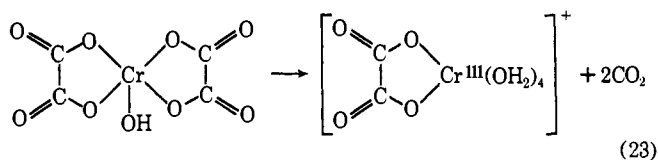
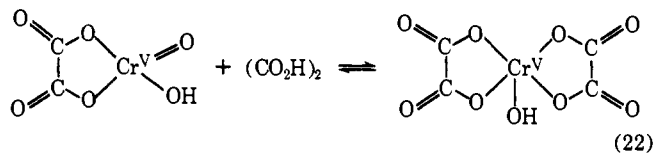
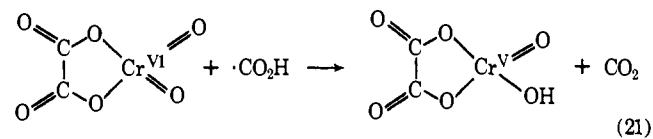


Scheme IV



reactivity of chromium(V) to chromium(VI) with respect to oxalic acid.

The independence of the ratio of k_2/k_1 indicates that the oxidation of oxalic acid by both chromium(VI) and chromium(V) follows the same kinetic dependence on the oxalic acid and hydrogen ion concentration. As the oxidation of oxalic acid within the region studied in this work is second order in oxalic acid,⁸ it follows that the same order can be assumed for the chromium(V) oxidation, which leads to the conclusion that the chromium-

(V) oxidation of oxalic acid proceeds through a dioxyato complex of chromium(V). This conclusion is in full agreement with earlier observations that around 50% of chromium(III) produced during the reaction contains oxalic ligands.^{8,10} The main reaction involving chromium(V) and taking place during the chromic acid oxidation of oxalic acid can be tentatively summarized in Scheme IV.

The results of our study thus indicate that the mono-oxalato complex of chromium(V) is relatively stable and is responsible for the accumulation of chromium(V) during the chromic acid oxidation of oxalic acid. Further reduction of chromium(V) to chromium(III) seems to occur only after a second molecule of oxalic acid enters the complex.

Acknowledgments. The authors acknowledge the assistance received from Dr. David J. Goon in devising the computer programs used in this work and from Professor Robert N. Schwartz in applying the esr technique to kinetic study. Helpful comments from Professors Robert Walter and Robert N. Schwartz, University of Illinois at Chicago Circle, and Dr. Matiur Rahman of Tee-Pak, Inc., Danville, Ill., are gratefully acknowledged. We are particularly grateful to Drs. Fariza Hansan and George F. Vandegrift for carrying out several crucial experiments and for their help in the preparation of this manuscript.

Fenton's Reagent. IV. Structure and Reactivity Relations in the Reactions of Hydroxyl Radicals and the Redox Reactions of Radicals¹

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Abstract: Reactivities of a variety of alcohols, ethers, and amides toward hydroxyl radicals have been examined. Results are in encouraging agreement with radiation chemistry results. Reactivities of different C-H bonds have been dissected from the data and indicate that the hydroxyl radical is a strongly electrophilic species, so that electron supply is more important than C-H bond strength in determining reactivity. Comparison with gas-phase data shows similar reactivity patterns, but considerably faster reactions in H₂O. Radicals α to -OH, -OR, and amide N are readily oxidized by Fe³⁺; *tert*-alkyl radicals are oxidized with more difficulty and allyl radicals hardly at all. In contrast, radicals RC(OH)CCl₃ are reduced by Fe²⁺. Results are consistent with a fast oxidation of easily oxidized radicals by Fe³⁺ via electron transfer, and a slower more general oxidation of radicals by Cu²⁺ via a RCu(III) intermediate.

In a series of recent papers^{2,3} we have described a re-examination of the reaction of Fenton's reagent, Fe²⁺-H₂O₂, with a variety of organic substrates. This paper reports results with some additional substrates and summarizes our conclusions, comparing our results with hydroxyl radical reactivity data obtained

from radiation chemistry, and data on the oxidation and reduction of radicals by metal ions (Cu²⁺, Fe³⁺, and Fe²⁺) obtained by other techniques.

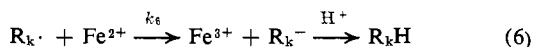
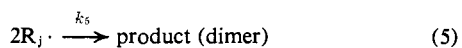
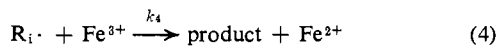
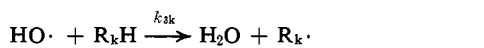
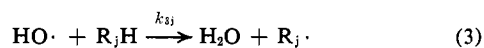
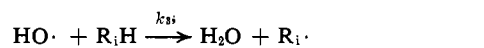
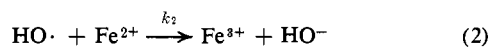
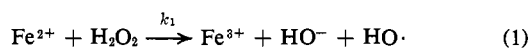
The basis of our approach is that, if H₂O₂ is added to an aqueous system containing an organic substrate and excess Fe²⁺ at pH 0-2, the hydroxyl radicals generated attack the substrate and the subsequent course of the reaction and stoichiometry (moles of Fe²⁺ oxidized/mole of H₂O₂ added, $\Delta[\text{Fe}^{2+}]/\Delta[\text{H}_2\text{O}_2]$) depend upon the fate of the organic radicals so pro-

(1) Support of this work by a grant from the National Science Foundation is gratefully acknowledged (Grants No. GP36620X and GP-24300).

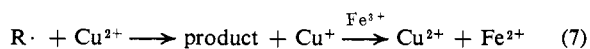
(2) C. Walling and S. Kato, *J. Amer. Chem. Soc.*, **93**, 4275 (1971).

