Table III. Correlation between Experimentally Determined Dihedral Angle θ and ΔI for Cyclic and Bicyclic Peroxides

compd	θ , deg (ref)	ΔI	(ref)	
2a	0-2 (7)	2.3	a	
3a	$14 \pm 2 (7)$	1.8	а	
4a	$44 \pm 2 (7)$	1.2	а	
5	$50 \pm 2^{\circ} (5)$	1.27	2	
6	$80 \pm 2^{\circ} (5)$	< 0.4	5	

^aThis work.

Discussion

Since a rigorous geometry optimization at the 4-31G level was not undertaken, the results remain qualitative in character. Nevertheless the calculations help us to understand the electronic structure of **2b**.

The sequence of the highest occupied MO's of 1b and **2b** can be derived by a simplified perturbation treatment including the highest occupied MO's of the peroxy group $(\pi_{-}, n_{-}, n_{+}, \pi_{+})$ shown in the center of Figure 3 and those of the cyclopentane (left) and cyclohexane fragment (right). Note that the basis orbital energies of the five-membered rings are lower than those of six-membered ring. The main interaction encountered between the ribbon orbitals of the six-membered ring¹⁵ and the peroxy group is that between $a'(\sigma)$ and $a'(\pi_+)$, which leads to a destabilization of the ribbon orbital. In the case of the five-membered ring fragment, $a''(\sigma)$ interacts with $a''(\pi)$ and thus enlarges the gap between $a''(\pi_--\sigma)$ and $a''(n_-)$. The n_+ and n_- MO's of the peroxy moiety do not interact with the ribbon orbitals of proper symmetry of both rings since σ - and n-orbitals are orthogonal to each other.

(15) Hoffmann, R.; Mollère, P. D.; Heilbronner, E. J. Am. Chem. Soc. 1973, 95, 4860.

To provide a firm basis for clarifying the nature of the relationship between the C-O-O-C dihedral angle (θ) and the split (ΔI) of bands in the PE spectrum assigned to ionizations from n₋ and π_- , it is essential to measure PE spectra of peroxides for which the dihedral angle has been determined experimentally. The measured ΔI and experimentally determined θ for **2a-4a** are listed in Table III together with similar data for the two monocyclic peroxides **5** and **6** which, as far as we are aware, are the



only other peroxides for which such information is available. Although a considerable step forward, these data are not yet sufficient to decide whether a $\Delta I/\theta$ or a $\Delta I/(\cos \theta)$ correlation should be used.

Experimental Section

The preparation of the peroxides has been reported elsewhere.⁶ The PE spectra of the pure samples were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer equipped with a He(I) source. All spectra were recorded at room temperature and were calibrated with xenon and argon. A resolution of ± 0.05 eV was achieved for the single bands and of ± 0.1 eV for the shoulders.

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Formation of Olefins from Alkyl Radicals with Leaving Groups in the β -Position

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A reaction of ethanol with Fe^{2+} -ethylenediaminetetraacetate (EDTA)- O_2 to give ethylene is described. This olefin-forming reaction was observed with a wide variety of compounds (alcohols, halides, ethers, acetates, ethyl sulfide, and *N*,*N*-diethylaniline). Olefins were also produced with Cu^+-O_2 in acidic solution and Fe^{2+} -EDTA- H_2O_2 and in some cases with $Fe^{2+}-H_2O_2$. The effect of H^+ , H_2O_2 , EDTA, Fe^{2+} , and O_2 concentrations on olefin formation was investigated. A mechanism involving formation of a β -substituted radical, followed by a simultaneous electron transfer and elimination of the leaving group (reductive elimination) is proposed.

In connection with work on the mechanism of the Fe^{2+} -ethylenediaminetetraacetate (EDTA)-O₂ hydroxylating system we have observed the formation of ethylene in the presence of ethanol. This olefin-forming reaction was found to occur with a wide variety of compounds (alcohols, halides, ethers, acetate, ethyl sulfide, and N,Ndiethylaniline). Olefins were also produced with Cu⁺-O₂¹ in acidic solution and with Fe^{2+} -EDTA-H₂O₂ and in some cases with Fe^{2+} -H₂O₂. In this paper we present the results of these studies and a discussion of the mechanism of this radical induced formation of olefins.

Results and Discussion

We have studied the effect of Fe^{2+} , EDTA, and O_2 concentration on the formation of isobutylene from *tert*butyl alcohol. These results are shown in Table I. The highest yield of isobutylene was obtained with equal amounts of Fe^{2+} and EDTA (10^{-2} M) and in air-saturated aqueous solutions. If the reaction was carried out in oxygen-saturated solution (10^{-3} M) or in argon saturated (deoxygenated) solution the yield of isobutylene decreased considerably. The small amount of isobutylene (25×10^{-6}

re (London) 1964, 204, 343). considerably. The small a

⁽¹⁾ In a similar system (Cu^{2+} -ascorbic acid) the formation of ethylene from ethanol and ethyl ether was noted by Lieberman and Mapson (Lieberman, M.; Mapson, L. W. Nature (London) 1964, 204, 343).

