*Anal.* Calcd for $C_9H_8ClNO$: C, 59.51; H, 4.41. Found: C, 59.72; H, 4.20.

***cis*-2-Methoxy-3-chloro-3-phenyl-4-methyl-1-azetine (12).** A mixture of 0.110 g (0.51 mmol) of **9a** and 0.050 g (0.95 mmol) of sodium methoxide in 7 ml of methanol was stirred at 25°. After 22 hr, tlc showed no more starting material. The mixture was evaporated to 1 ml of liquid and placed on a silica gel preparative tlc plate. Elution with 10:85:5 chloroform–Skellysolve B–ethanol gave a band at $R_f$ 0.60 which yielded 30 mg (28%) of **12** as a light yellow oil: ir (neat) 1633 $cm^{-1}$ (C=N); nmr ($CCl_4$) $\tau$ 2.7 (s, 5, aromatic), 5.99 (s, $OCH_3$), 6.02 (q, $J = 6.7$ Hz, CH, total area of 5.99 and 6.02 peaks is 4), and 9.12 (d, 3, $J = 6.7$ Hz, $CH_3$); mass spectrum *m/e* (rel intensity) 209, 211 (78, 46, $M^+$), 208, 210 (41, 29, $M^+ - 1$), 194, 196 (64, 22, $M^+$ − Me), 174 (100, $M^+$ − Cl), and 159 (43, $M^+$ − Me − Cl).

*Anal.* Calcd for $C_{11}H_{12}ClNO$: C, 63.01; H, 5.77; Cl, 16.91. Found: C, 63.05; H, 5.93; Cl, 16.84.

***N*-(Benzylidene)-α,β-dichloro-α-styrylamine (13).** A solution of 2.0 g (6.4 mmol) of **6c** was stirred in 40 ml of DMSO under a $N_2$ atmosphere while 0.84 g (7.5 mmol) of potassium *tert*-butoxide in 25 ml of DMSO was added dropwise. Addition took 45 min and stirring was continued for 6 hr. The resulting mixture was poured into 100 ml of salt solution and extracted with 120 ml of chloroform in two portions. The combined organic layers were dried over $MgSO_4$, decolorized with charcoal, and filtered, and the solvent removed *in vacuo*. The resulting yellow solid was placed on a column of 30 g of silica gel and eluted with 10% chloroform–petroleum ether. A light yellow band separated and was collected. Removal of solvent gave **13** as a yellow oil which crystallized at −20° and was very hygroscopic: ir (neat) 1605 $cm^{-1}$ (C=N); nmr ($CCl_4$) $\tau$ 2.2–2.9 (m, aromatic) and 1.62 (s, CH).

*Anal.* Calcd for $C_{15}H_{11}Cl_2N$: C, 65.23; H, 4.02; N, 5.07; Cl, 25.68. Found: C, 65.00; H, 4.22; N, 5.21; Cl, 25.41.

**Hydrolysis of 13.** Using the same procedure as in the hydrolysis of **6a** to **11a**, **13** was hydrolyzed in 20 hr to a 1:1 ratio of benzaldehyde and α-chlorophenylacetonitrile. The yield of the mixture was 20% with 50% of **13** remaining unchanged. Hydrolysis for 45 hr at 25° gave a 52% yield of benzaldehyde but only a 10% yield of the nitrile. These components were separated on preparative silica gel plates. Elution with 60% chloroform–petroleum ether gave the benzaldehyde at $R_f$ 0.45, and the nitrile at $R_f$ 0.55. Benzaldehyde was identified by comparing the ir with an authentic sample as well as vpc comparison using a 3% XE-60 column at 75°. In addition, the mass spectrum showed a parent peak at *m/e* of 106. α-Chlorophenylacetonitrile was identified by its mass spectrum, *m/e* (rel intensity) 151, 153 (19, 6.5, $M^+$), 116 (100, $M^+$ − Cl), 89 (19, M − Cl − HCN); a metastable peak at *m/e* 68 indicates that the *m/e* 89 peak is derived from the 116 peak by loss of 27 (HCN). In addition the nmr spectrum ($CCl_4$) shows $\tau$ 2.53 (m, 5, aromatic) and 4.5 (s, 1, CH).

