Reaction of Methyl Radicals with Metal Powders Immersed in Aqueous Solutions

Irena Rusonik,[a] Hurriyet Polat,[a,b] Haim Cohen,[a,c] and Dan Meyerstein*[a,d]

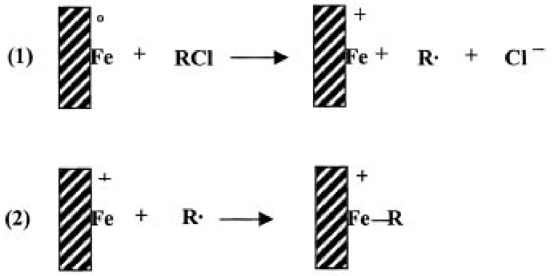
Keywords: Carbon / Energy transfer / Radicals / Oxidation

Methyl radicals radiolytically produced in aqueous solutions react efficiently with Cr^0, Mn^0, Fe^0, Ni^0, Cu^0 and Zn^0 powders immersed in the solution. The Cr^0, Mn^0, Fe^0, Ni^0 and Zn^0 powders reduce the radicals to form methane. On the other hand the Cu^0 powder seems to oxidize the radicals. Surprisingly a part of the energy absorbed by the Cr^0, Fe^0, Ni^0 and Zn^0 powders is transferred to the aqueous solution, thus increasing the radical yield. CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 are formed when an aqueous deaerated buffer solution, pH 4–5, is added to powders of analytical iron, zinc, manganese and chromium. The source of these gases is carbon traces present, as atoms or atom clusters, in the "analytical" metal powders. These carbon atoms, when present on the surface of the metals, are reduced by the metal particles in aqueous solutions. This mechanism might be the source of light alkanes and alkenes in the prebiotic era.

Introduction

Extensive use of halogenated aliphatic compounds, as solvents and degreasing agents in industry, and as pesticides in agriculture, has led to environmental problems of contamination of groundwater systems. Therefore, there is considerable interest in developing methods for removing halogenated organic compounds from industrial and agricultural wastes. Zero-valent iron,[1−11] Fe^0, is an effective reagent for the dehalogenation process of contaminated water streams. Despite recent significant progress in the elucidation of this mechanism,[9,12,13] many basic questions remain unanswered. The principle goal of our research program is a detailed investigation of the dehalogenation mechanism. The elucidation of this mechanism is of scientific interest and might enable to improve the process.

The mechanism of the dehalogenation process probably involves in the first stage the reactions:[2,6,14]



Thus, it seemed of interest to study the mechanism of reaction 2 and the mechanism of the decomposition of the transient I formed in it. For this purpose it was decided to form the radicals $R^{\cdot}$ in the vicinity of iron powder using radiation chemical techniques. The methyl radical was chosen due to its simplicity and reactivity as a strong oxidizing and reducing agent.[15,16] However blank experiments revealed that light alkanes and alkenes are formed when "analytical" iron is dissolved in slightly acidic aqueous solutions. This observation, which partially corroborates an earlier study,[17] might affect the nature of the final products obtained and was therefore also studied. For comparison purposes the analogous processes in the presence of other metal powders were also studied.

Results and Discussion

Formation of Alkanes during the Dissolution of Analytical Metals in Aqueous Solution

Light alkanes and alkenes are formed when analytical iron is dissolved in He-saturated, CO_2-free, slightly acidic

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[a] Department of Chemistry, Ben-Gurion University of the Negev,
Beer-Sheva, Israel
[b] Department of Chemistry, Ismir Institute of Technology,
Ulra-Izmir, Turkey
[c] Nuclear Research Centre Negev,
Beer-Sheva, Israel
[d] Department of Biological Chemistry College of Judea and Samaria,
Ariel, Israel
Fax: (internat.) +972 39067440
E-mail: danmeyer@bgumail.bgu.ac.il