(3) C. Walling and G. M. El-Taliawi, *ibid.*, **95**, 844, 848 (1973).

duced. For a system containing a variety of C-H bonds the postulated reaction steps are²



In the case of unsaturated molecules (3) may also represent stoichiometrically equivalent addition reactions, but in either case it is assumed that under our conditions, the resulting radicals belong to three distinct classes: those oxidized by Fe^{3+} , $\text{R}_i\cdot$; those which are inert and dimerize $\text{R}_j\cdot$; and those which undergo reduction by Fe^{2+} , $\text{R}_k\cdot$. Simple alkyl radicals, such as arise by hydroxyl radical attack on β -methyl groups of alcohols, are inert toward both Fe^{2+} and Fe^{3+} , but addition of Cu^{2+} makes them oxidizable as well *via* the sequence



Thus the effect of added Cu^{2+} on the Fenton's reagent system provides a useful tool for its analysis.

With a single substrate, reactions 1-6 lead to the rectified stoichiometric equation

$$R = 2ar(1 - R) + b \quad (8)$$

where $R = \Delta[\text{Fe}^{2+}]/2\Delta[\text{H}_2\text{O}_2]$, the ratio of equivalents of Fe^{2+} oxidized to H_2O_2 reacted or reciprocal of the kinetic chain length, $r = [\text{Fe}^{2+}]/2[\text{RH}]$, $a = k_2/\Sigma k_3's$, and $b = (k_{3j} + 2k_{3k})/2\Sigma k_3's$. From (8), a plot of R vs. $r(1 - R)$ for a set of experiments in which r is varied and R measured should be linear with slope and intercept yielding a and b , respectively. In our previous papers we have shown that (8) is generally obeyed, and it provides the basis for our analysis of additional systems here.⁴

Results

Alcohols. Since our previously reported value of k_3/k_2 for methanol, 4.30, was appreciably higher than that derived from radiation chemistry measurements, and since we have frequently used methanol as a competitive standard in other reactions,³ we have re-examined this substrate in more detail (Table I). Seven independent series of experiments at initial Fe^{2+} concentrations at 0.0078-0.0391 M , plotted according to (8), yield $a = 0.248 \pm 0.005$, $b = 0.004 \pm 0.001$, the uncertainties being standard errors of the means. Included in the series were three sets, one followed by iodometric rather than dichromate titration, a second containing added Fe^{3+} , and the third 0.50 M

(4) Although (8) is the most convenient form for treatment and visual presentation of data, solution for $1/R$ and nonlinear curve fitting to determine a and b give a better weighting of experimental error, and have often been used in our analyses here.

Table I. Reaction of Methanol with Fe^{2+} - H_2O_2

[Fe^{2+}], M	Additive (M)	a	b	n^a	r^b
0.0391		0.245	0.006	7	0.999
0.0198		0.260	0.006	9	0.998
0.0148		0.236	0.002	3	0.999
0.0078		0.241	0.003	7	0.999
0.0272		0.237	0.010	6	0.996
0.0196	Fe^{3+} (0.0178)	0.269	-0.002	6	0.988
0.0198	NaClO_4 (0.50)	0.249	0.005	8	0.999
0.0148	Cu^{2+} (0.004)	0.273	-0.004	4	0.997
0.021	Cu^{2+} (0.02)	0.271	0.004	4	0.999
0.0148	Cu^{2+} (0.04)	0.361	0.000	4	0.998
0.0148	Cu^{2+} (0.04)	0.373	-0.004	4	0.999
0.021	Cu^{2+} (0.04)	0.351	-0.001	4	0.999
0.021	Cu^{2+} (0.08)	0.442	-0.001	4	0.999
0.0148	Cu^{2+} (0.04) Fe^{3+} (0.02)	0.329	0.001	4	0.998

^a Number of experimental points, at varying $\text{Fe}^{2+}/\text{MeOH}$ ratios.

^b Correlation coefficient.

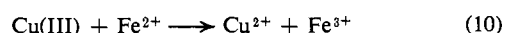
NaClO_4 to increase the ionic strength. None showed any significant effect on the plots. From these data, $k_3/k_2 = 4.03 \pm 0.08$, slightly lower than our previous value, but still larger than the radiation results, a discrepancy discussed further below.

In addition, we have also examined further the effect of added Cu^{2+} on the reaction stoichiometry. We now find that, at higher concentrations, Cu^{2+} gives a significant decrease in slope of our plots of (8), although they remain linear and yield the same intercepts. In retrospect, such an effect would be expected from radiation data. Baxendale⁵ has reported that Cu^{2+} reacts with hydroxyl radicals to yield Cu(III) with a



rate constant $k_9 = 3.5 \times 10^8$.

Since Cu(III) is a strong oxidizing agent (9) should be followed by



As a consequence the term $ra = k_2[\text{Fe}^{2+}]/2k_{3i}[\text{R}_i\text{H}]$ in (8) should be replaced by

$$(k_2[\text{Fe}^{2+}] + k_9[\text{Cu}^{2+}])/2k_{3i}[\text{RH}] \quad (11)$$

so that sufficient Cu^{2+} should have the same qualitative effect on reaction stoichiometry as additional Fe^{2+} . If (11) is correct

$$a/a_0 = 1 + k_9[\text{Cu}^{2+}]/k_2[\text{Fe}^{2+}] \quad (12)$$

where a_0 represents the slope of (8) in the absence of Cu^{2+} . A plot of the data in Table I according to (12) is satisfactorily linear and gives $k_9/k_2 = 0.2$. This value is smaller than would be anticipated from Baxendale's result⁵ which indicated that hydroxyl radicals react with Cu^{2+} and Fe^{2+} at almost identical rates. However, Meyerstein⁶ has recently concluded that, in acid solution, below pH 3 Cu(III) decomposes too rapidly for measurement to regenerate Cu^{2+} and hydroxyl radicals, *i.e.*, reaction 9 is significantly reversible which could account for our lower value.

In order to round out our survey of substrate reactivities, several other alcohols were investigated.

(5) J. H. Baxendale, E. M. Fielden, and J. P. Keene, "Pulse Radiolysis," M. Elbert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press, New York, N. Y., 1965, p 217.