Table I. Effect of Fe^{2+} , EDTA, O_2 , H_2O_2 , pH, and Cu^{2+} Ions on the Formation of Isobutylene from *tert*-Butyl Alcohol

expt	reactants, 10 ² M				produ	ict, ^a 10 ⁶ mol
no.	t-BuOH	Fe ²⁺	EDTA	$soln^b$	H_2O_2	isobutylene
1	5.0	1.0	1.0	air	0	220
2	5.0	2.0	1.0	air	0	220
3	5.0	2.0	2.0	air	0	174
4	5.0	1.0	1.0	O_2	0	44
5	5.0	1.0	1.0	Ar	0	25
6	5.0	0.5	0.5	air	0	108
7	5.0	0.2	0.2	air	0	12
8	5.0	1.0	0.2	air	0	30
9	5.0	1.0	0	air	1.4	trace
10	5.0	2.0	0	air	0.7	trace
11	5.0	1.0	1.0	air	1.4	181
12	5.0	1.0	1.0	air	0.7	215
13	5.0°	1.0	0	air	1.4	trace
14	1.0	1.0	1.0	air	0	89
15	1.0 ^d	1.0	1.0	air	0	1
16	1.0	1.0	1.0	air	1.4	93
17	5.0	1.0	1.0	Ar	0.7	208,° 210'
18	5.0 ^g	1.0	1.0	Ar	0.7	53e
19	5.0	1.0	1.0	Ar	1.4	190,° 190'
20	5.0	1.0	1.0	Ar	0	14,° 25⁄
21	1.0 ^h	1.0	1.0	air	0	64
22	1.0^{i}	1.0	1.0	air	0	0

^a The product was determined after 30 min of reaction time (shaking in a mechanical shaker) unless otherwise indicated. ^bO₂ or Ar was bubbled through 500 mL of a solution of *tert*-butyl alcohol and EDTA for 30 min prior to the addition of the other reagents. Saturation was enhanced by occasional shaking. ^cHClO₄, 7 × 10⁻² M. ^dCu²⁺, 10⁻² M. ^eReaction time 5 min. ^fH₂SO₄, 3.7 × 10⁻² M. ^hH₂SO₄, 10⁻² M.

mol) formed in argon-saturated solution shows that under our experimental conditions (30 min of bubbling argon through 500 mL of aqueous solution under occasional shaking) the argon did not remove all the oxygen. If H_2O_2 is added to an argon saturated solution the yield of isobutylene increased about 8-fold. However, if EDTA was omitted no isobutylene was formed. Similar results were obtained with ethanol (Table III). These results show that for the formation of olefin we require OH radicals (or in the Fe²⁺-EDTA-O₂ system a radical at least closely resembling OH radical in its reactivity): Fe²⁺ + H₂O₂ \rightarrow Fe³⁺ + OH⁻ + ·OH.

The reaction further requires the presence of Fe^{2+} and EDTA. With OH radicals alone, produced by H_2O_2 photolysis no olefin was produced.²

The reactions of alcohols with Fenton's reagent $(Fe^{2+}-H_2O_2)$ was studied by Walling and Kato.³ These authors observed that in the presence of Cu^{2+} , which oxidizes the β -hydroxyethyl radical (HOCH₂CH₂· + Cu²⁺ H_{2Q} ·HOCH₂CH₂CH₂OH + Cu⁺ + H⁺) about 1.8% of ethylene glycol is formed and only about 0.13% of 1,4-butanediol. From these results we can conclude that about 2% of the OH radicals react with ethanol at the β position to produce the β -hydroxyethyl radical. On the basis of this result and considering the following competing reactions,

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^{-\alpha}$$

 $k = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ (ref 4)}$

$$CH_{3}CH_{2}OH + \cdot OH \rightarrow R \cdot + H_{2}O$$

k = 1.8 × 10⁹ M⁻¹ s⁻¹ (ref 4)

EDTA +
$$\cdot$$
OH \rightarrow EDTA \cdot + H₂O
 $k = 2.76 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} (\text{ref 5})$

Table II. Effect of H_2O_2 Concentration on the Formation of Isobutylene from *tert*-Butyl Alcohol by Fe^{2+} -EDTA- H_2O_2

expt no.	H ₂ O ₂ , ^{a,b} 10 ³ M	isobutylene, 10 ⁶ mol	yield, ^c %
1	14	190	8
2	7	190	16
3	4.2	238	33
4	2.8	176	37
5	1.4	132	55
6	1.4	125	52
7	0.7	78	65
8	0.35	43	72

^a tert-Butyl alcohol, 5×10^{-2} M; Fe²⁺, 10^{-2} M; EDTA, 10^{-2} M. ^bA 500-mL solution of tert-butyl alcohol and EDTA was saturated with argon for 30 min. Fe²⁺ was added and then the H₂O₂ solution was injected through a rubber septum and the solution shaken for 5 min. In expt no. 1–5, 10, 5, 3, 2, and 1 mL of 2.5% H₂O₂ solution was injected and in expt no. 6–8, 10, 5, and 2.5 mL of 0.25% H₂O₂ solution was injected. ^c For the calculation of the yield see text.

and assuming the following concentrations, $Fe^{2+} 10^{-2}$ M, EDTA 10^{-2} M, and ethanol 5×10^{-2} M, we can calculate that only 75% of OH radicals react with ethanol. (Because of the small rate constant for $H_2O_2 + OH$ of 2.25×10^7 M⁻¹ s⁻¹ (ref 4) this competing reaction can be ignored.) Only 2% of these OH radicals reacting with ethanol react to give β -hydroxyethyl radical or a total of 1.5%. The results in Table III (expt no. 6) show that 7.0×10^{-3} mol of H_2O_2 give 115 $\times 10^{-6}$ mol of ethylene (1.64%). The conversion of β -hydroxyethyl radicals to ethylene is therefore quantitative.