DOI: 10.1002/ejic.200300403

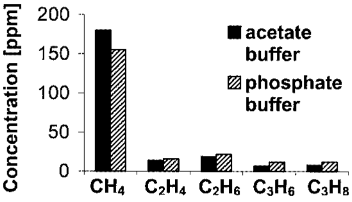


Figure 1. Yield of alkanes and alkenes in the gas phase: 10 g Fe^0, 2.5 mL 0.5 M acetate buffer pH 4.0 or 10 g Fe^0, 2.5 mL 0.1 M phosphate buffer pH 4.0; t = 3 h, T = 25 °C

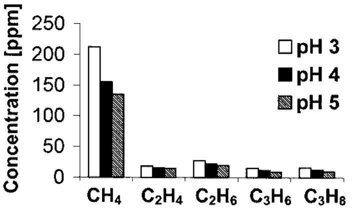


Figure 2. pH dependence of the dissolution of iron in phosphate buffer 0.1 M: 10 g Fe^0, 2.5 mL phosphate buffer 0.1 M; t = 3 h, T = 25 °C; error limit ± 15%

buffers. Typical results are summed up in Figure 1. The major product is always methane. The results suggest that the nature of the buffer slightly affects the relative yields of the different products. The larger methane yield in the acetate buffer is tentatively attributed to the larger buffer capacity of acetate at this pH.

As, at least in the phosphate buffer, the source of the organic gases has to be the iron, an analysis of the carbon content of the iron powder was performed. Indeed the results point out that the carbon/carbide content of the analytical iron is 450 ppm by weight, though this is not mentioned in the analytical data given by Merck. As expected, analysis of the iron ions formed indicates that over 95% of the iron is present as $Fe^{II}_{(aq)}$ and not as $Fe^{III}_{(aq).}$ The yield of $H_{2(g)}$, not shown, is very similar to that of $Fe^{II}_{(aq)}$ and corroborates the previous observation.

Analysis of the time dependence of the process shows that no induction period is observed and the product gases are formed within the first 20 min of the process, during which the pH at the metal surface presumably increases thus stopping, or slowing down, the process. The observation that the process is over within the first 20 min could alternatively suggest that the carbon atoms are present only at the surface of the iron particles. In order to check this possibility, the iron powder was activated in sulfuric acid (0.1 M) for 30 min, it was then washed with excess distilled water, and was bubbled with He for one hour. The water was then removed and the bulb was closed and deaerated with He before adding the phosphate buffer. After a further 20 min the gas phase was analyzed. The gas composition and concentrations were the same as in the previous experiments. This result points out that the carbon atoms are present in the iron bulk.

The emission of organic gases during the dissolution of iron powder in slightly acidic aqueous solutions is surprising. The yield of the organic gases increases with the decrease in pH of the solution (see Figure 2). It seemed of interest to check whether similar results are obtained for other analytical metal powders. The results obtained are summed up in Table 1. The results clearly demonstrate that light alkanes and alkenes are also formed during the dissolution of “analytical” Cr^0, Mn^0 and Zn^0. However, the relative yields of the different gases depend on the nature of the metal.

As the main purpose of our research was to study the mechanism of reaction 2 and the mechanism of decomposition of the transient **I** formed in it, the influence of radiation on the dissolution process of the metal power was studied. When the samples (10 g activated metal powder, 2.5 mL water at pH 4.0) are irradiated in a ^{60}Co γ-source with a dose of 480 Gy, the yield of the alkanes and alkenes increases somewhat. Typical results are shown in Table 1. Clearly the radiation enhances the rate of dissolution of the metals; this might be due to the reactions of the radicals formed by irradiating the aqueous solutions (see below) with the metals.