(6) D. Meyerstein, *Inorg. Chem.*, 10, 638 (1971).

All gave good linear plots of eq 8 with results summarized in Table II. Saturated alcohols are considered

Table II. Reactions of Further Alcohols with Fe^{2+} - H_2O_2

Alcohol	Additive (M)	<i>a</i>	<i>b</i>
<i>n</i> -Propyl	Cu^{2+} (0.004)	0.0885	0.2020
	Cu^{2+} (0.04)	0.0941	0.0369
Isobutyl	Fe^{3+} (0.04)	0.1491	0.0153
	Cu^{2+} (0.004)	0.0712	0.1531
Neopentyl	Fe^{3+} (0.04)	0.0661	0.0820
	Cu^{2+} (0.004)	0.0816	0.0282
"Hexyl" ^a	Cu^{2+} (0.004)	0.0833	0.2343
	Cu^{2+} (0.04)	0.0689	0.1238
Allyl	Cu^{2+} (0.04)	0.1024	0.0446
	Fe^{3+} (0.04)	0.0713	0.343
Allyl	Fe^{3+} (0.04)	0.0634	0.236
	Cu^{2+} (0.04)	0.109	0.439
		0.183	0.130

^a 2,3-Dimethyl-2-butanol.

further below, but we note here that the intercept, *b*, for isobutyl alcohol is surprisingly low and is reduced further by added ferric ion. This we attribute to oxidation of the tertiary 2-hydroxymethyl-2-propyl radical, as well as the 1-hydroxy isobutyl radical by Fe^{3+} , in contrast to the behavior of unactivated primary and secondary alkyl radicals. In confirmation, glc examination of reaction products shows that 1,2-dihydroxy-2-methylpropane is produced in the absence as well as presence of Cu^{2+} .

2,3-Dimethyl-2-butanol, which lacks α hydrogens, shows the same effect. Even without added Fe^{3+} *b* = 0.34, rather than 0.5 as expected if no radical oxidation were occurring, and is further decreased by added Fe^{3+} .

Allyl alcohol finally shows a relatively large intercept, which is, however, reduced by Cu^{2+} . We interpret this as arising from predominantly (88%) addition of hydroxyl radicals to the double bond, a result in good agreement with Volman and Chen's qualitative conclusions⁷ and Leyshon and Volman's estimate of 92% addition to allyl alcohol-3,3-*d*₂,⁸ both based upon hydrogen peroxide photolyses, and on esr spectra of radicals produced in the H_2O_2 - Ti^{3+} -allyl alcohol system.⁹

Negatively Substituted Alcohols. Our previous results³ have shown that, while α -hydroxy radicals are oxidized by Fe^{3+} , radicals with strong electron-withdrawing groups are instead reduced by Fe^{2+} . In order to see where the crossover in reaction path occurs, we have examined a series of negatively substituted alcohols. Acetol (hydroxyacetone) data, plotted according to eq 8, give *a* = 0.2, *b* = <0.03 corresponding to long kinetic chains (*i.e.*, ready oxidation of the intermediate radical) but a slightly lower reactivity than ethanol.

2,2,2-Trifluoroethanol behaves rather similarly, but with markedly reduced reactivity, *a* = 1.81, and a larger intercept, *b* = 0.128, indicating that not all radicals undergo oxidation. Addition of 0.02 M Fe^{3+} to the system reduces the intercept to 0.04 without significant change in slope, and we conclude that now

(7) D. H. Volman and J. C. Chen, *J. Amer. Chem. Soc.*, **81**, 4141 (1959).

(8) L. N. Leyshon and D. H. Volman, *ibid.*, **87**, 5565 (1965).

(9) P. Smith, J. T. Pearson, P. B. Wood, and T. C. Smith, *J. Chem. Phys.*, **43**, 1535 (1965).

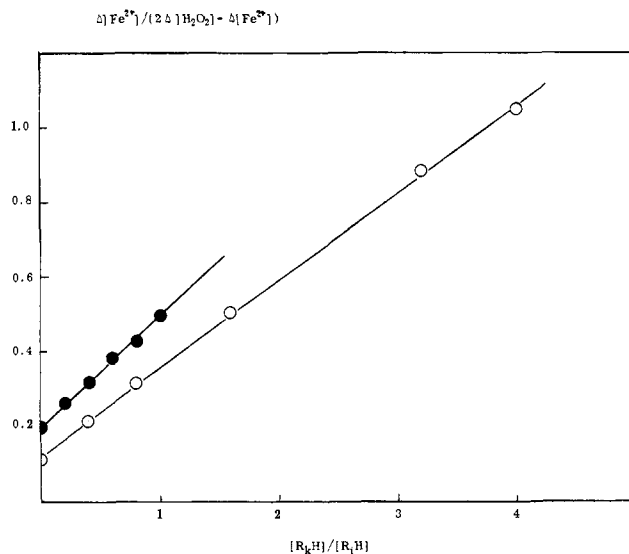


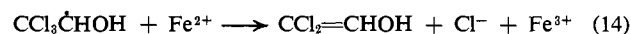
Figure 1. Plots of eq 9, 0.02 M Fe^{2+} : (O) $\text{CCl}_3\text{CHOHCH}_3$, 0.025 M CH_3OH ; (●) $\text{CCl}_3\text{CH}_2\text{OH}$, 0.05 M CH_3OH .

radical oxidation is becoming slow enough that radical coupling is significant at low Fe^{3+} concentration.

