ on the metal surfaces, thus slowing the dehalogenation and dissolution processes.[12] No buffers were used, because these affect the dissolution process.[12]

After 3 h of reaction, the gas phase above the metal was analyzed using gas chromatography (HP model 5890 GC, fitted with a flame ionization detector (FID) detector (Poropaq QS GC column, 10 ft in length, 1/8 in. in diameter, Supelco). Helium was used as the carrier gas (30 mL/min, $T = 70$ °C). The concentration of the gases measured are reported in units of parts per million (ppm) of the gas phase, because, in most systems studied, only the relative yields of the different gases are discussed. In Tables 2, 8, and 11 (presented later in this work), the yields of $C_4H_8$ are also expressed in G and/or M units, to enable comparisons with the total radical yield and with nongases products. Some of the samples were irradiated for 2 h, within the 3 h time span, in a $^{60}Co$ $\gamma$ source with a dose rate of 4 Gy/min, as determined by the Fricke dosimeter. (The unit Gy refers to the absorption of 1 J/kg of the sample.)

The $Cl^-$ ion concentrations were analyzed using a colorimetric method.[17]

**Formation of Radicals with Ionizing Radiation.** When ionizing radiation ($\gamma$ radiation) is absorbed by a dilute aqueous solution, the following initial products are formed:[18]

$$H_2O \xrightarrow{\gamma,\, e^-} {}^\bullet H\ (0.60),\ {}^\bullet OH\ (2.65),\ e^-_{aq}\ (2.65),\ H_2O_2\ (0.75),\ H_2\ (0.45) \qquad (6)$$

where the G values are given in parentheses (G values are defined as the number of molecules of each product per 100 eV of radiation absorbed by the solution). In concentrated solutions, the yields of the radicals are somewhat higher and those of $H_2O_2$ and $H_2$ are somewhat lower.[18] In $N_2O$-saturated solutions, the hydrated electron is converted to the hydroxyl radical:[19]

$$e^-_{aq} + N_2O \xrightarrow{H^+} N_2 + {}^\bullet OH \qquad (k = 8.7 \times 10^9\ M^{-1}\ s^{-1}) \qquad (7)$$

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(12) Rusonik, I.; Polat, H.; Cohen, H.; Meyerstein, D. *Eur. J. Inorg. Chem.* **2003**, *23*, 4227.

(13) van Eldik, R.; Meyerstein, D. *Acc. Chem. Res.* **2000**, *33*, 207.

(14) Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D.; Cho, J. K.; Shaik, S. S. *Inorg. Chem.* **1992**, *31*, 798.

(15) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. I* **1988**, *84*, 4157.

(16) Cohen, H.; Meyerstein, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *97*, 785−787.

(17) Florence, T. M.; Farrar, Y. J. *Anal. Chim. Acta* **1971**, *54*, 373.

(18) Matheson, M.; Dorfman, L. *Pulse Radiolysis*; MIT Press: Cambridge, MA, 1969.

(19) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

**Table 2.** $\beta$-Elimination Reaction of ·$CH_2(CH_3)_2COH$ Radical with Surfaces of Different Metal Powders[a]

| sample[b] | radiation | $E^{\circ c}$ [V] | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] | $G(C_4H_8)$ |
|---|---|---|---|---|---|---|---|---|---|
| no metal | + |  | 43.3 |  |  |  |  | 10[d] | 0.04[d] |
| Ni°(activ) | + | −0.21 | 289 |  | 152 |  | 41 | 411 | 1.4 |
| Ni°(activ) | - | −0.21 | 234 |  | 133 |  | 36.9 | 9.3 |  |
| Ni°(no activ) | + | −0.21 | 19 |  | 7.8 |  | 25 | 33 | 0.1 |
| Ni°(no activ) | - | −0.21 | 2.2 |  |  |  |  |  |  |
| $NiCl_2$ 0.005 M[e] | + | −0.21 | 9 |  |  |  | 1.6 | 32 | 0.1 |
| Co°(activ) | + | −0.25 | 82 |  | 4.8 |  | 1.6 | 204 | 0.7 |
| Co°(activ) | - | −0.25 | 29 |  | 4.6 |  |  | 4.2 |  |
| Co°(no activ) | + | −0.25 | 26 |  | 4 |  |  | 145 | 0.5 |
| Co°(no activ) | - | −0.25 | 5 |  |  |  |  | 3.5 |  |
| $CoCl_2$ 0.005 M[e] | + | −0.25 | 8.3 |  |  |  | 1.6 | 50.5 | 0.2 |
| Fe°(activ) | + | −0.44 | 74 | 19 | 15 | 3.5 | 3.9 | 970 | 3.4 |
| Fe°(activ) | - | −0.44 | 14 | 16 | 10 | 2.5 | 3.5 | 11.6 |  |
| Fe°(no activ) | + | −0.44 | 31 | 14 | 8 | 3 | 3.1 | 101 | 0.3 |
| Fe°(no activ) | - | −0.44 | 12 | 12 | 7.9 | 2.5 | 3 | 10 |  |
| $FeSO_4$ 0.005 M[e] | + | −0.44 | 16 |  |  |  |  | 56 | 0.2 |
| Zn°(no activ) | + | −0.76 | 82 |  | 7.1 |  | 1.6 | 152 | 0.5 |
| Zn°(no activ) | - | −0.76 | 6 |  |  |  | 1.6 | 5.8 |  |
| $ZnSO_4$ 0.005 M[e] | + | −0.76 | 14 |  |  |  | 1.6 | 67 | 0.2 |
| Mn°(no activ) | + | −1.18 | 167 | 12 | 10 | 0.5 | 1.7 | 96 | 0.3 |
| Mn°(no activ) | - | −1.18 | 144 | 9.9 | 8.4 |  | 1.6 | 13 |  |
| $MnCl_2$ 0.005 M[e] | + | −1.18 | 17 |  |  |  | 1.6 | 42 | 0.15 |