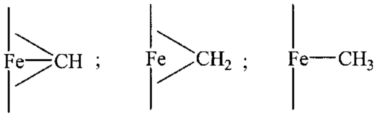
The mechanism of formation of the alkanes and alkenes probably involves in the first stage one of the following steps:

Table 1. The relative yields of the different gases depend on the nature of the metal and of the radiation[a]

Metal	Radiation	E [V]	Carbon [ppm]	CH_4 [ppm]	C_2H_4 [ppm]	C_2H_6 [ppm]	C_3H_6 [ppm]	C_3H_8 [ppm]
Cr^0	+	−0.41	3000	30.8	16.9	8	9	−
Cr^0	−			28	14	6	8	−
Fe^0	+	−0.44	450	29	17	11	4.9	3.9
Fe^0	−			21	10.1	8	−	3.7
Zn^0	+	−0.76	40	23.6	−	1.8	−	3.2
Zn^0	−			22.2	−	1.8	−	−
Mn^0	+	−1.18	50	87.8	−	5.1	0.4	−
Mn^0	−			72.9	−	3.1	−	−

[a] All samples contained 10 g of activated metal powder and 2.5 mL of water at pH 4.0, t = 3 hours, radiation dose 480 Gy. No buffer was added to these experiments.Error limit ± 15%.

1. Hydrogen atoms adsorbed to the iron particles migrate to exposed carbon atoms forming



groups.

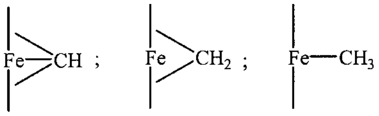
The migration of the hydrogen atoms is equivalent to that involved in the formation of $H_{2(g)}$ via the migration of two hydrogen atoms. The formation of transients containing Fe−alkyl bonds is analogous to the formation of transient complexes in the reaction of alkyl radicals with iron(II) complexes,[18] and other low valent transition metal complexes,[16] in homogeneous solutions.

2. The iron particles act as microelectrodes charging negatively the less electropositive exposed carbon atoms that then reduce the water.

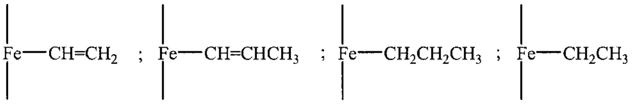
These two mechanisms might contribute in parallel to the process observed.

In addition, the next step might occur via two mechanisms:

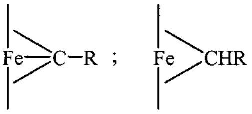
1. Migration of the alkyl groups of



in parallel to hydrogen atom migration, to form



2. The carbon atoms might be dispersed in the metal particles as C_1, C_2 and C_3, which are then reduced. This mechanism does not require migration of alkyl groups which at least for



seems to be difficult.

The results of the study of the mechanism of the reaction of $^{\cdot}CH_3$ radicals with metal powders (see below) seems to suggest that the latter mechanism is more probable. However the considerably smaller ratios of $[CH_4]/[C_2H_4]$ and $[CH_4]/[C_2H_6]$ in non-buffered solutions than in buffered solutions (see Table 2), suggests that the acid-catalyzed heterolysis of the metal−carbon σ-bonds[19,20] in the dissolution process of the metal powder, inhibits alkyl migration, thus increasing these ratios.

Table 2. Ratio comparison of gas concentrations formed in the dissolution process of analytical iron in the presence of a buffer and in its absence[a]

Presence of buffer	$[CH_4]/[C_2H_4]$	$[CH_4]/[C_2H_6]$
+	9.8	7.1
−	2.1	2.6

[a] Every sample contains 10 g of activated iron powder, 2.5 mL H_2O or 0.1 M phosphatebuffer pH 4.0, t = 3 hours, T = 25 °C, No radiation. Error limit ± 15%.

The last step of the mechanism clearly involves the heterolysis of the M−C σ-bonds, in an analogous mechanism to that observed for homogeneously dissolved complexes with metal−carbon σ bonds.[21−23]

The results clearly demonstrate that whenever the reduction of haloalkanes by metals is studied by following the kinetics of formation of the organic products,[24,25] the corresponding blank experiments, in the absence of organic substrates, have to be carried out.

