(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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Table I. Effect of Water and O_2 Concentration on the Reaction of Cu^+–Ascorbic Acid–O_2 with DMSO[a]

		products,[b] mol × 10^6					
		air satd			O_2 satd[c]		
H_2O, mL	DMSO, mL	CH_4	CH_3CH_3	C_2H_6/CH_4	CH_4	CH_3CH_3	C_2H_6/CH_4
0	25	78	21	0.27	7	7	1.0
1	24	60	20	0.33	20	19	0.95
2	23	85	22	0.26	33	23	0.70
5	20	150	14	0.09	131	70	0.53
10	15	208	9	0.04	127	62	0.49
15	10	243	10	0.04	255	39	0.15
20	5	222	10	0.04	183	32	0.17
23	2	199	10	0.05	133	25	0.19

[a] All experiments contained 0.25 × 10^{-3} mol of Cu^+ as $Cu(CH_3CN)_4(ClO_4)$ and 3 × 10^{-3} mol of ascorbic acid. [b] The products were analyzed after shaking the solutions in 150 mL bottles stoppered with rubber septums for about 45 min in a mechanical shaker. [c] Oxygen was bubbled through the H_2O–DMSO solutions for 15 min before addition of ascorbic acid and Cu^+.

Table II. Effect of Water, O_2 Concentration, and Ascorbic Acid Concentration on the Reaction of Cu^+–Ascorbic Acid–O_2 with DMSO[a]

			products, mol × 10^6					
			air satd			O_2 satd		
expt	H_2O, mL	DMSo, mL	CH_4	CH_3CH_3	C_2H_6/CH_4	CH_4	CH_3CH_3	C_2H_6/CH_4
1	0	25	17	15	0.88			
2	1	24	29	19	0.66			
3	2	23	39	19	0.49			
4	5	20	62	11	0.18			
5	10	15	53	4	0.08			
6	15	10	125	4	0.03			
7	20	5	32	3	0.09			
8	23	2	32	2	0.06			
9	0	25	96	17	0.18	78	31	0.40
10	1	24	125	19	0.15	67	50	0.75
11	2	23	157	15	0.09	60	49	0.82
12	5	20	215	9	0.04	124	46	0.32
13	10	15	232	5	0.02	139	7	0.05
14	15	10	142	5	0.03	85	4	0.05
15	20	5	191	1	0.005	64	2	0.03
16	23	2	95	2	0.02			
17	0	25	153	29	0.19	109	51	0.47
18	1	24	168	20	0.12	138	70	0.51
19	2	23	171	20	0.12	247	69	0.28
20	5	20	168	5	0.03	340	71	0.21
21	10	15	180	4	0.02	333	18	0.05
22	15	10	142	2	0.01	188	7	0.04
23	20	5	107	2	0.02	146	4	0.03
24	23	2	76	1	0.01	111	4	0.04

[a] All experiments contained 0.5 × 10^{-3} mol of Cu^+ and 10^{-3} (experiments 1–8), 3 × 10^{-3} (experiments 9–16), and 5 × 10^{-3} mol (experiments 17–24) of ascorbic acid.

proceeds in two steps to the H_2O_2 stage. The interesting part is that the reaction appears to stop at the H_2O_2 stage,[7] although it is well-known that Cu^+ reacts with H_2O_2 in a Fenton-like reaction (eq 7). This reaction proceeds with

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + {}^{\bullet}OH \qquad (7)$$

a faster rate than the Fenton reaction.[8] Previous results by us have clearly shown that reaction 7 is taking place at least in aqueous solutions.[9] In the cooxidation of Cu^+ and benzoin in dimethyl sulfoxide Gampp and Zuberbühler[10] reported a further reaction of H_2O_2 with dimethyl sulfoxide to give dimethyl sulfone.

Our present results on the Cu^+–O_2–DMSO reaction are shown in Tables I–IV. We find considerable amounts of methane and ethane. The oxidation requires the presence of protons. Without addition of H_2SO_4 or $HClO_4$ to the Cu^+ solution no CH_4 or CH_3CH_3 is obtained (Table IV). Other acids like oxalic acid are known to accelerate the Cu^+ autoxidation.[7] In presence of oxalic acid we actually found the highest yield of methane (about 40% based on Scheme I, followed by reaction 7, i.e. 1 CH_3 for 3 Cu^+ consumed). This is a high yield considering the low pH, which is known to decrease the conversion of OH to methane and ethane.[5] A high yield of CH_4 and C_2H_6 may be favored in this case by complexing of Cu^{2+} with oxalic acid,[7] thus suppressing the oxidation of CH_3 to CH_3OH or of the OH–DMSO adduct to $CH_3SO_2CH_3$.