[a] Determined under the following conditions: 10 g of metal powder; 2.5 mL solution, with a composition of 2-methyl-2-propanol, 0.65 M, pH 7.0; $N_2O$ sat.; radiation, 480 Gy. [b] M°(activ) denotes that the metal surface was activated by washing with $H_2SO_4$ (see experimental). M°(no activ) denotes that the metal powder was used as-is. [c] $E°$ is the standard redox potential of the metals. [d] This is a radiolytic yield. No alkenes were observed in non-irradiated blanks. [e] 0.005 M $MCl_2/MSO_4$ homogeneous solution.

At pH >3, all the solvated electrons react with $N_2O$, yielding ·OH as the major radical ($G(\cdot OH) = 6.0$).

In the samples that contain the metals, ca. 80% of the radiation is absorbed by the metals. However, only a minor portion of this energy is transferred to the aqueous solution and increases the radical yield in the solutions only by up to 80%, depending on the metal.[12] (The source of this increase is not clear at present; one of the reviewers suggested that it is due to Compton electrons, and we thank him for sharing this idea). The dose rate of 4 Gy/min is equal to <1 cal/(g min) and, therefore, does not heat the metal powders significantly.

**Preparation of ·$CR^1R^2CR^3R^4X$ Radicals by Radiation Chemical Techniques.** All these radicals were prepared via the general reactions

$$HCR^1R^2CR^3R^4X + \cdot OH/H\cdot \rightarrow \cdot CR^1R^2CR^3R^4X + H_2O/H_2$$

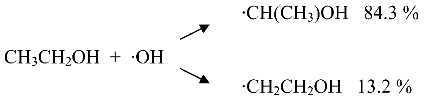
in $N_2O$ saturated solutions, i.e., in solutions in which $[\cdot OH]/[H\cdot] > 10$. Naturally, in some irradiated systems, different types of radicals are formed; however, the desired radical is the only radical with a good $\beta$ leaving group.

The radicals ·$CH_2C(CH_3)_2OH$ and ·$CH_2C(CH_3)_2NH_3^+$ were formed via

$$(CH_3)_3C{-}OH/NH_3^+ + \cdot OH \rightarrow \cdot CH_2C(CH_3)_2{-}OH/NH_3^+ + H_2O$$

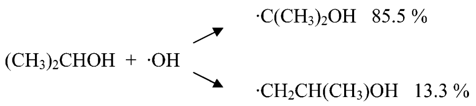
where $k_{OH} = 6.0 \times 10^8$ $M^{-1}$ $s^{-1}$ and $k_{NH_3} = 3.6 \times 10^9$ $M^{-1}$ $s^{-1}$.[19] Clearly, these are the only radicals that are formed in these systems.

The radicals ·$CH_2CH_2OH$ are formed via



$$CH_3CH_2OH + \cdot OH \rightarrow \cdot CH(CH_3)OH \; 84.3\,\% \;/\; \cdot CH_2CH_2OH \; 13.2\,\%$$

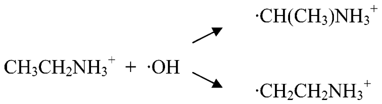
for which $k = 1.9 \times 10^9$ $M^{-1}$ $s^{-1}$,[19] and the radicals ·$CH_2CH(CH_3)OH$ are formed via



$$(CH_3)_2CHOH + \cdot OH \rightarrow \cdot C(CH_3)_2OH \; 85.5\,\% \;/\; \cdot CH_2CH(CH_3)OH \; 13.3\,\%$$

for which $k = 1.9 \times 10^9$ $M^{-1}$ $s^{-1}$.[19] Thus, in these systems, the desired radicals are only minor products. However, the reactions of ·$CH(CH_3)OH$ and ·$C(CH_3)_2OH$ with metals are not expected to yield alkenes in neutral solutions.[20]

The radical·$CH_2CH_2NH_3^+$ was formed via



$$CH_3CH_2NH_3^+ + \cdot OH \rightarrow \cdot CH(CH_3)NH_3^+ \;/\; \cdot CH_2CH_2NH_3^+$$

for which $k = 4.1 \times 10^8$ $M^{-1}$ $s^{-1}$.[19] The relative yields of these radicals were not reported. However, because $NH_3^+$ is a deactivating substituent,[19] one expects that the desired radical is the major product. Furthermore, $H_2C{=}CH_2$ is not expected as a product of any reaction of the ·$CH(CH_3)NH_3^+$ radicals.