Finally it is tempting to suggest that the production of alkanes and alkenes via this mechanism might have contributed to the formation of light organic compounds[26] including petroleum,[27] in the prebiotic era. Clearly this mechanism does not require the harsh conditions required by many alternative mechanisms.[28]

Reaction of Methyl Radicals

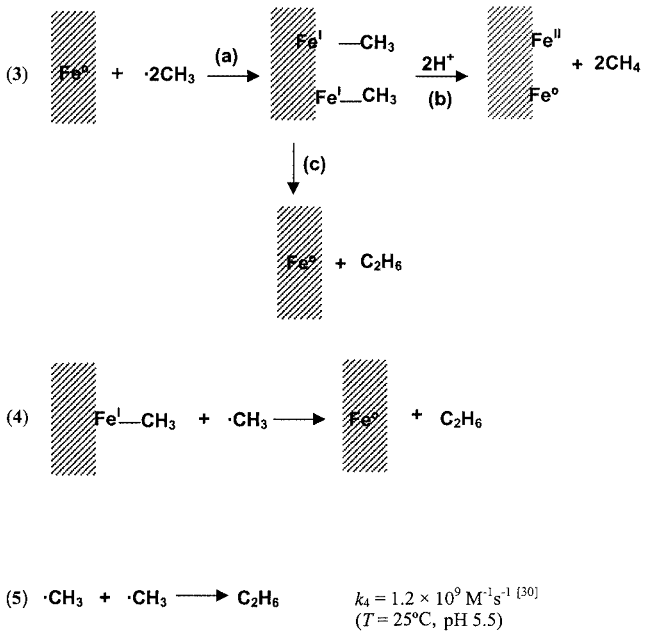
At first the reaction of activated iron powder with methyl radicals was studied. The results (see Table 3) clearly demonstrate that considerably more CH_4 is formed in the irradiated sample containing iron powder than in the sum of the blank experiments (non-irradiated sample and irradiated sample without iron powder). The gases formed in the non-irradiated blank experiment are due to the dissolution process of the iron powder, which contains 450 ppm of carbon by weight. A comparison of the yields of the gases formed in the irradiated sample containing iron powder and the same non-irradiated experiment (see Table 3), demonstrates that the C_2H_4, C_3H_6 and C_3H_8 gases formed in irradiated experiments originate from the dissolution of Fe^0. However the yield of CH_4 and C_2H_6 in this experiment is considerably larger than that in the non-irradiated experiment. It is suggested that the excess CH_4 and C_2H_6 formed in the irradiated samples containing iron powder are

Table 3. Emitted gas composition in reaction with $(CH_3)_2SO$[a]

Presence of Iron	Radiation	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
+	+	1598	18	147	4	5.7
+	−	45	17	11	3.9	5.7
−	+	990	−	122	−	−

[a] 10 g activated iron, 2.5 mL solution containing buffer acetate 0.1 M and $(CH_3)_2SO$ 0.05 M, pH 4.0, radiation dose 480 Gy, N_2O saturated. Error limit ± 15%.

formed via the mechanism outlined in Scheme 1. It is proposed that the reaction proceeds via the inner-sphere mechanism, as the formation of CH_3^- is endothermic in analogy to oxidations by hydrogen atoms.[30,31] The formation of M^I-CH_3 σ-bonds is analogous to the observed mechanism of reaction of $^\cdot CH_3$ radicals with a variety of low valent transition metal complexes.[16,21]



Scheme 1. CH_4 and C_2H_6 formation via reaction of methyl radicals with iron powder

It is of interest to note that the yield of $[CH_4] + 2[C_2H_6]$ in irradiated samples containing iron powder is considerably larger than in irradiated samples without iron powder, by at least a factor of two. This result proves that more methyl radicals are formed by radiation in the solution containing the iron powder. This result points out that some of the energy absorbed by the metal powder is transferred to the aqueous solution or to$(CH_3)_2SO$ molecules adsorbed to the powder surface. Energy transfer and charge transfer from irradiated solids to the solvent or to adsorbed molecules is a well-known phenomenon in the literature.[32−37] But the solid systems studied were porous silica, zeolites, porous glass and clay systems i.e. insulators. Nothing is known about energy transfer or charge transfer from irradiated metals to adsorbed molecules or to the solution. Obviously, the present results point out that, surprisingly, this phenomenon occurs also for iron, i.e. for a metal. This means that a band gap between the ground state and the excited state is not required for this process.