Since in the Fenton reaction with ethanol the Fe^{2+} is regenerated:

$$CH_3\dot{C}HOH + Fe^{3+} \rightarrow CH_3CHO + H^+ + Fe^{2+}$$

we obtain an increase in ethylene formation with increasing H_2O_2 concentration, even if H_2O_2 is in excess (i.e., all H_2O_2 is decomposed to OH radicals (expt 6 and 7, Table III). On the other hand *tert*-butyl alcohol can yield only β -hydroxy radicals, which according to the results of Walling and Kato³ are not oxidized by Fe^{3+} and thus Fe^{2+} is not regenerated. The yield of isobutylene does not increase if an excess of H_2O_2 is used (Table I, expt 11, 12, 17, and 19, and Table II). As a matter of fact the percentage yield of isobutylene increases with decreasing H_2O_2 concentration. At the lover H_2O_2 concentrations only a small fraction of Fe²⁺ is consumed and thus a high concentration of Fe²⁺ and EDTA is available for reduction of the radical (Table II). The yields were calculated by assuming the above rate constants for the reactions of OH with Fe^{2+} and EDTA and taking $(CH_3)_3COH + OH k = 4.2 \times 10^8 M^{-1}$ s^{-1} (ref 4) and the concentrations used in Table II. From these data we can calculate that about 40% of OH radicals react with tert-butyl alcohol. From these 40% only 86%³ react to give the β -hydroxy radical or a total of 34%.

Walling and Kato³ have shown that the β -hydroxyalkyl radicals produced from ethanol or *tert*-butyl alcohol are not oxidized by Fe³⁺ but are oxidized by Cu²⁺. Our results show that in the presence of Cu²⁺ (CuSO₄ × 5H₂O) the formation of ethylene from ethanol and of isobutylene from *tert*-butyl alcohol is almost completely suppressed (Table I, expt no. 15 and Table III, expt no. 3). Our results clearly show that the β -hydroxyalkyl radicals are the precursors of the olefin:

$$\cdot \mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{OH} \xrightarrow{\mathrm{Fe^{2+}-EDTA}} \mathrm{CH}_{2} \xrightarrow{=} \mathrm{CH}_{2} + \mathrm{OH}^{-1}$$

⁽²⁾ A 1-L solution of 0.1 M H_2O_2 and 0.1 M ethanol irradiated with a medium-pressure Hg lamp for 30 min gave 45×10^{-6} mol of methane and 0.4×10^{-6} mol of ethylene.

⁽³⁾ Walling, C.; Kato, S. J. Am. Chem. Soc. 1971, 93, 4275.

⁽⁴⁾ Dorfman, L. M.; Adams, G. E. Natl. Stand. Ref. Data (U.S. Nat. Bur. Stand.) 1973, NSRDS-NBS 46, 1973.

⁽⁵⁾ Bhattacharyya, S. N.; Kundu, K. P. Int. J. Radiat. Phys. Chem. 1972, 4, 31.

Table III. Effect of Fe²⁺, EDTA, O₂, H₂O₂, pH, and Cu²⁺ lons on the Formation of Ethylene from Ethanol

expt	reactan N	ts," 10" 1			time.	produ	icts, 10 ⁶ mol
no. e	ethanol	EDTA	soln^b	H_2O_2	min	CH_4	CH2=CH2
1	1.0	1.0	air	0	30	0.3	17
2	5.0	1.0	air	0	5	0.4	17
					15	0.4	32
					30	0.5	45
3	5.0^{c}	1.0	air	0	30	0.2	0
4	5.0	0	air	1.4	5	10	0.3
5	5.0	0	Ar	0.7	5	7.5	0
6	5.0	1.0	Ar	1.4	5	trace	115
					30	trace	115
7	5.0	1.0	Ar	0.7	5	trace	60
					30	trace	62
8	5.0	1.0	Ar	0	30	trace	3.6
9	5.0^{d}	0	Ar	0.7	5	3.6	0
10	5.0	1.0	Ar	0.7	5	trace	57
11	5.0^{e}	1.0	Ar	0.7	5	trace	66
12	5.0^{f}	1.0	Ar	0.7	5	trace	56
13	5.0^{g}	1.0	Ar	0.7	5	trace	41
14	5.0	1.0	air	0	30	0.5	47
15	5.0^{e}	1.0	air	0	30	0	27
16	5.0^{f}	1.0	air	0	30	0	0

^a All experiments were 10^{-2} M in Fe²⁺. ^b See foot note b, Table I. c Cu²⁺, 10^{-2} M. ^d HClO₄, 7×10^{-2} M. ^eH₂SO₄, 1.84×10^{-2} M. f H₂SO₄, 3.7×10^{-2} M. ^fH₂SO₄, 5.5×10^{-2} M.