2,2,2-Trichloroethanol and 1,1,1-trichloro-2-propanol show a striking change in oxidation stoichiometry. In both cases intercepts are approximately unity (0.975 and 0.875, respectively) with chain lengths independent of Fe^{2+} /substrate ratios, results implying that either both substrates are inert to hydroxyl radicals or that they yield radicals reduced by Fe^{2+} . The latter was shown to be the case by demonstrating that both retard the oxidation of methanol, and reactivities were measured by the same technique employed with acetone. Results using the modified stoichiometric equation³

$$\Delta[\text{Fe}^{2+}]/(2\Delta[\text{H}_2\text{O}_2] - \Delta[\text{Fe}^{2+}]) = \frac{k_2[\text{Fe}^{2+}]/k_{3i}[\text{R}_i\text{H}] + k_{3k}[\text{R}_k\text{H}]/k_{3i}[\text{R}_i\text{H}]}{1} \quad (13)$$

where subscript *i*'s refer to methanol and *k*'s to the chloro alcohols (which yield oxidizable and reducible radicals, respectively) are shown in Figure 1 and yield, for trichloroethanol, $k_{3k}/k_{3i} = 0.236$, and for the trichloropropanol 0.296. In these cases, the possibility arises that reduction does not regenerate starting material *via* reduction 6, but rather involves β -chloride loss, which if concerted, could account for its ease, *e.g.*, eq 14. However, since no ionic chloride could be



detected in reaction mixtures by AgNO_3 reagent, (14) can be eliminated as a reaction path.

Ethers and Amides. Four representative ethers and amides were investigated as additional structural types which might yield mixtures of oxidizable and non-oxidizable radicals. All gave good linear plots of eq 8 and results are summarized in Table III. Dioxane yields a single radical which is evidently oxidized by Fe^{3+} , since *b* is almost zero and insensitive to added Cu^{2+} . Tetrahydrofuran, in contrast, can yield two radicals, one of which (presumably arising from β attack) is only oxidized by Cu^{2+} . From the data we calculate that α attack is, however, the major reaction path (87%) as in the case of alcohols. The esr spectrum of radicals produced from Fenton's reagent-

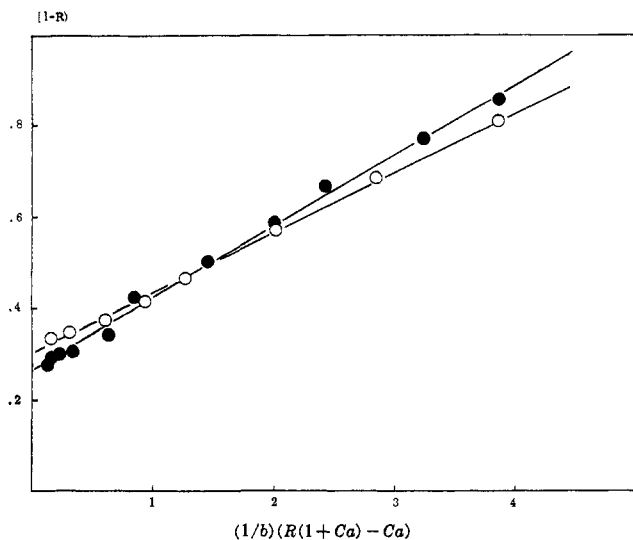


Figure 2. Plots of eq 15, 0.02 M Fe²⁺: (●) CH₃SOCH₃; (○) CD₃SOCD₃.

Table III. Reaction of Ethers and Amides with Fe²⁺-H₂O₂

Substrate	a ^a	b ^a
Dioxane	0.063 (0.063)	0.002 (0.002)
Tetrahydrofuran	0.148 (0.150)	0.07 (0.03)
Dimethylacetamide	0.188	0.08
Dimethylformamide	0.168	0.01

^a Values in parentheses in presence of Cu²⁺.

tetrahydrofuran has been reported by Norman and West¹⁰ as indicating only the β radical. Presumably, again as in the case of alcohols, the α-alkoxy radicals, although the major product, are too rapidly oxidized to be detected. This is also the conclusion to be drawn from product studies by Shono, *et al.*,¹¹ who obtained α-hydroxydioxane and α-hydroxytetrahydrofuran from these ethers, together with hydroxylated dimers, presumably arising from further oxidation of initial products.

Our results with dimethylacetamide show high reactivity and long kinetic chains, indicating predominant attack on *N*-methyl groups to yield Fe³⁺ oxidizable radicals. If, by analogy to acetic acid,^{4a} attack on acetyl methyl yields a radical reduced by Fe²⁺, from our intercept and slope we obtain $k_{3k}/k_2 = 0.043$ which is in fact comparable to the value for acetic acid, 0.094, although the small intercept makes the result not very reliable. Dimethylformamide shows similar overall reactivity, consistent with predominant *N*-methyl attack in both systems. The slightly larger reactivity but small intercept suggests some attack on formyl H to yield radicals which are also oxidized. Again, our findings are consistent with literature reports of predominant hydroxyl radical attack on *N*-alkyl groups of simple amides (based on fast spectroscopy)¹² and on the easy oxidation of α-aminoalkyl radicals.¹³ They also explain Shiga's observations¹⁴ that, with Ti³⁺-H₂O₂,

(10) R. O. C. Norman and P. R. West, *J. Chem. Soc. B*, 389 (1969).

(11) T. Shono, T. I. Kuni, and R. Oda, *Nippon Kagaku Zasshi*, **81**, 1344 (1960).

(12) (a) E. Hayon, T. Ibatani, N. N. Lichtin, and M. Simic, *J. Amer. Chem. Soc.*, **92**, 3898 (1970); (b) *ibid.*, **93**, 5388 (1971).

(13) R. O. C. Norman and N. H. Anderson, *J. Chem. Soc. B*, 993 (1971).

(14) T. Shiga, A. Boukhors, and P. Douzou, *J. Phys. Chem.*, **71**, 4264 (1967).

Table IV. Reaction of Butadiene with Fe²⁺-H₂O₂

[Fe ²⁺], M	Additive (M) ^a	Chain length ^c
0.02		1.10
0.02	Fe ³⁺ (0.021)	1.25
0.05	Fe ³⁺ (0.0025) ^b	1.07
0.05	Fe ³⁺ (0.0525) ^b	1.15
0.02	Cu ²⁺ (0.04)	5.45
0.02	Cu ²⁺ (0.04)	7.02

^a 0.1 M HClO₄, 0.001 M Fe³⁺, ca. 0.01 M butadiene present except as indicated. ^b 0.25 M HClO₄. ^c Chain length = 1/2R = Δ[H₂O₂]/Δ[Fe²⁺]. This assumes that essentially all HO· radicals add to butadiene.