## Results and Discussions

**Reactions of ·$CR^1R^2CR^3R^4X$ Radicals with Metal Powders.** It was decided to start this study with the reactions of the ·$CH_2(CH_3)_2COH$ radical, because it is the only radical formed in the solution. The reactions of the ·$CH_2(CH_3)_2COH$ radical with different metal powders were studied, the results are summarized in Table 2. The results clearly demonstrate that radiolytically produced ·$CH_2(CH_3)_2COH$ radicals react with the metal surface to form 2-methylpropene as the major gaseous product. The results thus indicate that the ·$CH_2(CH_3)_2COH$ radicals react with metal surfaces via the formation of a transient with metal−carbon $\sigma$ bonds that

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(20) Masarwa, A.; Meyerstein, D. *Adv. Inorg. Chem.* **2004**, *55*, 271.

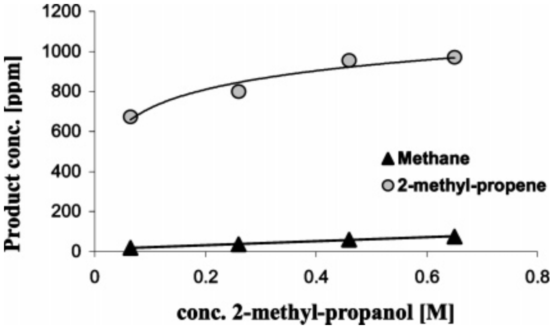


**Figure 1.** Dependence of methane and 2-methylpropene formation on initial 2-methyl-2-propanol concentration. Conditions were as follows: 10 g of activated iron powder; 2.5 mL solution, pH 7.0; $N_2O$ sat.; radiation, 480 Gy.

decompose, at least partially, via $\beta$-elimination reactions. This phenomenon is common for all the metal powders used.

Small yields of 2-methylpropene are obtained also by irradiating homogeneous solutions that contain $Ni_{(aq)}{}^{2+}$, $Co_{(aq)}{}^{2+}$, $Fe_{(aq)}{}^{2+}$, $Zn_{(aq)}{}^{2+}$, $Mn_{(aq)}{}^{2+}$, and 2-methyl-2-propanol. The mechanism of formation of the 2-methyl propene in these systems is probably due to the reaction sequence

$$M_{aq}{}^{2+} + e_{aq}{}^{-} \rightarrow M_{aq}{}^{+} \qquad (a)$$

followed by

$$M_{aq}{}^{+} + {\cdot}CH_2C(CH_3)_2OH \rightarrow (M^{II}{-}CH_2C(CH_3)_2OH)_{aq}{}^{+} \qquad (b)$$

$$(M^{II}{-}CH_2C(CH_3)_2OH)_{aq}{}^{+} \rightarrow M_{aq}{}^{2+} + H_2C{=}C(CH_3)_2 + H_2O \qquad (c)$$

The rate constants of reaction a are $1.3 \times 10^{10}\ M^{-1}s^{-1}$ for $Co_{aq}{}^{2+}$; $1.9 \times 10^{10}\ M^{-1}s^{-1}$ for $Ni_{aq}{}^{2+}$; $1.5 \times 10^{9}\ M^{-1}s^{-1}$ for $Zn_{aq}{}^{2+}$; $1.6 \times 10^{8}\ M^{-1}s^{-1}$ for $Fe_{aq}{}^{2+}$, and $2.0 \times 10^{7}\ M^{-1}s^{-1}$ for $Mn_{aq}{}^{2+}$.[19] Therefore, under the experimental conditions, reaction a competes somewhat with reaction 7 for $Co_{aq}{}^{2+}$, $Ni_{aq}{}^{2+}$, and $Zn_{aq}{}^{2+}$. Reactions analogous to reactions b and c are well-known.[13−16]

However, for the systems that contained $Fe_{aq}{}^{2+}$ and $Mn_{aq}{}^{2+}$, the source of the 2-methylpropene is probably the following reaction sequence:

$$M_{aq}{}^{2+} + {\cdot}CH_2C(CH_3)_2OH \rightarrow (M^{III}{-}CH_2C(CH_3)_2OH)_{aq}{}^{2+} \qquad (d)$$

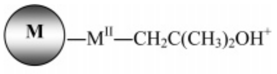
$$(M^{III}{-}CH_2C(CH_3)_2OH)_{aq}{}^{2+} \rightarrow M_{aq}{}^{3+} + H_2C{=}C(CH_3)_2 + H_2O \qquad (e)$$

Note that, for the metal powders, the yield of $C_4H_8$ and the other light gases in the non-irradiated blank experiments is somewhat larger than that observed when the metals are immersed in water in the absence of 2-methyl-2-propanol.[12] This is probably due to the reaction of the H atoms and alkyl radicals that are formed and bound to the metal surfaces during dissolution[12] with the 2-methyl-2-propanol, i.e. hydrogen abstraction from $C(CH_3)_3OH$ by the radicals that are formed on the metal surface during the dissolution process.