For the mechanism of this reaction we may consider the following possibilities:

(1) homolytic β -cleavage

$$\cdot CH_2CH_2OH \rightarrow CH_2 = CH_2 + \cdot OH$$

(2) heterolytic β -cleavage, followed by reduction

(3) reduction to an anion, followed by elimination of OH-

$$CH_2CH_2OH \rightarrow CH_2CH_2OH \rightarrow CH_2=CH_2 + OH^-$$

(4) concerted electron transfer and elimination (reductive elimination)

 $\cdot CH_2CH_2OH \rightarrow CH_2 = CH_2 + OH^-$

We can eliminate the first possibility by considering our photolysis results.² In the photolysis of H_2O_2 in aqueous ethanol we observe only the formation of methane and no ethylene.² The methane is formed via hydrogen abstraction from the OH group:

$$CH_{3}CH_{2}OH + \cdot OH \rightarrow CH_{3}CH_{2}O \cdot \rightarrow CH_{2}O + CH_{3} \cdot \rightarrow CH_{3}O + CH_{3} \cdot \rightarrow CH_{3}O + CH_{3}O +$$

In addition the reaction of Fe²⁺ and H₂O₂ with ethanol or *tert*-butyl alcohol did not produce any olefin. (Table I, expt no. 9 and 10 and Table III, expt no. 4 and 5). The homolytic β -elimination from β -hydroxyethyl radical requires a high activation energy ($E_{\rm a} \sim 33 \text{ kcal/mol}^6$ Homolytic β -cleavage however is a possibility in the case of β -halogenated alkyl radicals.⁷ Such reactions have been observed under other circumstances, particularly with β -bromoalkyl radicals.⁸

Our results with alkyl bromides and alkyl chlorides (Tables IV and V) show that olefins are formed with Fe^{2+}

Table IV. Effect of Fe²⁺, EDTA, O₂, H₂O₂, and pH on the Formation of Ethylene from Ethyl Bromide

expt	reactants, ^{a,b} 10 ² M				time.	CH_=CH_
no.	Fe	EDTA	solutn	H_2O_2	min	10 ⁶ mol
1	1.0	1.0	air	0	30	82
2	1.0	0	Ar	0.7	5	90
3	1.0	0	Ar	1.4	5	82
4	1.0	1.0	Ar	0.7	5	114
5	1.0	1.0	Ar	1.4	5	106
6	1.0	1.0	Ar	0	30	3
7	0.5	1.0	Ar	0.7	5	111
8	0.25	1.0	Ar	0.7	5	77
9	1.0	0	Ar	0.7	5	92
10	1.0^{c}	0	Ar	0.7	5	95
11	1.0^{d}	0	Ar	0.7	5	92
12	1.0^{e}	0	Ar	0.7	5	92

°A 500-mL solution containing EDTA or H_2SO_4 was saturated with argon for 30 min. Then Fe²⁺ and CH₃CH₂Br were added and finally a 2.5% H₂O₂ solution was injected through a rubber septum. ^bCH₃CH₃Br, 10⁻² M. ^cH₂SO₄, 1.84 × 10⁻² M. ^dH₂SO₄, 3.7 × 10⁻² M. ^eH₂SO₄, 5.5 × 10⁻² M.

Table V. Effect of Fe^{2+} , EDTA, O_2 , and H_2O_2 on the Formation of Propene from 1-Chloropropane and 1- and 2-Bromopropane

expt	reactar 1	nts,° 10² M			CH ₄ CH=CH ₂ , ^b
no.	halide	EDTA	soln	H_2O_2	10 ⁶ M
1	1.0 ^e	1.0	air	0	53
2	1.0^{e}	0	air	1.4	78
3	1.0^{e}	1.0	air	1.4	65
4	1.0^{\prime}	1.0	air	0	165
5	1.0^{f}	0	air	1.4	154, ^c 154
6	1.0^{f}	1.0	Ar	1.4	165
7	1.0^{g}	1.0	air	0	43,° 100
8	1.0^{g}	0	air	1.4	56,° 62
9	1.0^{g}	1.0	air	1.4	80,° 84
10	1.0 ^d ,g	0	air	1.4	82, ^c 80

^a All experiments were 10^{-2} M in Fe²⁺. ^b Analyzed after 30 min reaction time, unless stated otherwise. ^c Analyzed after 5 min. ^d H₂SO₄, 5 × 10^{-2} M. ^e CH₃CH₂CH₂Cl. ^f CH₃CH₂CH₂Br. ^g (CH₃)₂CHBr.

Scheme I





and H_2O_2 in absence of EDTA. This could be due to a homolytic β -cleavage:

$$\cdot CH_2CH_2Br \rightarrow CH_2=CH_2 + Br \cdot$$

Recent results by Schulte-Frohlinde and co-workers,⁹ however, have clearly shown that in aqueous solutions no

⁽⁶⁾ Calculated from D ((R)-OH) for ethanol (-91 Kcal/mol) and the π bond energy for ethylene (58 Kcal/mol).

⁽⁷⁾ An activation energy for the homolytic cleavage of the β -bromoethyl radical has been determined by Barker and Maccoll to be about 7.4 Kcal/mol (Barker, R.; Maccoll, A. J. Chem. Soc. 1963, 2839).

<sup>Kcal/mol (Barker, R.; Maccoll, A. J. Chem. Soc. 1963, 2839).
(8) Nonhebel, D. C., Walton, J. C., Eds. "Free Radical Chemistry";</sup> University Press: Cambridge, 1974; pp 472-475.