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# Mechanism of the Ferric Ion Catalyzed Decomposition of Hydrogen Peroxide. Effect of Organic Substrates[1]

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**Abstract:** The retardation of the $Fe^{3+}$ catalyzed decomposition of $H_2O_2$ in $HClO_4$ solution by a number of organic substrates has been examined. Results with acetone, acetic acid, and *tert*-butyl alcohol are consistent with the redox chain mechanism of Barb, Baxendale, George, and Hargrave on the assumption that the substrates trap hydroxyl radicals which otherwise react with $H_2O_2$. Data show the predicted form and yield ratios of rate constants in fair agreement with those derived from radiation chemistry and $Fe^{2+}$–$H_2O_2$ experiments. The treatment also predicts the observed dependence on [$H^+$], effect of $Cu^{2+}$, and primary isotope effect with $CD_3COCD_3$, and indicates kinetic chains of 30, much shorter than those estimated by Barb, *et al.*

Although the ferric ion catalyzed decomposition of hydrogen peroxide in acid solution has long been of interest and has received extensive study, two completely conflicting interpretations exist for its mechanism. The older scheme, elaborated by Barb, Baxendale, George, and Hargrave,[3] involves a redox radical chain

$$Fe^{3+} + H_2O_2 \xrightarrow{k_1} Fe^{2+} + HO_2\cdot + H^+ \quad (1)$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_2} Fe^{3+} + HO^- + HO\cdot \quad (2)$$

$$HO\cdot + H_2O_2 \xrightarrow{k_3} H_2O + HO_2\cdot \quad (3)$$

$$HO_2\cdot + Fe^{3+} \xrightarrow{k_4} H^+ + Fe^{2+} + O_2 \quad (4)$$

$$HO_2\cdot + Fe^{2+} \xrightarrow{k_5} HO_2^- + Fe^{3+} \quad (5)$$

leading to an overall rate expression at high $H_2O_2/Fe^{3+}$ ratios.

$$-d[H_2O_2]/dt = 2(k_1k_2k_4/k_5)^{1/2}[H_2O_2][Fe^{3+}] \quad (6)$$

More recently, Kremer and Stein[4] have proposed an alternative path not involving HO· or $Fe^{2+}$, but a series of intermediate complexes.

$$H_2O_2 + Fe^{3+} \rightleftharpoons H^+ + FeOOH^{2+} \longrightarrow HO^- + FeO^{3+} \xrightarrow{H_2O_2} O_2 + H_2O + Fe^{3+} \quad (7)$$

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[2] Visiting Professor on leave from the University of Port Elizabeth, Republic of South Africa.

[3] W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 591 (1951).

[4] M. L. Kremer and G. Stein, *ibid.*, **55**, 595 (1959); M. L. Kremer, *ibid.*, **58**, 702 (1962); **59**, 2535 (1963).