The dependence of the yield of 2-methylpropene on the initial 2-methyl-2-propanol concentration was examined, and only the yields of methane and 2-methylpropene were affected by this parameter (Figure 1). The highest radiolytic yield of 2-methylpropene obtained is $G = 3.4$. This yield is considerably lower than the yield of ${\cdot}CH_2C(CH_3)_2OH$ radicals formed in $N_2O$ saturated solutions ($G({\cdot}CH_2C(CH_3)_2OH) = 6.0$).[18,19] The lower yield of 2-methylpropene is due either to the reaction

$$2({\cdot}CH_2C(CH_3)_2OH) \rightarrow ({-}CH_2C(CH_3)_2OH)_2 \qquad (f)$$

which competes with the reaction of the radicals with the iron powder, and/or with a competing mechanism of decomposition of the transient



$$\text{M}{-}M^{II}{-}CH_2C(CH_3)_2OH^{+}$$

II

probably via heterolysis of the metal−carbon $\sigma$ bond (see below). Because both the heterolysis of metal−carbon $\sigma$ bonds and the metal-induced $\beta$-elimination reactions are acid-catalyzed,[21,22] it was decided to study the pH effect on the presently studied system. The results are summarized in Table 3. The results indicate that the yield of 2-methylpropene increases as the initial pH decreases. Thus, the results suggest that the acid-catalyzed decomposition of the transient II prefers $\beta$-elimination over heterolyses.

It is of interest to note that, in the blank solutions also, i.e., those which contain no metal, some 2-methylpropene is formed and its yield increases slightly as the pH decreases. This observation suggests the following reaction scheme, which is a side process to reaction f:

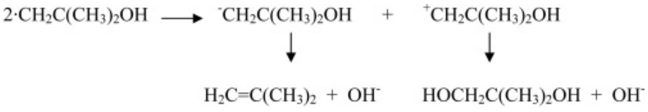
$${\cdot}CH_2C(CH_3)_2OH + H^{+} \rightleftarrows {\cdot}CH_2C(CH_3)_2OH_2{}^{+} \rightarrow {\cdot}CH_2{-}C(CH_3)_2{}^{+} + H_2O$$

$${\cdot}CH_2{-}C(CH_3)_2{}^{+} + {\cdot}CH_2C(CH_3)_2OH \xrightarrow{H_2O} H_2C{=}C(CH_3)_2 + HOCH_2C(CH_3)_2OH + H^{+}$$

or

$${\cdot}CH_2C(CH_3)_2OH_2{}^{+} + {\cdot}CH_2C(CH_3)_2OH \rightarrow H_2C{=}C(CH_3)_2 + HOCH_2C(CH_3)_2OH + H^{+}$$

This reaction scheme is preferable to the straight disproportionation reaction



because it is difficult to envisage why this process should be acid-catalyzed.

To determine that reactions analogous to those of ${\cdot}CH_2C(CH_3)_2OH$ radicals with metal surfaces occur, it was

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(21) Rotman, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 4158.
(22) Gaede, W.; van Eldik, R. *Inorg. Chim. Acta* **1994**, *215*, 173.

**Table 3.** pH Dependence of Reaction of the $\cdot CH_2(CH_3)_2COH$ Radical with Iron Powder Surfaces[a]

| sample | pH | radiation | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] |
|---|---|---|---|---|---|---|---|---|
| Fe° | 7.0 | + | 32 | 13.2 | 9 | 1.8 | 2.9 | 780 |
| Fe° | 7.0 | - | 7 | 12.5 | 9 | 1.5 | 2.7 | 6.1 |
| no metal | 7.0 | + | 6.1 | | | | | 8.7 |
| Fe° | 5.0 | + | 34 | 13.9 | 10.7 | 2.7 | 3.1 | 830 |
| Fe° | 5.0 | - | 7.2 | 13.3 | 10 | 2.3 | 2.9 | 6.5 |
| no metal | 5.0 | + | 6.0 | | | | 1.6 | 18 |
| Fe° | 3.0 | + | 37 | 13.6 | 10.9 | 2.9 | 3.2 | 890 |
| Fe° | 3.0 | - | 7.6 | 13.1 | 10.3 | 2.3 | 2.8 | 6.5 |
| no metal | 3.0 | + | 6.3 | | | | 1.6 | 21 |

[a] Determined under the following conditions: 10 g of activated metal powder; 2.5 mL solution, with a composition of 2-methyl-2-propanol, 0.26 M; $N_2O$ sat.; radiation, 480 Gy.

**Table 4.** Formation of the Corresponding Alkenes in the Reaction of Radiolytically Formed $\cdot CH_2CH_{2-n}(CH_3)_nOH$ ($n = 0, 1,$ or 2) and $\cdot CH_2C(CH_3)_2NH_3^+$ Radicals with Iron Powder[a]

| sample | radiation | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] |
|---|---|---|---|---|---|---|---|
| Fe, 2-propanol | + | 34 | 16 | 13 | 101 | 13 | |
| Fe, 2-propanol | - | 10.3 | 8 | 13.1 | 2.2 | 2.7 | |
| 2-propanol | + | 16 | | | 1.1 | | |
| $FeSO_4$, 0.005 M 2-propanol | + | 16 | | | 40 | | |
| Fe°, ethanol | + | 13 | 74 | 20 | 2.5 | 3.4 | |
| Fe°, ethanol | - | 10.1 | 8.2 | 12 | 2.0 | 2.7 | |
| ethanol | + | 10 | | | | | |
| $FeSO_4$, 0.005 M ethanol | + | 9.6 | 44 | | | | |
| Fe°, $C(CH_3)_3NH_3^+$ | + | 15 | 16 | 9.7 | 3.3 | 3 | 462 |
| Fe°, $C(CH_3)_3NH_3^+$ | - | 10.1 | 16 | 11.6 | 2.1 | 3.2 | 5.2 |
| $C(CH_3)_3NH_3^+$ | + | 6 | | | | | 4 |
| $FeSO_4$, 0.005 M $C(CH_3)_3NH_3^+$ | + | 6.9 | | | | | 28 |
| Fe°, $C(CH_3)_3OH$ | + | 74 | 19 | 15 | 3.5 | 3.9 | 970 |
| Fe°, $C(CH_3)_3OH$ | - | 14 | 16 | 10 | 2.5 | 3.5 | 11.6 |
| $C(CH_3)_3OH$ | + | 43 | | | | | 10 |
| $FeSO_4$, 0.005 M $C(CH_3)_3OH$ | + | 16 | | | | | 56 |