⁽⁹⁾ Koltzenburg, G.; Behrens, G.; Schulte-Frohlinde, D. J. Am. Chem. Soc. 1982, 104, 7311. These authors studied the pulse radiolysis of alkyl halides in aqueous solutions in the presence of N₂O. Under these conditions OH radicals are the only reactive intermediates. No olefin formation was observed. This example demonstrates the superiority of the radiolysis method for OH generation over the chemical method (Fenton's reagent), which besides OH radicals have a variety of other species present, thus complicating the mechanistic interpretation. The half-lives of the alkene radical cations (if formed at all) has been estimated to be shorter than 10^{-10} s in aqueous solution.

Table VI. Formation of Ethylene from Ethanol by Cu⁺-HClO₄-O₂

		produ	cts, ^b 10 ⁶ mol
expt no.	HClO_4 , ^a $10^2 \mathrm{M}$	CH4	CH2=CH2
1	0	0	0
2	1.4	6	80
3	2.8	4	92
4	4.2	3	95
5	7.0	3	96
6	14	4	80

^a Ethanol, 5×10^{-2} M; Cu⁺, 10^{-2} M, air saturated (not deairated). ^b Analyzed after 30 min reaction time.

such β -cleavage is taking place, but that instead a rapid hydrolysis to the β -hydroxyalkyl radical occurs, possibly via a radical cation intermediate.⁹ These reactions are shown in Scheme I. If the radical cation is a distinct intermediate we would expect olefin formation with $Fe^{2+}-H_2O_2$ from alcohols as well as from alkyl halides. The formation of olefin from alcohols however requires Fe^{2+} -EDTA. This result is inconsistent with the idea of a common intermediate in the two reactions.

Examples of heterolytic β -cleavage have been reported. Walling and Johnson¹⁰ have shown that hydroxycyclohexadienyl radicals undergo acid-catalyzed dehydration to a benzene radical cation. It has further been demonstrated that the acid-catalyzed isomerization of methylhydroxycyclohexadienyl radicals involves radical cation intermediates.^{11,12} In an aliphatic system the isomerization of β -hydroxyalkyl radicals involving radical cation intermediates was described by Gilbert et al.¹³ This isomerization however was observed only at very low pH (pH of 0).

Reductions of radicals by Cr²⁺ have been reported for alkyl radicals 14,15 and by $\rm Fe^{2+}$ for radicals with a $\rm NO_2$ group¹⁶ or a carbonyl group¹⁷ in the α -position. However the mechanism involving reduction followed by elimination of an anion may be rejected for the following reasons. The formation of a carbanion as a distinct intermediate¹⁸ in aqueous solutions would certainly lead to protonation back to starting materials:



Our results with ethanol have shown a quantitative conversion of the β -hydroxyethyl radical to ethylene (see above). In addition in the reaction of ethanol with Fe^{2+} -EDTA- H_2O_2 only a small effect of pH (Table III, expt no. 10-13) and in the reaction of ethyl bromide with $Fe^{2+}-H_2O_2$ no pH effect was observed (Table IV, expt no. 9-12). Furthermore in the reaction of isopropyl bromide with $Fe^{2+}-H_2O_2$ the pH had no effect on the yield of propene (Table V, expt no. 8–10). The reactions of Cu^+-O_2

Table VII. Formation of Isobutylene from tert-Butyl Alcohol by Cu⁺-HClO₄-O₂ and Cu⁺-HClO₄-H₂O₂

expt no.	HClO ₄ , ^a 10 ² M	soln	H_2O_2	isobutylene, ^b 10 ⁶ mol
1	0	air	0	0
2	0.7	air	0	195
3	1.4	air	0	240
4	2.8	air	0	230
5	14	air	0	200
6	2.8	Ar	0.7	294
7	2.8	Ar	0	trace

^a tert-Butyl alcohol, 5×10^{-2} M; Cu⁺, 10^{-2} M. ^b Analyzed after 30 min reaction time.

Table VIII. Formation of Olefins from a Variety of Compounds by Fe²⁺-EDTA-O₂

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reactants ^a (in M)	products (mol \times 10 ⁶)
2-propanol (10^{-2})	propylene (57)
ethyl acetate (10^{-2})	ethylene (29)
tert-butyl acetate (10^{-2})	isobutylene (23)
diethyl ether (10^{-2})	ethylene (14)
n-propyl acetate (10^{-2})	propylene (19)
ethyl trifluoroacetate (10^{-2})	ethylene (19)
N,N-diethylaniline (10^{-2})	ethylene (9)

^aAll experiments were carried out in 500 mL of nondeoxygenated water containing 10⁻² M EDTA. To this solution was added the organic compound and finally Fe²⁺ to make the solution 10^{-2} M in Fe²⁺. Products were analyzed after 30 min reaction time (shaking in a mechanical shaker).