The dependence of the yield of CH_4 and C_2H_6 on $(CH_3)_2SO$, in the range 0.02−0.08 M, was studied. The results (not shown) point out that the gas yields are independent of $(CH_3)_2SO$. This suggests that either the energy is transferred from the iron to the solution or that even at the lowest concentration the iron surface is saturated with adsorbed $(CH_3)_2SO$. The latter alternative seems less probable.

The results are pH independent in the range 4−6. Therefore it was decided to omit the acetate buffer from the solutions. This action decreases the $[CH_4]/[C_2H_6]$ ratio in the blank experiments that do not contain iron powder, because reaction 6 contributes to the methane yield.

$$\textbf{(6)}\ ^\cdot CH_3 + CH_3COO^- \longrightarrow CH_4 + {}^\cdot CH_2CO_2^- \quad k_6 = 600\ M^{-1}s^{-1}\ [38] \quad (T = 25°C,\ pH\ 1.0)$$

When N_2O-saturated blank solutions containing only 0.05 M $(CH_3)_2SO$ are irradiated, the methane and ethane are formed via reactions 7 and 5. Using the radiation dose 480 Gy and k_5 one can calculate k_7 from the results.

$$\textbf{(7)}\ ^\cdot CH_3 + (CH_3)_2SO \longrightarrow CH_4 + {}^\cdot CH_2S(O)CH_3 \quad k_7 = 100 \pm 20\ M^{-1}s^{-1} \quad (T = 25\ °C,\ pH\ 4.0)$$

The calculated value of k_7 is smaller than the k_6 value, therefore, in the absence of acetate buffer, the contribution of reaction 5 is larger and the yield of ethane is increased in comparison to the methane yield.

At the end of all the reactions the Fe^{II} and Fe^{III} concentrations were measured using a colorimetric method.[39] The measured concentrations of Fe^{III} ions are negligible $[(5 \pm 0.8) \times 10^{-5}$ M] compared to Fe^{II} $[(1.2 \pm 0.2) \times 10^{-3}$ M]. The Fe^{II} and Fe^{III} concentrations were the same at all pHs and for irradiated and non irradiated systems. The calculated concentration of Fe^{II} due to reaction 3, which yields 2100 ppm CH_4 (see Table 4) in the irradiated system is 1.1×10^{-4} M, i.e. within the experimental error of the non-irradiated sample.

Next it was checked whether the methane is formed via the reaction:

$$\textbf{(8)}\ Fe^{2+}_{aq} + {}^\cdot CH_3 \xrightarrow{H^+} Fe^{3+}_{aq} + CH_4$$

For this purpose N_2O-saturated solutions containing $FeSO_4$ were irradiated. The results (see Table 5) clearly point out that reaction 8 involving the Fe^{2+}_{aq} ions, formed in the corrosion process, is not the source of the methane formed in the presence of the iron powder.

Thus the results illustrate that methyl radicals react with the iron powder to form CH_4 and probably some C_2H_6. Assuming that all the ethane is formed via reaction 5, i.e. that reactions 3c and 4 do not contribute to the ethane yield, one can calculate the apparent rate of reaction 3a from the known dose rate and k_4. Thus $k_{3a} = 20 \pm 10\ s^{-1}$ and is calculated for this powder.

