and a minority high school student apprenticeship from the National Cancer Institute (S 03RR03408-02) to J. S.

Registry No. **1a**, 61229-08-1; (*Z*)-**1a**, 112375-60-7; **1b**, 404-86-4; (*Z*)-**1b**, 25775-90-0; **1c**, 58493-48-4; (*Z*)-**1c**, 112375-61-8; **1d**, 61229-09-2; **2a**, 28789-35-7; **2b**, 19408-84-5; **2c**, 20279-06-5; **3**, 121-33-5; **4a**, 2874-33-1; **4b**, 93249-67-3; **5**, 1196-92-5; **5**·HCl, 7149-10-2; **6a**, 13865-19-5; **6b**, 6026-86-4; **6c**, 6654-36-0; **6d**, 63857-17-0; **7a**, 22884-29-3; **7b**, 34009-07-9; (*Z*)-**8a**, 112375-41-4; (*E*)-**8a**, 112375-53-8; (*E*)-**8a** (acid), 61229-06-9; (*E*)-**8a** (acid chloride), 112375-57-2; (*Z*)-**8b**, 112375-42-5; (*E*)-**8b**, 112375-54-9; (*E*)-**8b** (acid), 59320-77-3; (*E*)-**8b** (acid chloride), 95636-02-5; (*Z*)-**8c**, 112375-43-6; (*E*)-**8c**, 112375-55-0; (*E*)-**8c** (acid), 61229-05-8; (*E*)-**8c** (acid chloride), 112375-58-3; (*Z*)-**8d**, 112375-44-7; (*E*)-**8d**, 112375-56-1; (*E*)-**8d** (acid), 61229-07-0; (*E*)-**8d** (acid chloride), 112375-59-4; **9a**, 96-48-0; **9b**, 542-28-9; **9c**, 502-44-3; **9d**, 57-57-8; **10a**, 925-57-5; **10b**, 14273-92-8; **10c**, 4547-43-7; **10d**, 6149-41-3; (*R**,*R**)-**12a**, 112375-45-8; (*R**,*S**)-**12a**, 112375-46-9; (*R**,*R**)-**12b**, 112375-47-0; (*R**,*S**)-**12b**, 112375-48-1; (*R**,*R**)-**12c**, 112375-49-2; (*R**,*S**)-**12c**, 112375-50-5; (*R**,*R**)-**12d**, 112375-51-6; (*R**,*S**)-**12d**, 112375-52-7; methoxyamine hydrochloride, 593-56-6; 1-bromo-2-methylpropane, 78-77-3.

The Reaction of OH Radicals with Dimethyl Sulfoxide. A Comparative Study of Fenton's Reagent and the Radiolysis of Aqueous Dimethyl Sulfoxide Solutions

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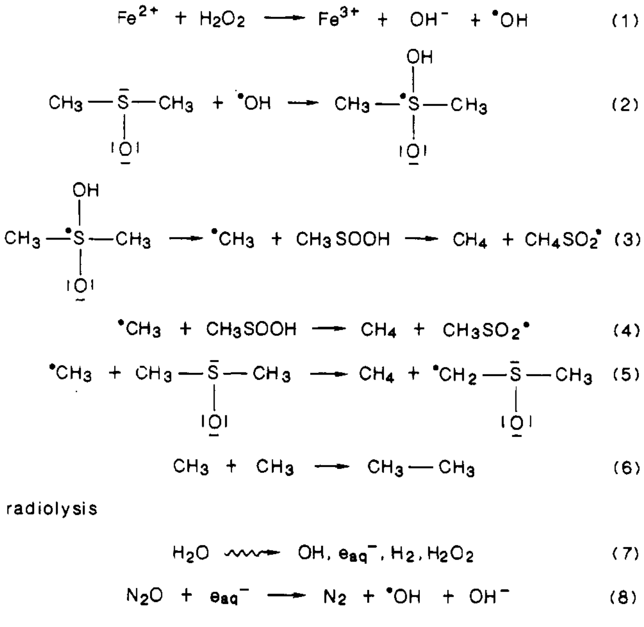
The reaction of OH radicals with dimethyl sulfoxide (DMSO) in aqueous solutions was investigated. The OH radicals were produced via radiolysis of N_2O saturated aqueous solutions and via Fenton's reagent. With Fenton's reagent we observed a quantitative conversion of OH radicals to CH_3 radicals, giving CH_4 and C_2H_6. The maximum yield in the radiolysis experiments was 86%. In both cases C_2H_6 was a major product with the C_2H_6/CH_4 ratio as high as 45. The C_2H_6/CH_4 ratio depends on the steady-state concentration of CH_3 radicals and on the DMSO concentration. Our results show that CH_3 radicals in addition to abstracting hydrogen from methanesulfinic acid also abstract hydrogen from DMSO to give CH_4. In the radiolysis of deuteriated DMSO we observed a much higher ethane/methane ratio than in the nondeuteriated DMSO. This isotope effect supports the hydrogen abstraction from DMSO by CH_3 radicals.