In all the experiments in presence of acid (H_2SO_4, oxalic acid) the almost exclusive product is methane (Table IV). This is contrary to our results with Fenton's reagent[5] and is due to the rapid reduction of CH_3 by Cu^+ in acid solution (eq 8 and 9). Reaction 8 competes effectively with the

$$ {}^{\bullet}CH_3 + Cu^+ \rightarrow \underset{\text{I}}{(Cu^+\ {}^{\bullet}CH_3)} \xrightarrow{H^+} Cu^{2+} + CH_4 \qquad (8)$$

$$2(Cu^+\ {}^{\bullet}CH_3) \xrightarrow[\text{aprotic solvent}]{\text{in}} 2Cu^+ + CH_3\text{-}CH_3 \qquad (9)$$

scavenging of CH_3 radicals by oxygen due to the considerable higher concentration of Cu^+ compared to O_2 in our experiments.[11]

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Table III. Effect of Water, O_2 Concentration, and Ascorbic Acid Concentration on the Reaction of Cu^+-Ascorbic Acid-O_2 with DMSO[a]

			products,[b] mol × 10^6					
			air satd			O_2 satd[c]		
expt	H_2O, mL	DMSO, mL	CH_4	CH_3CH_3	C_2H_6/CH_4	CH_4	CH_3CH_3	C_2H_6/CH_4
1	0	25	4	32	8.0			
2	1	24	5	34	6.8			
3	2	23	8	32	4.0			
4	5	20	36	34	0.96			
5	10	15	76	29	0.38			
6	15	10	94	19	0.20			
7	20	5	90	23	0.26			
8	23	2	77	25	0.32			
9	0	25	17	31	1.82	8	42	5.25
10	1	24	25	27	1.08	8	55	6.87
11	2	23	48	28	0.58	18	46	2.56
12	5	20	73	30	0.41	43	50	1.16
13	10	15	119	18	0.15	118	32	0.27
14	15	10	126	16	0.13	119	34	0.28
15	20	5	141	14	0.10	45	28	0.62
16	23	2	113	13	0.12	61	23	0.38

[a] All experiments contained 2.5 × 10^{-3} mol of Cu^+ and 1 × 10^{-3} (experiments 1–8) and 3 × 10^{-3} mol (experiments 9–16) of ascorbic acid. [b,c] See corresponding footnotes, Table I.

Table IV. Effect of Water and Acids on the Reaction of Cu^+-O_2 with DMSO[a]

reactants				products,[b] mol × 10^6 air satd	
H_2SO_4 or $HClO_4$, mL, or oxalic acid, mol		DMSO, mL	H_2O, mL	CH_4	CH_3CH_3
$HClO_4$	0.5	25	0	192	10
H_2SO_4	0.5	25	0	192	7
none		25	0	0	0
H_2SO_4	0.5	24	1	196	3
H_2SO_4	0.5	23	2	204	7
H_2SO_4	0.5	20	5	170	6
oxalic	10^{-2}	25	0	310	9
oxalic	2 × 10^{-2}	25	0	300	5
oxalic	10^{-2}	10	15	290	0

[a] All experiments contained 2.5 × 10^{-3} mol of Cu^+ as $Cu(CH_3CN)_4(ClO_4)$. [b] See footnote *b*, Table I.

Since protons are required for CH_3 radical formation the intermediate complex I, if formed at all, will have a very short lifetime. It occurred to us that if we could find conditions where CH_3 is formed in absence of strong acid and in aprotic solvent, then the (Cu^+ $^\bullet CH_3$) complex would have a longer lifetime and instead of giving CH_4 would give mainly CH_3CH_3 (reaction 9).

We have indeed found that the Cu^+ oxidation is accelerated by ascorbic acid. These results are shown in Tables I–III. In pure DMSO (aprotic solvent) we obtain very high CH_3CH_3/CH_4 ratios. At the lowest concentration of ascorbic acid used (4 × 10^{-2} M) we obtain in pure DMSO almost exclusively ethane (Table III, experiment 1). This is surprising since in our recent work with Fenton's reagent we have shown that CH_3 radicals abstract hydrogen from DMSO,[12] giving high CH_4, contrary to our results. This means that in pure DMSO the Cu^+ ions affect the reactivity of the CH_3 radicals in such a way as to favor the formation of ethane. These results constitute strong support for a (Cu^+ $^\bullet CH_3$) complex. Evidence for a CH_3–metal ion complex in aqueous solution has been presented by Kochi and Rust[13] for Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}. Our present results show for the first time that the lifetime of such a complex may be solvent dependent, being more stable in aprotic solvent (DMSO) than in protic solvent (H_2O).