A considerably larger $[CH_4]/[C_2H_6]$ ratio is observed in the irradiated samples containing iron powder than in the blank non-irradiated samples (see Table 4). In the irradiated samples the density of $-CH_3$ groups bound to the iron particles is clearly considerably higher than in the blank non-irradiated experiments. These observations suggest that the C_2H_6 formed in the blank experiments does not stem from the reaction:

Table 4. The role of metal powder activation and irradiation on the gas yields[a]

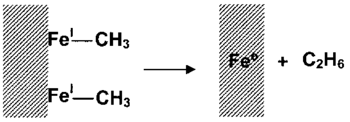
Metal	Activated	Irradiated	E^0 [V]	Carbon [ppm]	CH_4 [ppm]	C_2H_4 [ppm]	C_2H_6 [ppm]	C_3H_6 [ppm]	C_3H_8 [ppm]
$(CH_3)_2SO$	−	+			500		370		
Cu^0[a]	+	+	0.34	560	41		20		
	+	−			17		5.6		
	−	+			44		82		
	−	−			2				
Cr^0[b]	+	+	−0.41	3000	1500	72	160	32	30
	+	−			75	19	15	8	7.4
	−	+			466	28	37		
	−	−			58	13.7	5.3		
Fe^0[c]	+	+	−0.44	450	2100	63	240	1.2	4
	+	−			28.4	13	8.6	4.7	5
	−	+			753	22	85	2.7	1.7
	−	−			30	20	8.8	8	3.2
Zn^0[d]	+	+	−0.76	40	2060		553		
	+	−			12	2.6	1.6		
	−	+			903		150		
	−	−			1.8				
Mn^0[e]	+	+	−1.18	50	790		90		
	+	−			170		32		
	−	+			780		132		
	−	−			140		8		

[a] Composition of the gases formed in the reaction of 10 g activated/ non activated metal powders with 2.5 mL $(CH_3)_2SO$ 0.05 M solution, pH 4.0, t = 3 hours (radiation dose 480 Gy), T = 25 °C. All samples N_2O saturated. Error limit ± 15%. Cu^0 powder (Aldrich 99%, <10 μm). [b] Cr^0 powder (Alfa Aesar 99.8%, <10 μm). [c] Fe^0 powder (Merck 99%, ≤10 μm). [d] Zn^0 powder (Aldrich 98%, <10 μm). [e] Mn^0 powder (Aldrich 99%, 325 mesh).

Table 5. Dependence of gas formation in the presence of $Fe^{2+}{}_{aq}$ ions[a]

Sample composition	Irradiated	CH_4 [ppm]	C_2H_6 [ppm]
$FeSO_4$, $(CH_3)_2SO$	+	480	190
$FeSO_4$, $(CH_3)_2SO$	−	−	−
$(CH_3)_2SO$	+	500	370

[a] 2.5 mL of N_2O saturated solutions containing $FeSO_4$ (5×10^{-3} M), $(CH_3)_2SO$ (0.05 M), pH 4.0, t = 3 hours (radiation dose 480 Gy), T = 25 °C. Error limit ± 15%.



i.e. from the migration of -CH_3 groups bound to the iron particle. Thus the results corroborate the suggestion that the C_2H_4, C_2H_6, C_3H_6 and C_3H_8 gases formed in the non-irradiated blank experiments containing iron powder, originate from small carbon clusters present in the iron metal.

It was interesting to check whether analogous reactions of methyl radicals also take place with other metal powders. For this purpose the reactions of Cu, Cr, Zn and Mn powders with methyl radicals were studied. In addition, the role of metal powder activation on the gas yields was investigated; the results are summed up in Table 4. The effect of irradiating metal powders immersed in water at pH 4.0, in the absence of $(CH_3)_2SO$, on the yield of light alkanes is minor (see Table 1).