2-pyrrolidone shows the esr spectrum of radicals α to either nitrogen or carbonyl (the two could not be distinguished, but from our results they should be the former) but that with Fe²⁺ only the β radical could be detected.

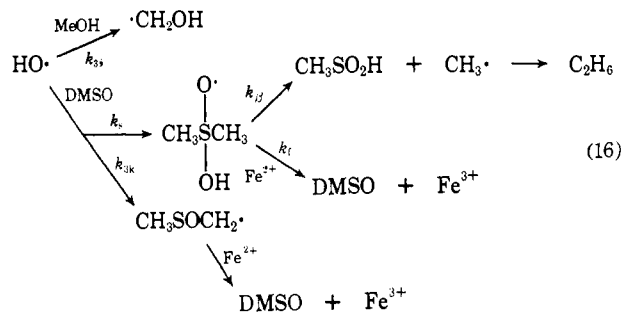
Butadiene. Our results with allyl alcohol show that an α-hydroxyallylic radical is readily oxidized by Fe³⁺, and earlier data on crotonic acid³ suggested that the same was true for relatively unactivated allylic radicals as well. In order to investigate the matter further, the stoichiometry of the Fe²⁺-H₂O₂ system was examined in butadiene saturated systems (Table IV).

With Fe²⁺ alone (*i.e.*, low Fe³⁺ concentration) chains are short, and are only slightly increased by added Fe³⁺, but markedly by Cu²⁺. We conclude that simple allylic radicals are readily oxidized by Cu²⁺, but only marginally by Fe³⁺, and thus behave much like simple saturated radicals in our system.

Dimethyl Sulfoxide. Bertilsson, Gustafsson, Kuhn, and Torssell¹⁵ reported that Fenton's reagent in aqueous solution readily cleaves sulfoxides to yield alkyl radicals which may then participate in further



reactions. Oxidation of dimethyl sulfoxide in our system and plotting the data according to eq 8 gave $a = 0.122$, $b = 0.75$. Experiments with added Cu²⁺ gave smaller intercepts, but were too irreproducible for analysis. The value of $b > 0.5$ indicates the formation of radicals reducible by Fe²⁺. The small value of a indicated a high reactivity for the sulfoxide, but its value was too near zero for accurate determination. Accordingly, the retardation of methanol oxidation by the sulfoxide was examined as well. Here, application of eq 13 gave nonlinear plots and it was necessary to turn to a more elaborate reaction scheme (eq 16)



(15) B. Bertilsson, B. Gustafsson, I. Kuhn, and K. Torssell, *Acta Chem. Scand.*, **24**, 3590 (1970). These authors propose a reaction scheme not involving hydroxyl radicals which, however, seems incompatible with our observations.

in which radicals from both hydrogen abstraction and addition are reduced by Fe^{2+} , but in the latter case reduction competes with β -scission to yield methyl radicals which dimerize.

Suitable manipulation of the stoichiometric equations arising from (16) yields a linear expression

$$1 - R = \frac{k_{3i}[R(1 + Ca) - Ca]}{b(k_{3k} + k_s)} - \frac{k_s(f - 1)}{2(k_{3k} + k_s)} \quad (17)$$

where $R = \Delta[\text{Fe}^{2+}]/2\Delta[\text{H}_2\text{O}_2]$, $a = [\text{Fe}^{2+}]/[\text{MeOH}]$, $b = [\text{DMSO}]/[\text{MeOH}]$, $C = k_2/k_{3i}$, and $f = k_t[\text{Fe}^{2+}]/k_\beta + k_t[\text{Fe}^{2+}]$, the fraction of adduct radicals reduced by Fe^{2+} . From (15), a plot of $1 - R$ vs. $[R(1 + Ca) - Ca]/b$ should be linear with a slope $k_{3i}/(k_{3k} + k_s)$. Typical plots are shown in Figure 2, and four sets at different Fe^{2+} concentrations yield an average slope of 0.141 ± 0.01 . Taking $C = 0.248$ from Table I, this corresponds to a reactivity of DMSO relative to Fe^{2+} of $1/0.141 \times 0.248 = 28.6$, or a rate constant of approximately 9×10^9 . We believe that this is a better estimate than that obtained directly *via* eq 8. Since intercepts were within experimental error, independent of Fe^{2+} , f must be zero, *i.e.*, there is no reduction of the intermediate adduct.

Since the average value of the intercepts from Figure 2 is 0.26, the results indicate $k_s/(k_{3k} + k_s) = 0.52$, or 48% of the reaction goes through hydrogen abstraction. However, this result seems too high, since electron-withdrawing groups, *e.g.*, in acetone and acetic acid, reduce rates for hydrogen abstraction from methyl groups to below 10^8 l./mol sec, and reaction of DMSO- d_6 (Figure 2) shows only a barely detectable kinetic isotope effect. In short, our reaction scheme is incomplete, although it shows convincingly that hydroxyl radical attack on DMSO is a very rapid process.