Dimethyl sulfoxide (DMSO) has been used as a probe for OH radicals in biological systems.[1] The mechanism of this reaction has been studied in detail both by ESR and by radiolysis techniques.[2,3] In a radiolysis study[4] the product of the reaction was found to be mainly methane with only small amounts of ethane. In this study the authors concluded that only a small fraction of OH radicals (about 25%) are converted to methyl radicals. On the other hand a pulse radiolysis study[3] reached the conclusion that OH radicals are converted quantitatively to methyl radicals. Because of the importance of this reaction for the detection of OH radicals we have studied the reaction of OH radicals with DMSO, producing OH radicals both by radiolysis of water and via the Fenton reaction.[5]

Scheme I



$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

$$CH_3-\bar{S}(O)-CH_3 + {}^{\bullet}OH \longrightarrow CH_3-{}^{\bullet}S(OH)(O)-CH_3 \quad (2)$$

$$CH_3-{}^{\bullet}S(OH)(O)-CH_3 \longrightarrow {}^{\bullet}CH_3 + CH_3SOOH \longrightarrow CH_4 + CH_4SO_2^{\bullet} \quad (3)$$

$${}^{\bullet}CH_3 + CH_3SOOH \longrightarrow CH_4 + CH_3SO_2^{\bullet} \quad (4)$$

$${}^{\bullet}CH_3 + CH_3-\bar{S}(O)-CH_3 \longrightarrow CH_4 + {}^{\bullet}CH_2-\bar{S}(O)-CH_3 \quad (5)$$

$$CH_3 + CH_3 \longrightarrow CH_3-CH_3 \quad (6)$$

radiolysis

$$H_2O \rightsquigarrow OH,\ e_{aq}^-,\ H_2,\ H_2O_2 \quad (7)$$

$$N_2O + e_{aq}^- \longrightarrow N_2 + {}^{\bullet}OH + OH^- \quad (8)$$

Results and Discussion

The results of the radiolysis experiments are shown in Tables I–III, and those using Fenton's reagent are shown in Tables IV–V. The reaction of OH radicals with DMSO to yield CH_3 radicals was first observed by Norman and co-workers.[6] Subsequent work by this research group using ESR techniques[2] and more recently by Asmus and co-workers[3] using pulse radiolysis have established the mechanism outlined in Scheme I. In the radiolysis of water OH radicals and e_{aq}^- are formed in about equal amounts along with some minor molecular products.[7] In presence of N_2O the solvated electrons are converted to OH radicals. The yield of these species is given by the *G* value (number of molecules produced per 100 eV of energy

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Table I. Effect of N_2O, Dose Rate, and pH on the *G* Values in the Radiolysis of Aqueous DMSO Solutions[a]