Conclusions

According to the experimental results the following conclusions can be drawn:

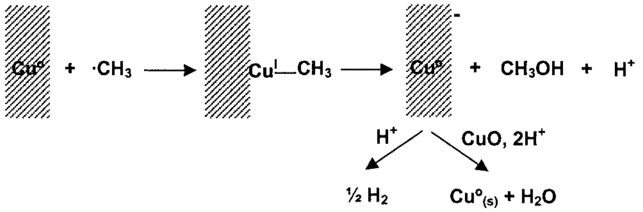
1. For all metals, except for Cu^0 and Mn^0, in the $\{M^0, (CH_3)_2SO, Ra\}$ system the radiolytic yield of methane is considerably larger than that obtained in the absence of the metal powder but the ethane yield decreases, except for the system containing activated Zn. Thus, the results point out that under the experimental condition the rate of reaction 9 is considerably higher than that of reaction 5.

$$\textbf{(9)}\quad M^o + \cdot CH_3 \xrightarrow{H^+} CH_4 + M^I$$

2. For all metals except for Cu^0, the total radiolytic alkane yield, $[CH_4]$ +2 $[C_2H_6]$, in solutions containing $(CH_3)_2SO$ and metal powder, is considerably larger than the sum of the yields of the two blank experiment, i.e. the non-irradiated solution containing metal powder and the irradiated solution containing only $(CH_3)_2SO$ without the metal. This result points out that some energy transfer from the irradiated metal to the solution or to adsorbed $(CH_3)_2SO$ occurs.

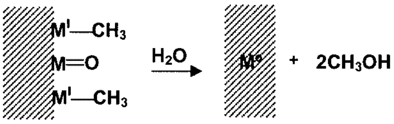
3. The addition of copper powder to $(CH_3)_2SO$ decreases the total radiolytic gas yield considerably (see Table 4). The logic explanation for this observation is that methyl radicals are oxidized by the copper particles. A mechanism for this process is presented in Scheme 2. It should be noted that the oxidation potential of $\cdot CH_3$ radicals is considerably higher than that of $Cu^0{}_{(s)}$. Thus, thermodynamically the methyl radicals can oxidize copper as they oxidize the other

metals. The copper system is still under investigation and the yield of the methanol and dihydrogen in the system will be determined.



Scheme 2. Reaction of methyl radicals with copper powder

4. Activation of the metal powders leads to an increase in the radiolytic gas yield. In the activation step oxides are removed from the metal surface, this probably transforms the metal particle into a stronger reducing agent. Oxides present on the surface might react via:



thus decreasing the yields of CH_4 and C_2H_6. Nevertheless, the activation step does not contribute to an increase in the radiolytic gas yield in the case of Cu^0 and Mn^0. The explanation for the Cu^0 system was outlined above. Mn^0 is the strongest reducing metal studied ($E^0 = -1.18$ V) thus, it probably tends to act only as a reductant.

It seemed of interest to check whether the use of metal nano-particles, prepared via reduction of the metal ions with BH_4^-,[40] affects the results. The results of these experiments are summed up in Table 6. A comparison of the results for iron in Tables 4 and 6 reveals that indeed the smaller particles scavenge a larger part of the methyl radicals thus increasing the methane yield and decreasing the ethane yield. Furthermore, the total gas yield, $[CH_4] + 2\,[C_2H_6]$, is larger for the "nano" particles, that is the smaller particles induce a larger energy transfer from the metal to the solution, as expected.

Table 6. Reaction of methyl radicals with synthesized metal powders[a]

Metal	Irradiated	CH_4 [ppm]	C_2H_6 [ppm]
Fe^0 (synth)	+	2600	152
	−	14	
Ni^0 (synth)	+	25000	606
	−	18	

[a] Gas product composition in reaction of 10 g activated nanoparticle metal powders with 2.5 mL N_2O saturated solution containing 0.05 M $(CH_3)_2SO$ solution, pH 4.0, t = 3 hours (2 h of radiation, 480 Gy), T = 25 °C. Error limit ± 15%.