Discussion

Relative Reactivities. In our first paper² we noted some discrepancies between our data on relative reactivities and those obtained by the quite different techniques of radiation chemistry. Since then we have investigated a number of additional substrates, and some radiation results have been revised, so in Table V

Table V. Relative Reactivities of Substrates toward $\text{HO}\cdot$

Substrate	$\Sigma k_s/k_2$	Lit.
Alcohols		
Methyl	4.03	2.67 ¹⁷
Ethyl	7.00 ²	6.17 ¹⁷
<i>n</i> -Propyl	11.3	8.74 ¹⁷
Isopropyl	6.65 ²	6.67 ¹⁷
Isobutyl	14.0	3.83 ¹⁶
<i>tert</i> -Butyl	1.90 ²	1.57 ¹⁷
Allyl	9.2	6.57 ¹⁷
Ethers		
Tetrahydrofuran	6.76	5.3 ¹⁶
Dioxane	15.9	5.0 ¹⁶
Carbonyl compounds		
Acetone	0.322 ³	0.289 ¹⁷
Acetic acid	0.089 ³	0.047 ¹⁶
Dimethylacetamide	5.3	12 ¹²
Dimethylformamide	6.0	5.7 ¹²

we repeat the comparison with our results in this and previous papers, with radiation data from Anbar and

Neta¹⁶ and from a new compilation by Dorfman.¹⁷ Reactivities are listed as substrate reactivities toward hydroxyl radicals relative to the Fe^{2+} reaction (2). In our case, these were measured directly or *via* competition with methanol for which we take $k_{3i}/k_2 = 4.03$ (Table I). This leads to a small correction to some of our previous values. Radiation results are calculated from published rate constants taking $k_2 = 3.0 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$.¹⁷ Thanks to the downward revision of both k_2 and our methanol reactivity, agreement is now more satisfactory, although our values average 20% lower and there are obvious discrepancies. Since the literature results are often averages of several values which may vary as much as 50%, we feel that the data now provide little reason to doubt that the same species, $\text{HO}\cdot$, is involved in both sets of reactions.¹⁸

For molecules containing two types of C-H bonds, one yielding oxidizable and the other nonoxidizable radicals, from the definitions of eq 8, $k_{3i}/k_2 = (1 - 2b)/a$, $k_{3j}/k_2 = 2b/a$. Reactivities *per hydrogen* relative to the Fe^{2+} reaction for a number of our substrates are summarized in Table VI. For *n*-propyl alcohol $k_j =$

Table VI. Dissection of Relative Reactivities per Hydrogen

Substrate	k_α/k_2	k_β/k_2	k_γ/k_2
Alcohols			
Methyl	1.34		
Ethyl ²	3.66	0.23	
<i>n</i> -Propyl	3.36	1.34	(0.625) ^d
Isopropyl ²	5.73	0.15	
Isobutyl	(3.04) ^d	4.22 (5.66) ^e	(0.625) ^d
<i>tert</i> -Butyl ²		0.21	
Neopentyl	2.11		0.625
"Hexyl" ^c		(0.2) (p.) ^d	(0.625) ^d
		9.07 (7.42) ^e	
Allyl	1.12		8.08 ^a
2,2,2-Trifluoroethyl	0.276		
2,2,2-Trichloroethyl	0.475		
Other substrates			
Acetone	0.054		
Acetic acid	0.030		
Dimethylformamide	0.97 ^b	~0.12	
Dimethylacetamide	0.87 ^b	~0.017	
Dioxane	1.99		
Tetrahydrofuran	1.45	0.23	

^a Addition. ^b Methyl hydrogens of the amide group. ^c 2,3-Dimethyl-2-butanol. ^d Assumed. ^e Calculated from $2b/a$ in presence of added Fe^{3+} assuming oxidation of all tertiary radicals.

$k_\beta + k_\gamma$, and the reactivity of the latter was assumed the same as in neopentyl alcohol. With isobutyl alcohol, in which we have shown that the tertiary β hydrogens are also somewhat oxidizable, k_α was further assumed the same as in other primary alcohols. A similar calculation was made for "hexyl" alcohol (2,3-dimethyl-2-butanol).

In the alcohol series reactivities for both α and β hydrogens increase smoothly in the order primary < secondary < tertiary, the slower β -hydrogen abstractions showing the larger change. Looking at the data as a

(16) M. A. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

(17) L. M. Dorfman and G. E. Adams, Report No. NSRDS-NBS-46, U. S. Government Printing Office, Washington, D. C., in press. We thank Professor Dorfman for making these data available.

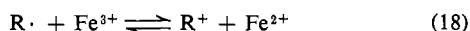
(18) A $\text{HO}\cdot\text{-Fe}^{3+}$ adduct, *e.g.* FeO^{2+} or FeOH^{3+} , would be kinetically equivalent to $\text{HO}\cdot$ in our scheme. However, one would then expect an ionic strength effect on reactivity. None has been detected (*cf.* Table I).

whole, it is evident that the reactivity of substrates is determined, not so much by bond strengths, as by the fact that HO· is a strongly electrophilic radical, preferentially attacking points of high electron density.¹⁹ Thus α -hydroxy C-H bonds are activated, β -hydroxy C-H bonds are deactivated (compare *tert*-butyl and neopentyl alcohols), and β halogens strongly reduce reactivity. Ether oxygen and amide nitrogen are slightly less effective than hydroxyl in activating α -C-H, while neighboring carbonyl decreases reactivity over tenfold (compare acetone and acetic acid with neopentyl alcohol).²⁰ It is plausible that the primary < secondary < tertiary order noted above is primarily such a polar effect,²¹ and the surprisingly low α -C-H reactivity of allyl alcohol, if real, may reflect the fact that vinyl is a more electronegative group than alkyl. The high rate of addition to allyl alcohol is consistent with our previous observations for a number of olefins and acetylenes.³ Except when a molecule possesses highly activated C-H bonds, addition is the preferred process. HO· is thus a "normal" radical and lacks the unexplained peculiarity of alkoxy radicals which preferentially attack allylic C-H bonds.²²

Finally some comparison can be made of our results with gas-phase data. Arrhenius parameters for reactions with ethane, propane, and isobutane at 300–500°K have been reported by Greiner.²³ Assigning "excess reactivity" of propane and isobutane to attack on secondary and tertiary hydrogens, we calculate the primary:secondary:tertiary ratio as 0.3:2.84:11.6 at 300°K, very close to the β -hydrogen sequence 0.2:1.34:6.6 in Table VI.