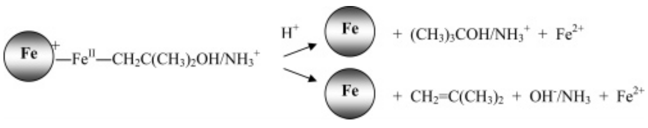
[a] Determined under the following conditions: 10 g of activated metal powder; 2.5 mL substrate, 0.65 M, pH 7.0; $N_2O$ sat.; radiation, 480 Gy.

**Table 5.** Relative Yields of the Different Gases Formed in the Dehalogenation Reaction of 2-Br-ethylamine[a]

| sample | $E^b$ [V] | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] |
|---|---|---|---|---|---|---|---|
| Ni°(activ), 2-Br-ethylamine | −0.21 | 260 | 1490 | 511.1 | | 40 | 9.2 |
| Ni°(activ), $H_2O$ | | 146 | | 110 | | 34 | 7.8 |
| Co°(activ), 2-Br-ethylamine | −0.25 | 25 | 7200 | | | 1.6 | 3.3 |
| Co°(activ), $H_2O$ | | 23 | | | | | 3.1 |
| Fe°(activ), 2-Br-ethylamine | −0.44 | 16.5 | 3800 | 21 | 3.2 | 4.3 | 5.8 |
| Fe°(activ), $H_2O$ | | 6.9 | 10 | 10.4 | | | 4.4 |
| Zn°(no activ), 2-Br-ethylamine | −0.76 | 10.4 | 24100 | | | | |
| Zn°(no activ), $H_2O$ | | 2.1 | | | | | |
| Mn°(no activ), 2-Br-ethylamine | −1.18 | explosion | | | | | |
| Mn°(no activ), $H_2O$ | | 153 | | 8.9 | | | 2.9 |

[a] Determined under the following conditions: 10 g of metal powder; 2.5 mL of 2-Br-ethylamine, 0.65 M, pH 3.0 or $H_2O$ pH 3.0; $N_2O$ sat.; $T = 25$ °C; $t = 3$ h. [b] The standard redox potentials of the metals.

decided to measure the reactions of the $\cdot CH_2CH_2OH$, $\cdot CH_2CH(OH)CH_3$, and $\cdot CH_2C(CH_3)_2NH_3$ radicals with iron powder. The results are summarized in Table 4. The results suggest that these radicals also react with the iron surfaces and that the corresponding alkenes are formed via $\beta$-elimination reactions. Therefore, it is concluded that radicals of the type $\cdot CR^1R^2CR^3R^4X$ (where X is a good leaving group) react with metal surfaces, according to reactions that are analogous to reaction b. These intermediates decompose, at least partially, via $\beta$-elimination reactions when the metal can be oxidized by the radical. Note that the yield of $H_2C{=}C(CH_3)_2$ is considerably smaller in the reaction of $\cdot CH_2C(CH_3)_2NH_3^+$ than in the reaction of $\cdot CH_2C(CH_3)_2OH$, although the yields of these radicals are identical. This result indicates that the relative rates of the two paths of decomposition of the transients,



differ considerably.

**Reactions of Haloorganic Compounds of the Type $YCH_2CR^1R^2X$, Where Y = Br or Cl and X = OH or $NH_3^+$ with Metal Powders**. Having established that radicals of the type $\cdot CH_2CR^1R^2X$ react with metal powders and that

**Table 6.** Products of Dehalogenation of $ClCH_2C(CH_3)_2OH$ by Metal Powders[a]

| sample | $E^b$ [V] | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] | $Cl^-$ [M] |
|---|---|---|---|---|---|---|---|---|
| Cl-tert. butanol | | 1.4 | | | | 1.6 | 4.4 | 0.0006 |
| Ni°, Cl-tert. butanol | −0.21 | 290 | | 140 | | 36 | 190 | 0.034 |
| Ni°, $H_2O$ | | 146 | | 110 | | 34 | 7.8 | |
| Co°, Cl-tert. butanol | −0.25 | 28 | 10 | 6.4 | 5 | | 10500 | 0.032 |
| Co°, $H_2O$ | | 24 | 8.9 | 4.5 | 1.4 | | 23.4 | |
| Fe°, Cl-tert. butanol | −0.44 | 11.8 | 11.5 | 8 | 3 | 4.7 | 5060 | 0.037 |
| Fe°, $H_2O$ | | 7.2 | 10 | 10.4 | | | 7.4 | |
| Zn°(no activ),Cl-tert. butanol | −0.76 | 6 | | | | 1.6 | 81 | not determined |
| Zn°(no activ), $H_2O$ | | 5.8 | | | | 1.6 | 3.2 | |
| Mn°(no activ),Cl-tert. butanol | −1.18 | 165 | | 10.2 | | | 300 | not determined |
| Mn°(no activ), $H_2O$ | | 153 | | 8.9 | | | 2.9 | |