Finally it should be pointed out that:

1. Methyl radicals which are strong reducing and oxidizing agents[15,16] oxidize Cr^0, Mn^0, Fe^0, Ni^0 and Zn^0 powders. The products of these reactions are methane and the corresponding $M^{2+}{}_{(aq)}$ ions. The analogous reaction with Cu^0 powders probably yields methanol and dihydrogen.

2. As the radicals formed in the dehalogenation reaction 1 are formed in the vicinity of the metal surface, it is clear that, since reaction 9 is fast, reaction 1 is followed by reaction 9.

3. The results suggest that if radioactive wastes are stored as aqueous solutions containing organic materials in metal containers, the formation of alkyl radicals will contribute to the corrosion of the container.

Experimental Section

The sources and properties of the metal powders used in this study are summed up in the footnotes of Table 4. All other chemicals were of AR grade and were used without further purification. The water used was deionized water, which was further purified by a Millipore Milli-Q setup with a final resistivity of > 10 MΩ. The solutions were deaerated by bubbling with N_2O (He was used for studying alkane formation during the dissolution of analytical metals in aqueous solutions) 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 was previously activated by H_2SO_4 (0.1 M) for two minutes and then washed 7−8 times by 8 mL portions of water. This bulb was also deaerated by N_2O (or He was used for studying alkane formation during the dissolution of the analytical metals in aqueous solutions) prior to the injection of the solution.

After three hours of reaction the gas phase above the metal was analyzed using an HP 5890 GC fitted with a FID detector (Poropaq QS GC column 10Ft 1/8 in, Supelco). The carrying gas was He (30 mL/min, T = 70 °C). Hydrogen was determined using a TCD detector (12 mL/min of N_2, 40 °C). Some of the samples were irradiated for two hours, within the three hour time span, in a ^{60}Co γ source with a dose rate of 4 Gy/min.

The Fe^{II} yield was measured using a colorimetric procedure based on *ortho*-phenanthroline.[39]

The amount of carbon in the metals was determinate using a Carbon-Elementary Analyzer, of LECO.

Metal nanoparticles were synthesized was by reducing $M^{II}/M^{III}{}_{(aq)}$ ions with $NaBH_4$ in He-saturated aqueous solutions.[40,41]

Formation of Radicals with Ionizing Radiation: When ionizing radiation (γ -radiation) is absorbed by a dilute aqueous solution, the following initial products are formed:[42]

$$\textbf{(10)}\quad H_2O \xrightarrow{\gamma,\, e^-} \cdot H\ (0.60),\ \cdot OH\ (2.65),\ e^-_{aq}\ (2.65),\ H_2O_2\ (0.75),\ H_2\ (0.45)$$

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 while those of H_2O_2 and H_2 are somewhat lower. In N_2O-saturated solutions the hydrated electron is converted into the hydroxyl radical:[43]

$$\textbf{(11)}\quad e^-_{aq} + N_2O \xrightarrow{H^+} N_2 + \cdot OH \qquad k = 8.7 \times 10^9\ M^{-1}\ s^{-1}$$

At pH > 3 the solvated electrons will all react with N_2O yielding $^{\cdot}OH$ as the major radical.

Preparation of the $^{\cdot}CH_3$ Radicals: The methyl radicals were formed[44] via the following reactions in N_2O-saturated solutions:

$$\textbf{(12)}\ {\cdot}OH + (CH_3)_2SO \longrightarrow (CH_3)_2S^{\cdot}(O)OH \qquad k = 7.0 \times 10^{9}\ M^{-1}\ s^{-1}$$

$$\textbf{(13)}\ (CH_3)_2S^{\cdot}(O)OH \longrightarrow (CH_3)_2S(O)OH + {\cdot}CH_3 \qquad k = 1.5 \times 10^{7}\ M^{-1}\ s^{-1}$$

Acknowledgments

This study was supported in part by a grant from the Budgeting and Planning Committee of The Council of Higher Education and the Israel Atomic Energy Commission. D. M. wishes to express his thanks to Mrs. Irene Evens for her ongoing interest and support.

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Received June 26, 2003