Interestingly, for molecules which can be compared, hydroxyl radical reactions are *slower* in the gas phase at 300°K than in water: H₂, 4.7×10^6 vs. 4.5×10^7 M⁻¹ sec⁻¹;^{16,24} CH₄, 5.8×10^6 vs. 1.4×10^8 ;^{16,23} CO, 8.5×10^7 vs. 6×10^8 .^{16,24} In the gas phase, rates per primary H are 3×10^7 ; for neopentyl alcohol we obtain 1.9×10^8 . One may speculate on the origin of the difference, but relative reactivities, the important quantities in determining reaction products, appear closely similar in the two media. Thus it seems reasonable that the extensive data on hydroxyl radical reactions in water can be applied to gas phase and atmospheric reactions as well.

Reactions of Fe³⁺, Fe²⁺, and Cu²⁺ with Radicals. Previously we have argued that radical oxidation by Fe³⁺ is an electron-transfer process and that the equilib-



rium lies to the right only for those radicals which yield relatively stable carbonium ions. The results in this paper are consistent with this model, with the tertiary radical from isobutyl alcohol providing a borderline case. The model is also supported by a rough estimate of the rate of the oxidation with methanol. Here essentially all radicals are oxidized, values of *b* in Table

(19) Similar conclusions have been reached by others, e.g., T. Bérces and A. F. Trotman-Dickenson [*J. Chem. Soc.*, 4281 (1961)] have suggested that HO· selectivity resembles that of Cl·.

(20) Consistent with this, P. D. Coffman, E. L. Jenner, and R. D. Lipscomb [*J. Amer. Chem. Soc.*, 80, 2864 (1958)] have shown that longer chain acids are attacked chiefly at points remote from -COOH.

(21) Since $D(\text{HO-H}) = 118$ kcal/mol, all H abstractions are strongly exothermic, so little sensitivity to bond strength might be anticipated.

(22) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, 83, 3877 (1961).

(23) N. R. Greiner, *J. Chem. Phys.*, 53, 1070 (1970).

(24) N. R. Greiner, *ibid.*, 51, 5049 (1969).

I indicating that less than 0.5% undergo coupling. Accordingly, from our earlier equations

$$R_i = k_4[R\cdot][Fe^{3+}] \quad (19)$$

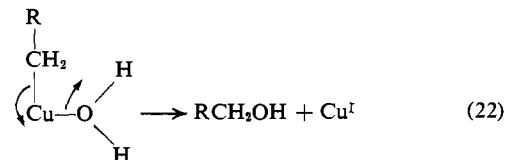
$$2k_3[R\cdot]^2 < 0.005k_4[R\cdot][Fe^{3+}] \quad (20)$$

Multiplying (19) and (20) together and solving for k_4 gives

$$k_4 > (2k_3R_i/0.005[Fe^{3+}]^2)^{1/2} \quad (21)$$

In our experiments, due to the high rate of (2), R_i , the rate of radical formation, is simply the rate of H₂O₂ addition (typically 1.25 mmol l⁻¹ min⁻¹),²⁵ and $[Fe^{3+}] \cong 10^{-4}$ M. Taking $k_3 = 2 \times 10^8$, a typical rate of coupling for simple radicals, gives $k_4 > 4 \times 10^8$. In contrast, rate constants for ligand exchange of Fe³⁺ are relatively slow, the rate for H₂O exchange being 3×10^3 .²⁶ Anything but an outer sphere electron-transfer process seems ruled out. A similar calculation for the rate of reduction of acetylonyl radicals by Fe²⁺, using data of Table II, ref 3, indicates a comparably rapid process, and suggests an electron-transfer mechanism here as well.

If oxidation of simple alkyl radicals by Fe³⁺ fails because of the reversibility of (18), it follows that their oxidation by Cu²⁺ (which has a lower oxidizing potential) must occur by a different mechanism. Radical oxidations by Cu²⁺ have been extensively studied by Kochi²⁷ who has proposed that they occur *via* an intermediate organocopper intermediate which, in his nonaqueous systems, decomposes either by β -proton loss to give olefin or by dissociation to ion pairs showing typical carbonium ion rearrangements. To the extent to which products have been investigated,² we find neither olefin nor rearrangements but rather oxidation to the corresponding alcohol. However, our results do appear compatible with the organocopper intermediate decomposing by a third path *via* insertion of a



neighboring ligand, somewhat analogous to the well-known carbonyl insertion reactions of transition metal chemistry.

Such a formulation is consistent with Kochi's conclusions and seems more plausible than a simple displacement on ligand water which has no analogy in radical chemistry. Although it is a more effective oxidant, radical oxidations by Cu²⁺ are evidently considerably slower than those by Fe³⁺. From Table I, 10^{-4} M Fe³⁺ effectively oxidizes all hydroxymethyl radicals in our system. In contrast (Table II), 4×10^{-2} M Cu²⁺ only partially oxidizes (β and α) radicals from *n*-propyl alcohol, a result consistent with Kochi's estimates of 10^6 – 10^8 for Cu²⁺ oxidation of a number of alkyl radicals. Since ligand exchange processes at Cu²⁺ are very rapid (k for H₂O exchange = 8×10^9 ²⁶),

(25) Actually, since H₂O₂ is added dropwise, R_i fluctuates and most radicals are produced at a higher rate than calculated above. If anything, therefore, our estimate must be low.

(26) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 152.

(27) J. Kochi in "Free Radicals," Vol. I, J. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 11.

such rates are certainly low enough for the mechanism we discuss.

Finally it is worth noting that simple hydrated Cu^{2+} fails to oxidize acetyl and similar negatively substituted radicals in contrast to many examples of such oxidation by Cu^{2+} -halide complexes,²⁷ supporting the idea that here another path, direct displacement on the ligand, is taking place.