			G values			
N_2O[b] presence	$[H_2SO_4]$, M	dose rate,[c] rad/min	CH_4	C_2H_6	C_2H_6/CH_4	% yield
		736	1.79	0.54	0.30	
		3360	1.36	0.61	0.45	
	5×10^{-2}	3360	1.54	0.41	0.27	
	5×10^{-1}	736	1.20	0.09	0.07	
	5×10^{-1}	3360	0.86	0.13	0.15	
N_2O		736	1.64	1.37	0.84	78
N_2O		3360	1.10	1.86	1.78	86
N_2O	5×10^{-2}	736	1.92	0.42	0.22	49
N_2O	5×10^{-2}	3360	1.56	0.51	0.33	46

[a] All experiments were carried out in 500-mL aqueous solutions containing 5×10^{-2} M DMSO. The solutions were deaerated by bubbling Ar through the solution for 15 min prior to irradiation. [b] N_2O containing solutions were prepared by bubbling Ar through it for 15 min and N_2O for 15 min, before irradiation. [c] Total dose was about 33 600 rad in all experiments.

Table II. Effect of DMSO Concentration on the *G* Values in the Radiolysis of N_2O-Saturated Aqueous Solutions[a]

		G values			
[DMSO], M	dose rate, rad/min	CH_4	C_2H_6	C_2H_6/CH_4	% yield[b]
5×10^{-3}	736	0.50	1.82	3.64	74
4×10^{-2}	736	1.13	1.50	1.33	74
5×10^{-2}	736	1.64	1.37	0.84	78
5×10^{-1}	736	2.79	0.32	0.11	61
5×10^{-3}	3360	0.45	2.0	4.44	79
4×10^{-2}	3360	0.80	2.0	2.5	86
5×10^{-2}	3360	1.0	1.87	1.87	85
5×10^{-1}	3360	2.92	0.73	0.25	78

[a] All experiments were carried out in 500-mL aqueous solutions, saturated with Ar (15-min bubbling) and N_2O (15-min bubbling) and irradiated for 45 min (736 rad/min) and 10 min (3360 rad/min), respectively. [b] Calculated assuming $G(^{\bullet}OH) = 5.6$ (see ref 7).

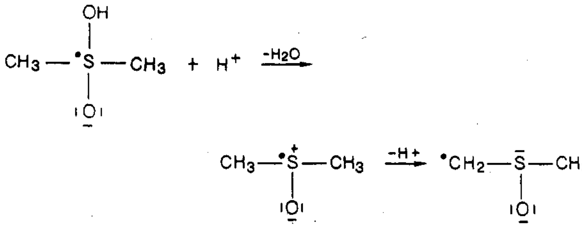
Table III. Yields of Methane and Ethane in the Radiolysis of Aqueous Perdeuteriated DMSO Solutions[a]

			G values[b]	
$[CD_3SOCD_3]$, M	dose rate, rad/min	irrad time, min	methane	ethane
5×10^{-3}	736	45	0.42 (0.50)	2.30 (1.80)
4×10^{-2}	736	45	0.75 (1.13)	1.80 (1.50)
4×10^{-2}	3360	10	0.40 (0.80)	2.40 (2.0)

[a] Conditions were the same as in Table II, footnote *a*. [b] *G* values in parentheses are those obtained from the irradiation of aqueous CH_3SOCH_3.