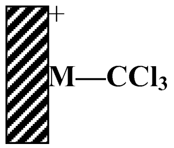
[a] Determined under the following conditions: 10 g of activated metal powder; 2.5 mL of Cl-tert. butanol, 0.65 M, pH 3.0 or $H_2O$ pH 3.0; $N_2O$ sat.; $T = 65$ °C (2 h); $t_{total} = 3$ h. [b] The standard redox potentials of the metals.

**Table 7.** Reaction of the $\cdot CH_2CH_2NH_3^+$ Radicals with Metal Powders[a]

| sample | radiation | $E^b$ [V] | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] |
|---|---|---|---|---|---|---|---|---|
| Ni°, ethylamine | + | −0.21 | 160 | 95 | 119 | | 28 | 5.8 |
| Ni°, ethylamine | - | | 140 | | 100 | | 22 | 4.9 |
| Co°, ethylamine | + | −0.25 | 23 | 180 | | | 1.6 | 3.1 |
| Co°, ethylamine | - | | 20 | 12 | 4.8 | | 1.6 | 3 |
| Fe°, ethylamine | + | −0.44 | 9 | 129 | 34 | | 2.7 | 4 |
| Fe°, ethylamine | - | | 6.4 | 19 | 10 | | 2.3 | 3.7 |

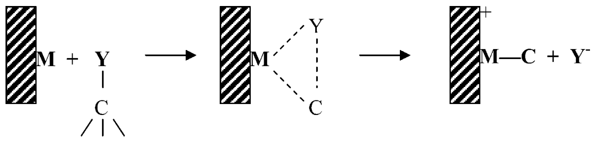
[a] Determined under the following conditions: 10 g activated metal powder; 2.5 mL of ethylamine, 0.65 M, pH 3.0; $N_2O$ sat.; radiation, 480 Gy; $T = 25$ °C (2 h); $t = 3$ h. [b] The standard redox potentials of the metals.

one of the products of these reactions is the corresponding alkene, it was decided to check whether the dehalogenation reactions of $YCH_2CR_1R_2X$ compounds by these metals yields the same alkenes. If, indeed, these alkenes are formed in the dehalogenation reactions, this will corroborate the suggestion that $\cdot CH_2CR^1R^2X$ radicals are formed as intermediates in the dehalogenation reaction (see reaction 1). For this purpose, the dehalogenation reactions of $BrCH_2CH_2NH_3^+$ and $ClCH_2(CH_3)_2COH$ were studied. Because the $Br^-$ species is a better leaving group, the dehalogenation reaction of $BrCH_2CH_2NH_3^+$ (see Table 5) is faster than that of $ClCH_2(CH_3)_2COH$. Therefore, the dehalogenation of $ClCH_2(CH_3)_2COH$ was accelerated by heating (see Table 6). The reaction of the $\cdot CH_2CH_2NH_3^+$ radical, which is formed radiolytically with the same metal powders, was studied; the results are summarized in Table 7. The results presented in this table indicate that $\cdot CH_2CH_2NH_3^+$ radicals react with the metal powders and that $C_2H_4$ is one of the gaseous products of this reaction. One of the products of the dehalogenation reaction of $BrCH_2CH_2NH_3^+$ is also $C_2H_4$ (see Table 5). In the dehalogenation of $BrCH_2CH_2NH_3^+$ by Ni°, considerable yields of ethane and methane also are observed. The results thus indicate that the dehalogenation of $BrCH_2CH_2NH_3^+$ by all metal powders first yields the $\cdot CH_2CH_2NH_3^+$ radical, which then reacts with the metal to yield ethylene as one of the products. When Ni° is used, more side reactions clearly occur. Similarly, $C_4H_8$ is formed in the dehalogenation of $ClCH_2C(CH_3)_2OH$ by all metal powders (see Table 6). Alternatively, the reactions that are occurring could be via Scheme 1, i.e., no radicals are formed as free transients. This mechanism seems less likely, at least for sterically hindered haloorganic compounds, e.g. $CCl_4$ for which the formation of the transient



was demonstrated.[23]

**Scheme 1.** Alternative Mechanism for the First Step of the Dehalogenation Process of Haloorganic Compounds Contains Formation of a Triangular Cyclic Transition State



It is of interest to note that the yield of $C_4H_8$ in the dehalogenation of $ClCH_2(CH_3)_2COH$ is dependent on the metal used, for Ni°, Co°, or Fe° powders (Co° > Fe° > Ni°), although the yield of $Cl^-$ is almost independent of the nature of the metal used (see Table 6). These results were unexpected, because, in the reaction of $\cdot CH_2(CH_3)_2COH$, radicals formed radiolytically (see Table 2), and the relative yield of $C_4H_8$ is Fe° > Ni° > Co°. Thus, the results suggest that the yield of $C_4H_8$ is dependent on the mode of formation of the $\cdot CH_2(CH_3)_2COH$ radicals, radiolytically or via the dehalogenation process. Moreover, the results indicate that, in the irradiated systems, the yield of $C_4H_8$ for Fe° powder

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(23) Rusonik, I.; Cohen, H.; Meyerstein, D. *Eur. J. Inorg. Chem.* **2005**, *7*, 1227.