In pure DMSO we obtain with increasing ascorbic acid concentration an increase in CH_4, but no corresponding decrease in CH_3CH_3. The increase in CH_4 could be due to a hydrogen abstraction reaction (eq 10).

$$^\bullet CH_3 + AH_2 \rightarrow CH_4 + AH^\bullet \qquad (10)$$

If these reactions of Cu^+–O_2 in presence of ascorbic acid are, however, carried out in DMSO–water mixtures, the total yield of CH_3 radicals increases considerably, the CH_4 yield increases many fold, and the CH_3CH_3 yield decreases as expected on the basis of the above mechanism (reactions 8 and 9).

In the Cu^+–ascorbic acid–O_2 system (Tables I–III) the highest yields of CH_3 radicals are obtained at the lowest Cu^+ concentration (Table I). Since in the presence of ascorbic acid the Cu^{2+} is again reduced to Cu^+ we obtain a redox chain. According to Scheme I, we expect to obtain from 0.25 × 10^{-3} mol of Cu^+ a maximum yield of 83 × 10^{-6} mol of CH_3 radicals, while the maximum yield obtained was 333 × 10^{-6} mol of CH_3 radicals (Table I, experiment 6 in O_2 saturated solution).

In all our experiments we observe that upon addition of water the total yield of CH_3 radicals increases. It has been reported by Zuberbühler[7] that the Cu^+–aquo complex is oxidized faster than the $Cu^+(CH_3CN)_4$ complex. We thus expect upon the addition of water an increase in the rate of oxidation and therefore an increase in the steady-state concentration of CH_3 radicals, which in turn should give a higher C_2H_6/CH_4 ratio. This faster rate of oxidation is most likely responsible for the small increase in ethane observed upon addition of small amounts of water (1–2 mL).

Ascorbic acid is known to reduce Cu^{2+} to Cu^+. Therefore, the Cu^{2+}–ascorbic acid–O_2 system should give the same products as the Cu^+–ascorbic acid–O_2 system. Our

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[11] A different situation exists in the reaction of Fenton's reagent with DMSO (ref 5) Fe^{2+} does not reduce CH_3 radicals to CH_4. In presence of oxygen we have to consider the competing reactions i–iii. In this case reaction iii can compete effectively with the slow reactions i and ii.

$$^\bullet CH_3 + CH_3SOOH \rightarrow CH_4 + CH_3SO_2^\bullet \qquad (i)$$

$$^\bullet CH_3 + CH_3SOCH_3 \rightarrow CH_4 + {}^\bullet CH_2SOCH_3 \qquad (ii)$$

$$^\bullet CH_3 + O_2 \rightarrow CH_3O_2^\bullet \qquad (iii)$$

[12] Formation of CH_4 by hydrogen abstraction from DMSO by CH_3 was also postulated by Gollnick and Stracke (Gollnick, K.; Strake, H. V. *Pure Appl. Chem.* **1973**, *33*, 217) in the photolysis of neat DMSO.

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Table V. Effect of Water, O_2, Cu^{2+} Concentration, and H_2SO_4 on the Reaction of Cu^{2+}-Ascorbic Acid-O_2 with DMSO[a]

			products,[b] mol × 10^6			
			air satd		O_2 satd[c]	
expt	H_2O, mL	DMSO, mL	CH_4	CH_3CH_3	CH_4	CH_3CH_3
1	0	25	81	29	31	35
2[d]	0	25	0	0	0	0
3	1	24	129	32	58	54
4	2	23	160	30		
5	5	20	190	12	150	57
6	7	18	186	8		
7	10	15	195	6	204	21
8	15	10	152	5		
9	23	2	55	1		
10	0	25	75	34	45	57
11	1	24	107	35		
12	2	23	120	31		
17	5	20	173	19		
16	7	18	158	12		
15	23	2	56	1		

[a] Experiments 1–9 contained 0.5 × 10^{-3} mol of $CuSO_4$ and 3 × 10^{-3} mol of ascorbic acid; experiments 10–15 contained 1 × 10^{-3} mol of $CuSO_4$ and 3 × 10^{-3} mol of ascorbic acid. [b,c] See corresponding footnotes, Table I. [d] Experiment 2 was identical with experiment 1 except that 0.5 mL concentrated H_2SO_4 was added before addition of ascorbic acid and $CuSO_4$.

results are shown in Table V.