absorbed). The *G* value for both OH and e_{aq}^- is 2.8. In presence of N_2O we therefore have a system in which OH is the only reactive intermedite with a *G* value of 5.6.[7] From the results in Table I and II we can clearly see that the OH radicals are converted in high yield to methyl radicals and that ethane is a major product. As expected from the mechanism outlined in Scheme I the CH_3CH_3/CH_4 ratio depends on the steady-state concentration of CH_3. With increasing dose rate (increasing steady state concentration) we expect an increase in the CH_3CH_3/CH_4 ratio as was indeed observed. The maximum yield was 86% in good agreement with the pulse radiolysis experiments by Asmus and co-workers.[3] The question arises: Where does the hydrogen in methane come from? It is generally assumed that CH_4 is formed via reaction 4 (Scheme I). ESR measurements in the Ti^{3+}–H_2O_2 reaction supported this reaction and no evidence for CH_2SOCH_3 (reaction 5, Scheme I) was obtained.[2] Other investigators have used CD_3SOCD_3 to study this problem.[1] Under their specific conditions they found no CD_4 but only CD_3H, thus supporting the ESR data. On the other hand a group of Swedish investigators[8] reported the formation of CD_4 in addition to CD_3H. However, no quantitative data are reported. Our radiolysis results (Table II) as well as our results with Fenton's reagent (Table IV), however, show a big increase in the CH_4/CH_3CH_3 ratio with increasing DMSO concentration, thus indicating the formation of CH_4 via H abstraction from DMSO (reaction 5, Scheme I). It is well-known that the interpretation of ESR data alone without any product analysis can lead to erroneous conclusions. This was pointed out many years ago by Walling.[5] The experiments with deuteriated DMSO leads in this case also to the wrong conclusions, due to a considerable isotope effect (Table III). Our results show that in the deuteriated experiments the CD_3 preferentially dimerizes which means that from the absence of CD_4 we cannot conclude that CH_3 does not abstract a hydrogen from CH_3SOCH_3.

The formation of considerable methane in the radiolysis of aqueous perdeuteriated DMSO indicates that (assuming all methane is CD_3H as formerly reported[1]) in addition to reaction 5 H abstraction from methanesulfinic acid (reaction 4) makes a major contribution to the formation of methane. In previous radiolysis work only traces of C_2H_6 were reported.[4] On the basis of our present results this is due to a number of factors: low dose rate, absence of N_2O, and low pH. Under these conditions we also find only very low yields of C_2H_6 (Table I). The decrease in CH_4 and C_2H_6 at low pH was also observed in the experiments with Fenton's reagent (Table IV, experiments 8, 9). We suggest the reactions in eq 9.



$$CH_3-\overset{OH}{\underset{O^-}{{}^{\bullet}S}}-CH_3 + H^+ \xrightarrow{-H_2O} CH_3-\overset{+}{\underset{O^-}{{}^{\bullet}S}}-CH_3 \xrightarrow{-H^+} {}^{\bullet}CH_2-\underset{O^-}{\bar{S}}-CH_3 \quad (9)$$

In the reactions with Fenton's reagent we observed the same behavior as in the radiolysis work. We obtain a quantitative conversion of OH radicals to CH_3 radicals. In presence of Cu^{2+} (Table IV, experiment 7) we obtain no gaseous products due to the oxidation of either the OH–DMSO adduct or the CH_3 radical. The effect of pH and DMSO concentration are the same in the two sets of experiments. The most striking result with Fenton's reagent is the very high yield of ethane. This can be expected on the basis of the rate constants[2] of reactions 4 and 6. The CH_3CH_3/CH_4 ratio is as high as 45. With increasing Fe^{2+} concentration we observed no significant change in C_2H_6 but a small decrease in CH_4 (Table IV, experiments 1–6). These results show that there is no reduction of CH_3 radicals to CH_4 by Fe^{2+}. The high C_2H_6/CH_4 ratio could

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Table IV. Effect of DMSO, Fe^{2+}, H_2O_2, and O_2 Concentrations and pH on the Yields of CH_4 and C_2H_6