**Table 8.** Mass Balance of the Dehalogenation Process of Cl-tert. Butanol[a]

| sample | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] | $C_4H_8$ [M] | 2-methyl-2-propanol [M] | $Cl^-$ [M] |
|---|---|---|---|---|---|---|---|---|---|
| Fe° | 8 | 5.3 | 4.9 | 0 | 0 | 5200 | 0.00067 | 0.028 | 0.030 |
| no metal | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00015 | 0.00056 |
| no metal, no heating | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00011 | 0.00038 |

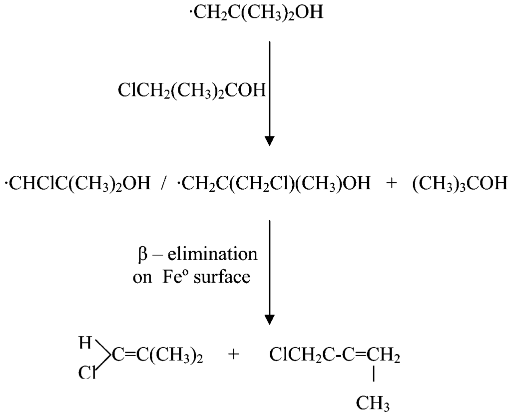
[a] Determined under the following conditions: 10 g of activated metal powder; 2.5 mL of $ClCH_2C(CH_3)_2OH$, 0.05 M, pH 3.0; $N_2O$ sat.; $T = 65$ °C (8 h); $t_{total} = 9$ h.

**Table 9.** Dependence of $\beta$-Elimination Process on tert. Butanol Concentration[a]

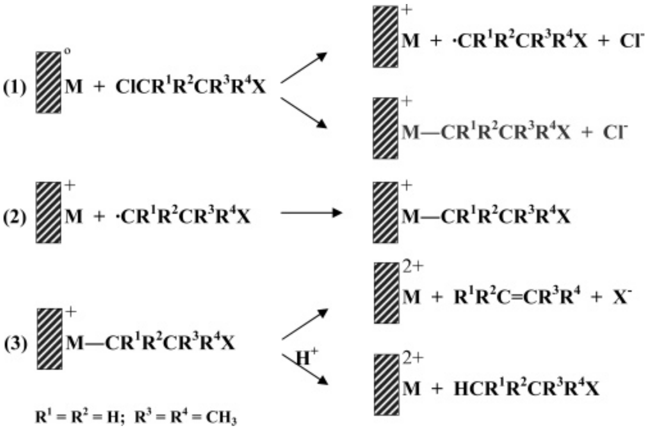
| sample | tert. butanol [M] | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] | $Cl^-$ [M] |
|---|---|---|---|---|---|---|---|---|
| no metal | | 1.1 | | | | | 4.1 | 0.0003 |
| Fe°(activ) | | 10 | 13.3 | 9.5 | 2.7 | 3.9 | 1200 | 0.0085 |
| Fe°(activ) | 0.05 | 9.5 | 11 | 9.4 | 2.1 | 3.7 | 1056 | 0.0082 |
| Fe°(activ) | 0.3 | 9.7 | 11.8 | 8.9 | 2.8 | 3.2 | 1040 | 0.0078 |
| Fe°(activ) | 0.65 | 10.5 | 12.6 | 9.7 | 2 | 3.6 | 950 | 0.0073 |
| Fe°(activ) | 1 | 9 | 12.4 | 9.6 | 2.1 | 3.2 | 900 | 0.0066 |

[a] Determined under the following conditions: 10 g of metal powder; 2.5 mL of Cl-tert. butanol, 0.05 M, pH 3.0; $N_2O$ sat.; $T = 65$ °C (2 h); $t_{total} = 3$ h.

**Scheme 2.** Possible Reactions of ·$CH_2(CH_3)_2COH$ Radicals with $ClCH_2(CH_3)_2COH$



**Scheme 3.** Mechanism of the Dehalogenation Process of Haloorganic Compounds That Contain a Good Leaving Group in the $\beta$ Position



is $G = 3.4$ (i.e., 54% of the radical yield; see Table 2); on the other hand, in the dehalogenation process, the yield of $C_4H_8$ is only 2% of the $Cl^-$ yield (see Table 8). Accordingly, only a small percentage of the ·$CH_2(CH_3)_2COH$ radicals formed in the first step of the dehalogenation process of $ClCH_2(CH_3)_2COH$ yield $C_4H_8$. The question that remains is: What happened to the rest? Probably, most of the radicals formed in the dehalogenation process react via one or both of the following processes: (i) reduction of the ·$CH_2(CH_3)_2$-COH radical on the metal surface to yield 2-methyl-2-propanol, and (ii) reaction with $ClCH_2(CH_3)_2COH$ via the mechanism outlined in Scheme 2.