with ethanol and tert-butyl alcohol at different HClO₄ concentrations did not show any significant effect (Tables VI and VII). From these results we conclude that the reduction and the anion elimination proceed in a synchronous fashion:

$$\cdot \mathrm{CH}_{2}\mathrm{CH}_{2}^{\delta +} \to \mathrm{OH}^{\delta -} \xrightarrow{\mathrm{Fe}^{2^{+}} - \mathrm{EDTA}} \mathrm{CH}_{2} = \mathrm{CH}_{2} + \mathrm{OH}^{-}$$
$$\cdot \mathrm{CH}_{2}\mathrm{CH}_{2}^{\delta +} \to \mathrm{Br}^{\delta -} \xrightarrow{\mathrm{Fe}^{2^{+}}} \mathrm{CH}_{2} = \mathrm{CH}_{2} + \mathrm{Br}^{-}$$

We would like to call this reaction reductive elimination¹⁹ in analogy to oxidative elimination. The reaction depends on the energy level of the singly occupied molecular orbital (SOMO) and on the leaving group. Br⁻ or Cl⁻ are less nucleophilic than OH⁻ and are better leaving groups. The β -halogenated ethyl radicals are thus reduced to the olefins by the less efficient Fe^{2+} , whereas reduction of the β -hydroxyethyl radicals requires the greater reducing power of Fe^{2+} -EDTA (redox potential $E_0 = -0.12$ at pH 7 vs. E_0 = -0.77 for Fe²⁺).²⁰ The radical cation may be preformed in the transition state, but will not be a free distinct intermediate for the reasons already discussed. In the β halogenated alkyl radicals the rate of reductive elimination by Fe²⁺ must be faster than the rate of hydrolysis to the β -hydroxyalkyl radicals, since olefin formation from these latter radicals require both Fe²⁺ and EDTA. This competition between hydrolysis and reductive elimination may be responsible for the somewhat lower yields of ethylene from ethyl bromide in the absence of EDTA (Table IV, expt 4 and 9). β -halogenated alkyl radicals have been invoked as intermediates in the Cr^{2+} induced dehalogen-ation of vicinal dihalides.^{21,22} However efforts to scavenge

⁽¹⁰⁾ Walling, C.; Johnson, R. A. J. Am. Chem. Soc. 1975, 97, 363 and references cited therein.

 ⁽¹¹⁾ Eberhardt, M. K. J. Org. Chem. 1977, 42, 832.
 (12) Walling, C.; Camaioni, D. M. J. Am. Chem. Soc. 1975, 97, 1603.
 (13) Gilbert, B. C.; Norman, R. O. C.; Williams, P. S. J. Chem. Soc. (15) Gilbert, B. C., Forman, R. G. C., Williams, F. G. C. Stern, 2011
(14) Castro, C. E., Kray, W. C., Jr. J. Am. Chem. Soc. 1963, 85, 2768.
(15) Kochi, J. K.; Mocadlo, P. E. J. Org. Chem. 1965, 30, 1134.
(16) Eberhardt, M. K. J. Phys. Chem. 1975, 79, 1913.
(17) William G. D. T. Thilting, C. M. J. Am. Chem. Soc. 1972, 95, 844.

⁽¹⁷⁾ Walling, C.; El-Taliawi, G. M. J. Am. Chem. Soc. 1973, 95, 844.

⁽¹⁸⁾ Carbanions may however be distinct intermediates in special cases where these anions are stabilized by resonance like in the conversion of maleic acid to malic acid by $Fe^{2+}-H_2O_2$ observed by Walling and Taliawi (ref 17).

⁽¹⁹⁾ The term reductive elimination was used by Kochi and Mocadlo (ref 15) to describe a variety of elimination reactions from vicinal dihalides, halo esters, halo hydrins, and halo amines by Cr²⁺, Zn, Mg, Na, and I⁻.

⁽²⁰⁾ Dearden, M. B.; Jefcoate, C. R. E.; Lindsay Smith, J. R.
"Oxidation of Organic Compounds III"; Gould, R. F., Ed.; American Chemical Society: Washington, D.C., 1968; Vol. 77, pp 260-278.
(21) Kray, W., Jr.; Castro, C. J. Am. Chem. Soc. 1964, 86, 4603.

Table IX. Effect of Fe²⁺, EDTA, and H₂O₂ on the Formation of Ethylene and Ethane from Ethyl Sulfide

	EDTA.ª		reactn	products, 10 ⁶ mol		
expt no.	10 ² M	H_2O_2	time, min	$\overline{CH_2}=CH_2$	CH ₃ CH ₃	
1	1.0	0	30	23	trace	
2	0	1.4	5	59	51	
3	0	1.4	30	62	59	
4	1.0	1.4	5	48	6	
5^b	0	1.4	30	66	40	

^a $(C_2H_5)_2S$, 10^{-2} M; Fe²⁺, 10^{-2} M; air saturated (not deairated). ^bContains 5 × 10⁻² M, H₂SO₄.

these intermediate radicals have been unsuccessful.²²

While in the reaction of ethanol with Fe^{2+} -EDTA-H₂O₂ no pH effect was observed, a considerable effect was observed in the reaction with Fe²⁺-EDTA-O₂ (Table III, expt no. 14-16). We suggest that this difference is due to a slower rate of formation of the hydroxylating species at lower pH, thus leading to a decrease in the formation of β -hydroxyethyl radicals.

In addition to alcohols and halides we have examined the reactions of a number of other compounds with Fe^{2+} -EDTA-O₂. These results are summarized in Table VIII. In the reaction of Fe^{2+} -EDTA-O₂ with ethyl acetate no methane was produced. This result confirms the idea that no homolytic β -cleavage is taking place.