	reactants[a]					products,[b] mol × 10^6	
expt	[DMSO], M	atmos	[H_2SO_4], M	[Fe^{2+}], M	[H_2O_2], M	CH_4	C_2H_6
1	5×10^{-2}	Ar		2×10^{-3}	1.76×10^{-3}	76	390
2	5×10^{-2}	Ar		10×10^{-3}	1.76×10^{-3}	25	400
3	5×10^{-2}	Ar		20×10^{-3}	1.76×10^{-3}	18	400
4	5×10^{-2}	Ar		2×10^{-3}	1.76×10^{-4}	4	44
5	5×10^{-2}	Ar		10×10^{-3}	1.76×10^{-4}	2	50
6	5×10^{-2}	Ar		10×10^{-3}	1.76×10^{-4}	1	45
7[c]	5×10^{-2}	Ar		2×10^{-3}	1.76×10^{-3}	0	0
8	5×10^{-2}	Ar	5×10^{-2}	2×10^{-3}	1.78×10^{-3}	52	200
9	5×10^{-2}	Ar	5×10^{-1}	2×10^{-3}	1.28×10^{-3}	30	55
10	5×10^{-3}	Ar		2×10^{-3}	1.78×10^{-3}	60	300
11	5×10^{-1}	Ar		2×10^{-3}	1.78×10^{-3}	145	320
12	5	Ar		2×10^{-3}	1.78×10^{-3}	478	51
13	5×10^{-2}	air		2×10^{-3}	1.78×10^{-3}	91	180
14	5×10^{-2}	O_2		2×10^{-3}	1.78×10^{-3}	0	0
15	5×10^{-2}	Ar		2×10^{-3}	3.56×10^{-3}	106	258
16	5×10^{-2}	Ar		2×10^{-3}	17.8×10^{-3}	292 (690)[d]	152 (152)[d]
17	5×10^{-2}	Ar		2×10^{-4}	1.78×10^{-3}	35 (68)[d]	41 (41)[d]

[a] All reactions were carried out in 700-mL bottles containing 500-mL solutions. The solutions were saturated with Ar or O_2 for 30 min, then Fe^{2+} was added, and 10-mL H_2O_2 solution was injected through a rubber septum. [b] Analysis was carried out after 10 min of shaking. [c] This experiment contained 2×10^{-3} M $CuSO_4$. [d] Results in parentheses represent analysis carried out after 1 day.

Table V. Effect of EDTA[a] or DTPA[b] on the Product Yields in the Reaction of Fenton's Reagent with DMSO

	reactants[c]					products, mol × 10^6	
expt	[DMSO], M	EDTA or DTPA (M)	atmos	[Fe^{2+}], M	[H_2O_2], M	CH_4	C_2H_6
1	5×10^{-2}	0	Ar	2×10^{-3}	1.76×10^{-3}	76	390
2	5×10^{-2}	EDTA (2×10^{-3})	Ar	2×10^{-3}	1.76×10^{-3}	35	410
3	5×10^{-2}	DTPA (2×10^{-3})	Ar	2×10^{-3}	1.76×10^{-3}	73	400

[a] EDTA: ethylenediaminetetraacetate disodium salt. [b] DTPA: diethylenetriaminepentaacetic acid. [c] Reaction conditions were the same as described in Table IV, footnote *a*.

Table VI. The Yields of CH_4 and C_2H_6 in the Reaction of Fe^{3+}–H_2O_2–DMSO

reactants[a]				products, mol × 10^6			
				after 10 min		after 18 h	
[DMSO], M	atmos	[Fe^{3+}], M	[H_2O_2], M	CH_4	C_2H_6	CH_4	C_2H_6
5×10^{-2}	Ar	2×10^{-3}	1.76×10^{-3}	0	0	66	3
5×10^{-2}	Ar	2×10^{-3}	17.6×10^{-3}	0	0	823	2

[a] 500-mL DMSO solutions were deaerated by bubbling Ar through the solution for 30 min. Then Fe^{3+} ($FeNH_4(SO_4)_2\cdot 12H_2O$) was added, the bottle stoppered, and 10-cm³ H_2O_2 solution (0.3% or 3%, respectively) injected through the rubber stopper.