Comparing the two sets of experiments (Table V and Table II, experiments 9–16) we note the same general behavior: a high C_2H_6/CH_4 ratio in pure DMSO and increasing CH_4 and decreasing C_2H_6 yields with increasing water concentration. The most striking difference between these experiments is the effect of H^+. Whereas the Cu^+–O_2 system requires the addition of H_2SO_4 or $HClO_4$ (Table IV) for CH_4 and CH_3CH_3 formation, the addition of these acids completely suppresses product formation in the Cu^{2+}–ascorbic acid–O_2 system (Table V, experiment 2).

The mechanism of the oxidation of ascorbic acid by Cu^{2+} and O_2 has been studied by a number of investigators. All of this work has been summarized by Gampp and Zuberbühler.[14] The mechanism outlined in Scheme II is essentially one proposed by Shtamm et al.[15] The reactions

Scheme II

$$2Cu^{2+} + AH^- \rightarrow 2Cu^+ + A + H^+ \qquad (11)$$

$$Cu^+ + O_2 \rightarrow CuO_2^+ \qquad (12)$$

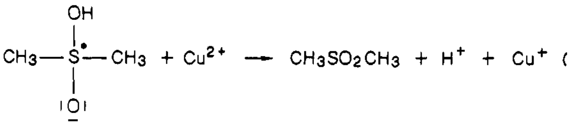
$$CuO_2^+ + AH^- \rightarrow Cu^+ + A + HO_2^- \qquad (13)$$

$$2H^+ + CuO_2^+ + Cu^+ \rightarrow 2Cu^{2+} + H_2O_2 \qquad (14)$$

in Scheme II are followed by eq 15. The pH effect can be explained by the decrease in AH concentration, thus decreasing the rate for reaction 11. At the lowest Cu^{2+} concentration we again obtain the highest yield of CH_3 radicals. With increasing Cu^{2+} the yields of CH_4 and C_2H_6 do not change significantly due to competing oxidation reactions 16 and 17.

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + {}^\bullet OH \qquad (15)$$

$${}^\bullet CH_3 + Cu^{2+} \xrightarrow{H_2O} CH_3OH + H^+ + Cu^+ \qquad (16)$$


$$CH_3-\overset{OH}{\underset{O^-}{S^\bullet}}-CH_3 + Cu^{2+} \longrightarrow CH_3SO_2CH_3 + H^+ + Cu^+ \qquad (17)$$

The mechanism by which metal ion–O_2 systems hydroxylate aromatic compounds has been studied extensively.[2] The marked dependence of phenolic isomer ratios on the initial metal ion concentration has been used as an argument against OH radicals.[16] However, we have shown in a number of studies[17] that the isomer ratio in the hydroxylation of aromatics with OH radicals (produced by γ radiolysis) varies sometimes dramatically depending on the presence of O_2, pH, and oxidizing or reducing metal ions.[18] Nofre et al.,[1b] who first discovered the hydroxylating properties of metal ion–O_2 systems in absence of ascorbic acid, proposed the OH radical as intermediate. The results of Zuberbühler[6,7] on the Cu^+ autoxidation together with our present results with Cu^+–O_2–DMSO support the OH radical hypothesis at least in the Cu^+–O_2 system.

Experimental Section

$Cu(CH_3CN)_4(ClO_4)$ was prepared according to the procedure described by Hemmerich and Sigwart.[19] The reactions were all carried out in 150-mL bottles with rubber septums. The reagents were mixed in 25-mL aqueous DMSO solutions, immediately stoppered, and shaken in a mechanical shaker for 45 min. Analysis of CH_4 and C_2H_6 was carried out by gas chromatography using a 6-ft Carbosieve B (Supelco) stainless steel column at 130 °C. The gas was withdrawn from the bottles with a 1-mL gas-tight syringe.

Calibrations were carried out with Scotty II calibrated gases (Supelco Inc.). All our results represent averages of at least two but mostly three or more determinations with a maximum deviation of ±5%.

Acknowledgment. We thank Dr. Angel A. Román Franco for his interest and support. Financial support from NIH (NIH-MBRS Grant 506-RR 8224-03) is gratefully acknowledged.

Registry No. Cu^+, 17493-86-6; O_2, 7782-44-7; Cu^{2+}, 15158-11-9; CH_4, 74-82-8; C_2H_6, 74-84-0; $(Cu^+ \cdot CH_3)$, 67049-30-3; DMSO, 67-68-5; ascorbic acid, 50-81-7.

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