The reactions of ethyl sulfide were studied with Fe²⁺-EDTA- O_2 and with Fenton's reagent in the presence and in the absence of EDTA. In all cases we observed ethylene formation (Table IX). In addition we found in the reaction with Fenton's reagent ethane. The ethane yield decreased considerably in presence of EDTA. We suggest that following reactions:

CH3CH2SCH2CH3 + •OH - •CH2CH2SC2H5 + CH3CHSC2H5



 C_2H_6 $CH_3CHO + HSC_2H_5$

 Fe^{3+} -EDTA is a stronger oxidizing agent than Fe^{3+} . It oxidizes the precursor of the ethyl radicals and thus decreases the ethane yield. The formation of ethylene from the β -(ethylthio)ethyl radical may in this case also proceed via homolytic β -cleavage. This type of cleavage has been proposed by Pryor and Tang²³ in the mechanism of ethylene formation from methional and OH radicals in aqueous solutions at 40 °C. These authors produced OH radicals via Fenton's reagent ($Fe^{2+}-H_2O_2$). In the presence of Fe²⁺ ethylene may also be produced by reductive elimination:

$$\cdot CH_2 CH_2 SC_2H_5 \longrightarrow CH_2 == CH_2 + C_2H_5 S$$

$$\downarrow Fe^{2+}$$

$$CH_2 == CH_0 + C_2H_5 S^- + Fe^{3+}$$

It is guite possible that in this case both pathways are operating and that their relative importance depends on temperature (high temperature favoring homolytic cleavage) and Fe^{2+} concentration (high Fe^{2+} concentration and low temperature favoring reductive elimination). Still another mechanistic pathway may involve radical cations, which have been deduced by ESR spectroscopy^{24,25} in the reaction of OH radicals with some substituted sulfides and by pulse radiolysis.²⁶ The mechanism of ethylene formation from ethyl sulfide may thus be rather complex and its elucidation is beyond the scope of the present investigation.

In conclusion we can state that a number of alkyl radicals with leaving groups in the β -position react with Fe^{2+} -EDTA, Fe^{2+} , or Cu⁺ in acidic solution by *reductive* elimination to yield olefins. Radical cations may however be involved in the reduction of other β -hydroxy radicals like hydroxycyclohexadienyl radicals, which are known to undergo acid-catalyzed heterolytic cleavage to a radical cation.10

$$\begin{array}{c} H \\ \hline (\cdot) \\ \hline (\cdot) \\ \end{array} + H^{+} = \begin{array}{c} \hline (\cdot) \\ \hline (\cdot) \\ \end{array} + H_{2} 0 \end{array}$$

Heterolytic β -cleavage is favored in this case because of the greater stability of the aromatic radical cation as compared to an aliphatic radical cation. In the reaction of Fe^{2+} with the o- and p-OH adducts to nitrobenzene however, where nitrobenzene radical cation formation is unfavorable,^{16,27} the reduction possibly follows the reductive elimination pathway.

Experimental Section

All reagents used were of highest available purity. Water was deionized and distilled twice.

Reactions with Fe²⁺-EDTA-O₂. Deionized and twice distilled water (500 mL) containing ethylenediaminetetraacetate disodium salt (EDTA) was placed in a 700-mL bottle. The appropriate amount of organic compound was added and the solution was shaken if required to dissolve the organic compound. Then 1.96 g of $FeSO_4(NH_4)_2SO_4\cdot 6H_2O(10^{-2} \text{ M})$ was added at once and the bottle was stoppered and shaken for 30 min in an automatic shaker. After this time the product yield had reached its maximum. Gas samples were withdrawn with a 2-mL gas-tight syringe and analyzed in a gas chromatograph. For the analysis of methane, ethylene, and ethane we used a 6 ft Carbosieve B column (Supelco, Inc.) at a temperature of 130 °C and a flow of 30 mL of He/min. The gases appeared in the following sequence: methane 1 min, ethylene 6 min, and ethane 10 min. For the analysis of propylene and isobutylene we used a 2 m 80/100 CarbopakC/0.19% picric acid column (Supelco) at 50 °C and a flow of 15 mL of He/min. The retention times were propylene 2.3 min and isobutylene 8 min. Calibrations were carried out with known gas mixtures.

Reactions with $Fe^{2+}-H_2O_2$ (with or without EDTA). To a 500-mL solution of water containing EDTA or no EDTA was added the organic compound and Fe²⁺. Then the bottle was stoppered and 10 mL of 2.5% H_2O_2 (1.4 × 10⁻² M) or 5 mL of 2.5% H_2O_2 (0.7 × 10⁻² M) was injected into the bottle with a syringe. The bottle was shaken for 5 min and gas samples were withdrawn and analyzed as described above. The reaction was finished after 5 min. A very rapid color change can be observed upon addition of H_2O_2 .

Reactions with $\tilde{C}\tilde{u}^+-O_2$ in Acidic Solutions. To 500 mL of water containing different concentrations of HClO₄ was added ethanol (5 × 10^{-2} M). Then 600 mg of CuOCOCH₃ was added and the bottle stopperd and shaken for 30 min.