be explained by a [$Fe^{2+}\cdot CH_3$] complex which stabilizes the CH_3 radicals and thus leads to more ethane formation. This type of complexation has been invoked previously.[9] However, in our case we feel that this complexation hypotheses is not required to explain the result. The reason for the high CH_3CH_3/CH_4 ratio is the high steady-state concentration and the small rate constant for H abstraction. This explanation is supported by our radiolysis experiments, where the same dependence of the C_2H_6/CH_4 ratio on the steady state concentration of CH_3 radicals was observed in absence of Fe^{2+}. Actually our results with EDTA and DTPA (Table V) support the latter explanation. If a Fe^{2+}–CH_3 radical complex were responsible for the high CH_3CH_3/CH_4 ratio, then in presence of EDTA or DTPA which complexes Fe^{2+} we should expect a decrease in the CH_3CH_3/CH_4 ratio contrary to our results.

If we use an excess of H_2O_2 over Fe^{2+} (Table IV, experiments 16, 17) we observe a considerable increase in CH_4 and a decrease in C_2H_6. This increase in CH_4 is due to reaction 10. With a 10-fold increase in H_2O_2 (compare

$$^{\bullet}CH_3 + H_2O_2 \rightarrow CH_4 + HO_2^{\bullet} \qquad (10)$$

experiments 1 and 16) we observe only a 4-fold increase in CH_4. This is less than expected on the basis of reaction 10 above. We have to realize that with increasing H_2O_2 concentration we obtain a higher steady-state concentration of CH_3 radicals, which is expected to cause a decrease in CH_4.

The reactions with Fenton's reagent are very fast. The reactions are complete in less than 10 min. If we use, however, an excess of H_2O_2 over Fe^{2+} (Table IV, experiments 15–17) we have after the Fenton reaction is finished an excess of H_2O_2 and Fe^{3+}. These two reactants undergo a slow reaction, giving rise to almost exclusively CH_4 (Table VI), according to reactions 11–14.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \qquad (11)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (12)$$

$$^{\bullet}OH + CH_3SOCH_3 \rightarrow {}^{\bullet}CH_3 + CH_3SOOH \qquad (13)$$

$$^{\bullet}CH_3 + H_2O_2 \rightarrow CH_4 + HO_2^{\bullet} \qquad (14)$$

Due to the slow first step the overall reaction is much slower than with Fenton's reagent and the steady-state concentrations of OH and CH_3 radicals are low, giving rise to almost exclusive methane formation (Table VI). Since in this case we always have an excess of H_2O_2 reaction 14 is responsible for the high yield of CH_4. In experiments 16 and 17 we therefore observe two stages of the reaction: (1) a fast Fenton reaction, giving both CH_4 and C_2H_6, and

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(2) a slow reaction of Fe^{3+} with H_2O_2, giving almost exclusively CH_4.

In conclusion, we have shown that OH radical react with DMSO to give in high yield CH_3 contrary to previous reports[4] and in good agreement with pulse radiolysis data.[3] The relative yields of CH_4 and C_2H_6 depends on the steady-state concentration of CH_3 and on a number of competing reactions.

Experimental Section

Irradiations. The irradiations were carried out in 700-mL bottles containing 500 mL of DMSO solutions. These solutions were saturated with Ar (15 min) and N_2O (15 min) and irradiated with a ^{137}Cs source at the desired dose rate sufficiently long to give a total dose of 33 600 rad. The analyses were carried out by withdrawing a sample with a 1-mL gas tight syringe and analyzing the sample by gas chromatography using a 6-ft Carbosieve B column (Supelco) at 130 °C. Calibrations were made with Scotty II (Supelco) calibrated gases. The results in Tables I–III are averages of at least two determinations with a deviation of ±0.1 *G* value units.

Reactions with Fenton's Reagent. These reactions were all carried out in 700-mL bottles containing 500 mL of DMSO solutions. These solutions were deaerated by Ar bubbling (30 min), then Fe^{2+} was added, and after it had dissolved, 10 mL of H_2O_2 solution was injected through a rubber septum. Analysis was carried out after about 10 min of shaking.