To check these possibilities, the mass balance for the dehalogenation process of $ClCH_2(CH_3)_2COH$ was studied (see Table 8). The yield of 2-methylpropene is 2%, relative to the $Cl^-$ yield; i.e., only a small percentage of the ·$CH_2(CH_3)_2COH$ radicals formed in the first step of the dehalogenation of $ClCH_2(CH_3)_2COH$ undergo the $\beta$-elimination reaction, all the other radicals yield 2-methyl-2-propanol. To check the contribution of the hydrogen abstraction reaction (Scheme 3), two experiments were performed:

(1) 2-Methyl-2-propanol was added to the Cl-tert. butanol dehalogenation experiment. This is expected to increase the 2-methylpropene yield if the hydrogen abstraction reaction has an important role in this system. The results (given in Table 9) indicate that this is not the case, because the ratio $[C_4H_8]/[Cl^-]$ is concentration independent.

(2) 2-Propanol was added to the same system. This is expected to decrease the 2-methylpropene yield. The results (given in Table 10) contradict this expectation.

Thus, the results suggest that the difference between the radiolytic experiments and the dehalogenation experiments originate from another source. One other source of this difference could be the temperature of the experiments. Therefore, the dehalogenation experiment was performed at different temperatures, and the results are summarized in Table 11. The results indicate the following:

(1) The source of the difference between the dehalogenation and radiolytic experiments is not the temperature.

(2) The activation energy for the dehalogenation process, as derived from the $Cl^-$ yield, is 68 kJ/mol.

(3) The ratio $[C_4H_8]/[Cl^-]$ increases as the temperature increases.

(4) In the GC analysis, a peak of an unknown product, with a larger retention time than $C_4H_8$, was observed. Its yield also increases as the temperature increases.

An alternative explanation to the different results in the dehalogenation and radiolytic experiments is that, in the former, the flux of radicals is considerably larger. This suggests that, plausibly, the number of radicals bound

**Table 10.** Dependence of $\beta$-Elimination Process on 2-Propanol Concentration[a]

| sample | 2-propanol [M] | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [ppm] | tert. butanol [M] | $Cl^-$ [M] |
|---|---|---|---|---|---|---|---|---|---|
| no metal | 1 | 1.2 | | | | | | 0.00044 | 0.00045 |
| Fe° | | 10 | 13.3 | 9.5 | 2.7 | 3.9 | 1540 | 0.009 | 0.0086 |
| Fe° | 1 | 9.5 | 9 | 6.4 | 1.2 | | 1570 | 0.010 | 0.0092 |

[a] Determined under the following conditions: 10 g of activated metal powder; 2.5 mL of Cl-tert. butanol, 0.05 M, pH 3.0; $N_2O$ sat.; $T = 65$ °C (2 h); $t_{total} = 3$ h.

**Table 11.** Dependence of $ClCH_2(CH_3)_2COH$ Dehalogenation on the Temperature[a]

| sample | temp, $T$ [° C] | $CH_4$ [ppm] | $C_2H_4$ [ppm] | $C_2H_6$ [ppm] | $C_3H_6$ [ppm] | $C_3H_8$ [ppm] | $C_4H_8$ [M] | $Cl^-$ [M] | $[C_4H_8]/[Cl^-] \times 100$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| no metal | 40 | 1 | | | | | | $4.9 \times 10^{-4}$ | |
| Fe° | 40 | 6.4 | 9.6 | 7.4 | 1.6 | 3.3 | $9.2 \times 10^{-6}$ | $1.8 \times 10^{-3}$ | 0.7 |
| no metal | 50 | 1 | | | | | | $5.3 \times 10^{-4}$ | |
| Fe° | 50 | 8.2 | 11.3 | 8.6 | 2 | 3.5 | $6.1 \times 10^{-5}$ | $5.4 \times 10^{-3}$ | 1.25 |
| no metal | 65 | 1.1 | | | | | | $5.5 \times 10^{-4}$ | |
| Fe° | 65 | 10.5 | 12.6 | 9.7 | 2 | 3.6 | $1.7 \times 10^{-4}$ | $7.3 \times 10^{-3}$ | 2.3 |
| no metal | 80 | 1.1 | | | | | | $8.4 \times 10^{-4}$ | |
| Fe° | 80 | 10 | 12 | 9 | 2.9 | 3.1 | $7.6 \times 10^{-4}$ | $2.6 \times 10^{-2}$ | 3 |

[a] Determined under the following conditions: 10 g of activated metal powder; 2.5 mL of Cl-tert. butanol, 0.05 M, pH 3.0; $N_2O$ sat.; $t_{testing} = 2$ h; $t_{total} = 3$ h.

coherently to each iron particle is larger in the dehalogenation experiments; the larger number of $-CH_2C(CH_3)_2OH$ groups bound to the metal is expected to decrease the redox potential of the metal particle. This effect probably favors heterolysis over $\beta$-elimination in the dehalogenation process, in accord with the experimental results.

## Concluding Remarks

Radicals of the type $\cdot CR^1R^2CR^3R^4X$ (where X is a good leaving group) react with metal powders to form transients with metal$-$carbon $\sigma$ bonds. These transients decompose via the $\beta$-elemination of X or via the heterolysis of the metal$-$carbon $\sigma$ bond. The same products, although with different relative yields, are formed during the dehalogenation of $YCR^1R^2CR^3R^4X$. These results are consistent with the suggestion that the dehalogenation proceeds via the mechanism outlined in Scheme 3.

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