Experimental Section

Stoichiometry of the Fe^{2+} - H_2O_2 -substrate reactions was determined as in our previous papers^{2,3} by slow addition of H_2O_2 to

stirred Fe^{2+} -substrate solutions under N_2 , followed by determination of Fe^{2+} consumed by dichromate titration or of Fe^{3+} formed by spectrophotometric determination of its thiocyanate complex. DMSO systems developed a pronounced yellow color during reaction and products were apparently unstable since Fe^{3+} titers changed on standing. Accordingly products were analyzed immediately after reaction *via* the thiocyanate method.

Isobutyl alcohol products were determined qualitatively by flame ionization glc of reaction solutions. Isobutylene glycol (2-methyl-1,2-propanediol) was detected in approximately 20% yield both with and without added Fe^{3+} . In the presence of 0.04 M Cu^{2+} the yield was 14% plus 8% methallyl alcohol, present only in traces in the absence of Cu^{2+} . Evidently some oxidative elimination occurs with copper in this system.

Structure and Unimolecular Reactions of Gaseous $\text{C}_2\text{H}_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ Ions¹

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Abstract: Collisional activation (CA) spectra of $\text{C}_2(\text{H},\text{D})_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ ions from a wide variety of compounds show that the immonium ion isomers, and only those isomers, are the stable structures of lifetimes $>10^{-5}$ sec. Ions formed initially as $^+\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{N}^+\text{H}$ isomerize to $\text{CH}_3\text{CH}=\text{N}^+\text{H}_2$ (b), and those formed as $\text{CH}_3\text{-N}^+\text{CH}_3$ isomerize to $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2$ (d). Deuterium labeling shows that a substantial proportion of the decompositions of b and d do not involve loss of the positional identity of the hydrogen atoms. $\text{C}_3\text{H}_8\text{N}^+$ ions of the immonium structures $\text{CH}_3\text{CH}_2\text{N}^+\text{H}=\text{CH}_2$ (f), $(\text{CH}_3)_2\text{C}=\text{N}^+\text{NH}_2$ (g), $\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+\text{H}_2$ (h), $\text{CH}_3\text{N}^+\text{H}=\text{CHCH}_3$ (i), and $(\text{CH}_3)_2\text{N}^+=\text{CH}_2$ (j) have lifetimes $>10^{-5}$ sec. Contrary to previous evidence,³ g does not isomerize completely to h before metastable decomposition, nor does f isomerize to i, unless the activation energy for the latter isomerization is nearly as high as that for decomposition. Thus in several cases the information supplied by metastable ion decompositions, including the width of flat-topped peaks, has provided misleading evidence as to the structure of the corresponding undecomposed ions in the mass spectrum. In contrast, CA spectra provide reliable evidence for the structures of $\text{C}_2\text{H}_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ ions, and thus for the structure of molecules giving such ions in their mass spectra.

Structure and reactivity of gaseous organic cations have been examined in a variety of recent investigations.^{1,3,4} Such information on ion behavior free of solvent interactions has been valuable in application to, for example, fundamental concepts of basicity,^{4a} theoretical prediction of ion structure and properties,^{4b,c} and understanding of mass spectral reactions.^{1,3,4} The study reported here of $\text{C}_2\text{H}_6\text{N}^+$ and $\text{C}_3\text{H}_8\text{N}^+$ ions was undertaken because of conflicting evidence of the behavior of such ions, which are simple examples of the important class of even-electron $\text{C}_n\text{H}_{2n+2}\text{N}^+$ ions found in the mass spectra of saturated amines.

The saturated amine group is well known for its unusual ability to direct mass spectral fragmentations;⁵

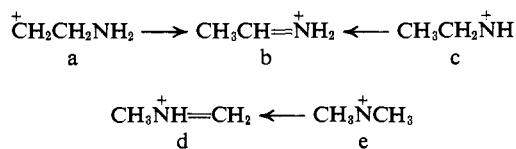
(1) Metastable Ion Characteristics. XXVII. Part XXVI: K. Levsen, F. W. McLafferty, and D. M. Jerina, *J. Amer. Chem. Soc.*, **95**, 6332 (1973).

(2) (a) Postdoctoral Fellow, 1972. (b) John Simon Guggenheim Memorial Foundation Fellow, 1972. (c) We are indebted to the National Institutes of Health (GM 16575 and 16609) and the Army Research Office (8246-C) for generous financial support.

(3) N. A. Uccella, I. Howe, and D. H. Williams, *J. Chem. Soc. B*, 1933 (1971).

(4) (a) E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972); (b) P. Ausloos, R. E. Rebert, L. W. Sieck, and T. O. Tiernan, *ibid.*, **94**, 8939 (1972); (c) D. J. McAdoo, F. W. McLafferty, and P. F. Bente III, *ibid.*, **94**, 2027 (1972); (d) N. A. Uccella and D. H. Williams, *ibid.*, **94**, 8778 (1972).

— NH_2 and — $\text{N}(\text{CH}_3)_2$ have been ranked as the most effective groups of the common functionalities.⁶ Addition of a single amine group can have a profound influence on the mass spectrum of a large molecule; for example, the mass spectrum of *n*-octadecylamine has CH_2N^+ as its largest peak, and other $\text{C}_n\text{H}_{2n+2}\text{N}^+$ ions account for a large part of the remaining ion abundance.⁵ This has been assumed to be due in substantial part to the high stability of the $\text{C}_n\text{H}_{2n+2}\text{N}^+$ ions, which stability is thought to result from the unusual electron-donating ability of nitrogen, for example, $^+\text{CH}_2\text{NH}_2 \leftrightarrow \text{CH}_2=\text{N}^+\text{H}_2$. This would predict that the quaternary immonium ions b and d would be the most stable of the possible $\text{C}_2\text{H}_6\text{N}^+$ isomers a–e (the indicated isomerizations will be discussed below). The $\text{CH}_3\text{CH}=\text{O}^+\text{H}$ and $\text{CH}_3\text{O}^+=$



(5) R. S. Gohlke and F. W. McLafferty, *Anal. Chem.*, **34**, 1281 (1962); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 8.

(6) G. Remberg and G. Spiteller, *Chem. Ber.*, **103**, 3640 (1970).