The results with Fenton's reagent represent the average of at least two determinations with a deviation of ±5%.

Acknowledgment. We thank Dr. Gabriel Infante of the Catholic University for the use of the ^{137}Cs irradiation facility and the National Institute of Health for financial support (MIH-MBRS Grant SO6-RR 8224-03). Thanks are also due to Dr. Angel A. Roman Franco for his continuing interest in and support of our research.

Registry No. DMSO, 67-68-5; H_2, 1333-74-0; D_2, 7782-39-0; Me·, 2229-07-4; HO·, 3352-57-6; N_2O, 10024-97-2; Fe^{2+}, 15438-31-0; H_2O_2, 7722-84-1; MeH, 74-82-8; EtH, 74-84-0.

The Reaction of Cu^+–O_2 and Cu^{2+}–Ascorbic Acid–O_2 with Dimethyl Sulfoxide. The Effect of Solvent

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The reaction of Cu^+–O_2 and Cu^{2+}–ascorbic acid–O_2 with dimethyl sulfoxide (DMSO) was investigated. The products of these reactions are CH_4 and C_2H_6 in high yields. The ratio of ethane to methane varies greatly from about 8 to 0.01, depending on the concentration of Cu^+, O_2, ascorbic acid, oxalic acid, mineral acids, and solvent. With a polar aprotic solvent like pure DMSO we observe a high C_2H_6/CH_4 ratio, while with a polar protic solvent like water a low C_2H_6/CH_4 ratio is observed. This solvent effect is consistent with the intermediate formation of a (Cu^+ $^\bullet CH_3$) complex, which in turn reacts in protic solvents or in the presence of mineral acids to give mainly CH_4 and mainly C_2H_6 in aprotic solvents.

Some transition-metal ion–O_2 systems have been known for a long time to hydroxylate aromatic compounds.[1] The mechanisms by which these systems hydroxylate has been studied extensively with quite contradictory results.[2] Arguments for and against the involvement of OH radicals have been presented. DMSO has been used as a probe for OH radicals in biological and chemical systems.[3] The use of DMSO as a OH radical probe has been called into question by a radiolysis study which claimed that only a small fraction of OH radicals (25%) are converted to CH_3 radicals.[4] In the preceding paper,[5] however, we have shown that OH radicals, produced via radiolysis of water and via Fenton's reagent, react with DMSO to give in high yields CH_3 radicals, which lead to methane and ethane as final products. Although the autoxidation of Cu^+ in DMSO has been studied in great detail,[6,7] no gaseous products derived from DMSO have been reported. We have therefore reexamined the Cu^+–O_2 as well as the Cu^{2+}–ascorbic acid–O_2 system in DMSO and DMSO–H_2O solutions.

Results and Discussion

The autoxidation of Cu^+ in DMSO was studied extensively by Zuberbühler and co-workers.[6,7] Their proposed mechanism is summarized in Scheme I. The oxidation

Scheme I

in aprotic solvent[6]

$$Cu^+ + O_2 \rightleftharpoons CuO_2{}^+ \rightleftharpoons Cu^{2+} + O_2{}^{\bullet -} \qquad (1)$$

$$CuO_2{}^+ + Cu^+ \rightleftharpoons Cu_2O_2{}^{2+} \qquad (2)$$

$$Cu_2O_2{}^{2+} \rightleftharpoons 2\,Cu^{2+} + O_2{}^{2-} \qquad (3)$$

in aqueous solution[7]

$$Cu^+{}_{aq} + O_2 \rightleftharpoons CuO_2{}^+ \qquad (4)$$

$$CuO_2{}^+ + H^+ \rightleftharpoons Cu^{2+} + HO_2{}^\bullet \qquad (5)$$

$$Cu^+{}_{aq} + HO_2{}^\bullet + H^+ \rightarrow Cu^{2+} + H_2O_2 \qquad (6)$$

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