⁽²²⁾ Singleton, D. M.; Kochi, J. K. J. Am. Chem. Soc. 1967, 89, 6547. (23) Pryor, W. A.; Tang, R. H. Biochem. Biophys. Res. Commun. 1978, 81 498

⁽²⁴⁾ Gilbert, B. C.; Larkin, J. P.; Norman, R. O. C. J. Chem. Soc. Perkin Trans. 2 1973, 272.

⁽²⁵⁾ Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. J. Chem. Soc. Perkin Trans. 2 1973, 1748. (26) Bors, W.; Lengfelder, E.; Saran, M.; Fuchs, C.; Michel, C. Bio-

chem. Biophys. Res. Commun. 1976, 70, 81.
 (27) Shevchuk, L. G.; Vysotskaya, N. A. Zh. Org. Khim. 1968, 4, 1936.

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Registry No. EDTA, 60-00-4; EDTA-2Na, 139-33-3; Fe²⁺. 15438-31-0; O₂, 7782-44-7; H₂O₂, 7722-84-1; Cu²⁺, 15158-11-9; CH₄, 74-82-8; HClO₄, 7601-90-3; H₂SO₄, 7664-93-9; FeSO₄(NH₄)₂SO₄, 10045-89-3; CuOCOCH₃, 598-54-9; Cu⁺, 17493-86-6; tert-butyl alcohol, 75-65-0; ethanol, 64-17-5; ethyl bromide, 74-96-4; 1chloropropane, 540-54-5; 1-bromopropane, 106-94-5; 2-bromopropane, 75-26-3; ethyl sulfide, 352-93-2; 2-propanol, 67-63-0; ethyl acetate, 141-78-6; tert-butyl acetate, 540-88-5; diethyl ether, 60-29-7; n-propyl acetate, 109-60-4; ethyl trifluoroacetate, 383-63-1; N,N-diethylaniline, 91-66-7; propylene, 115-07-1; ethylene, 74-85-1; isobutylene, 115-11-7; ethane, 74-84-0.

A ¹³C¹³C Spin-Spin Coupling Matrix for Azulene

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All resolvable ¹³C¹³C spin-spin coupling constants in 1-methylazulene (2) and 5-methylazulene (3) have been measured by the 2D-INADEQUATE technique in natural abundance. The data are compared with the results of various ¹³C-labeled azulenes and it is shown that the ¹³C¹³C spin-spin coupling constants are quite different from those in the naphthalene system.

¹³C¹³C spin-spin coupling constants can provide a detailed picture of the electronic framework of a molecule.¹ In our earlier work on ¹³C¹³C spin-spin coupling constants in azulenes,^{2,3} we have labeled various substituted and unsubstituted azulenes 1 with one or two ¹³C atoms to



enable the determination of ¹³C¹³C spin-spin coupling constants in these nonalternate aromatic compounds with respect to the labeled center.

Although considerable synthetic effort has been spent during this project, a complete description of the spin-spin coupling matrix could not be achieved. Especially the most interesting spin-spin coupling constant of the central bond between C-9 and C-10 is still missing.

With the publication of the INADEQUATE technique^{4a} in its two-dimensional version,4b it is now possible to measure these values in natural abundance. We have shown that nearly all theoretically possible spin-spin coupling constants in naphthalenes can be obtained by this technique, including the small values over two and three bonds.⁵ In this paper, we have extended these studies to 1-methylazulene (2) and 5-methylazulene (3) in order to compare



the values of these molecules with the data of the labeled compounds of our earlier work. Furthermore, a comparison of the magnetic frameworks of the azulene and the naphthalene system is given.

Results and Discussion

The ¹³C¹³C spin-spin coupling constants measured in this work are given in Table I; included are the values from partially unpublished labeling studies. For azulene itself the data originate from 4-, 4,7-, and 6-13C-labeled azulene 1 as well as from 1D-INADEQUATE measurements. The data for 4-methylazulene (4) have been obtained from the $4-^{13}C$



compound, the data for 1-phenylazulene (5) from the 1-, the 3-, and the 4-13C-labeled compound and the data for 2-phenylazulene 6 from the 2-¹³C-labeled compound. The 2D-INADEQUATE spectra of 2 and 3 confirm nicely the chemical shift assignment given by Braun.⁶

By comparing the data in the vertical columns of Table I, it becomes evident that the chosen substituents, the phenyl and methyl group, do not have a pronounced effect

⁽¹⁾ For an authorative recent review, see: Marshall, J. L. In "Methods of Stereochemical Analysis"; Marchand, A. P., Ed.; Verlag Chemie International: Deerfield Beach, FL,; Vol. 2, pp 1-241.

Berger, S.; Zeller, K. P. Tetrahedron 1980, 36, 1891-1893.
 Zeller, K. P.; Berger, S. Z. Naturforsch. B: Anorg. Chem., Org. Chem. 1981, 36B, 858-864.

^{(4) (}a) Bax, A.; Freeman, R.; Kempsell, S. P. J. Am. Chem. Soc. 1980, 102, 4849-4851. (b) Mareci, T. H.; Freeman, R. J. Magn. Reson. 1982, 48, 158-163.

⁽⁵⁾ Berger, S. Org. Magn. Reson. 1984, 22, 47-51.

⁽⁶⁾ Braun, S.; Kinkeldei, J. Tetrahedron 1977, 33, 1827-1832.