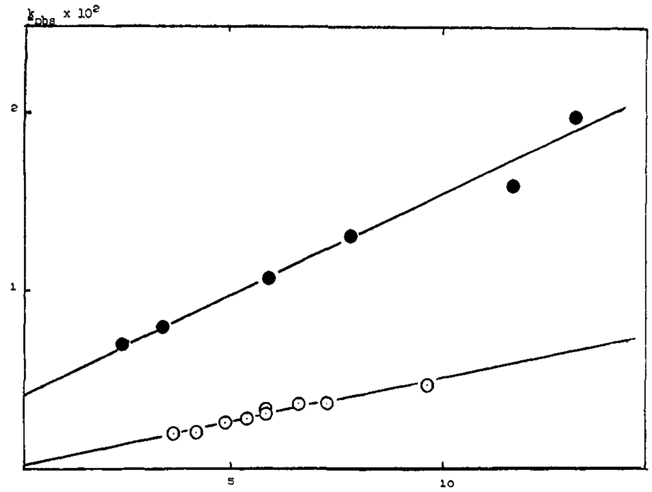

Figure 1. Effect of acetone on the $Fe^{3+}$-catalyzed decomposition of $H_2O_2$: (●) $H_2O_2$ consumption; (○) $O_2$ evolution; $[H^+]$, 1.92 × $10^{-2}$ *M*; $[Fe^{3+}]$, 3.92 × $10^{-3}$ *M*; $[H_2O_2]$, 3.92 × $10^{-1}$ *M*; temperature 30°.

Although both schemes predict second-order kinetics at high $H_2O_2/Fe^{3+}$ ratios[5] and an inverse dependence on $[H^+]$,[6] a recent review[7] favors the Kremer and Stein formulation.

Addition of organic substrates alters the rate of the decomposition, and Kremer[8] has interpreted its retardation by acetone as support for (7). However, our recent work[9-12] on $Fe^{2+}$–$H_2O_2$–organic substrate systems has suggested to us that organic substrates should act as HO· radical traps in the Barb scheme, and alter the kinetics in a predictable manner.

Specifically, they introduce the step

$$HO\cdot + RH \xrightarrow{k_6} H_2O + R\cdot \qquad (8)$$

which (in light of the rates of $O_2$ evolution discussed below) we propose is followed in $O_2$ saturated solutions by

$$R\cdot + O_2 \longrightarrow RO_2\cdot \xrightarrow[H^+]{Fe^{2+}} ROOH + Fe^{3+} \qquad (9)$$

If the reaction is *strongly* retarded, (8) replaces (9) as the termination step, leading, with the usual steady-state assumptions for transient intermediates, to the rate expressions

$$-d[H_2O_2]/dt = 2k_1[H_2O_2][Fe^{3+}] \times (1 + (k_3/k_6)[H_2O_2]/[RH]) \qquad (10)$$

$$d[O_2]dt = (k_1k_3/k_6)[H_2O_2]^2[Fe^{3+}]/[RH] \qquad (11)$$

From (10) and (11) plots of observed second-order rate constants, $k_{obsd}$, for $H_2O_2$ disappearance or $O_2$ evolution *vs.* $[H_2O_2]/[RH]$ should be linear with intercepts of $2k_1$ and zero, respectively, and with slopes differing by a factor of 2. Furthermore, while intercepts in plots of (10) should be pH dependent, they should be independent of RH; *i.e.*, limiting rates at high substrate concentration should be independent of the substrate involved.

In this paper, we show that the predicted behavior is observed for several organic materials, that the data yield values for $k_3/k_6$ consistent with other measurements, and that failure in some other systems is plausibly accounted for on the basis of expected reactions not included in the kinetic scheme just given.

**Acetone** was examined in greatest detail in view of Kremer's conclusions[8] and since we have recently investigated its reaction with hydroxyl radicals ourselves.[10,11] Typical results in which $k_{obsd}$'s have been calculated from initial reaction rates are shown in Figure 1. Since $k_{obsd}$ for the unretarded reaction under these conditions is 12 × $10^{-2}$ l./(mol sec), our assumption of strong retardation should be valid, and we see that the data yield the predicted linear plots with zero intercept for $O_2$ evolution and a ratio of slopes close to 2 (2.08).

Table I. $Fe^{3+}$-Catalyzed Decomposition of $H_2O_2$ in the Presence of Acetone[a]

| $10^2[H^+]$ | $10^3[Fe^{3+}]$ | $10[H_2O_2]_0$ | $10^3k_1$, $M^{-1}$ sec$^{-1}$ | $k_3/k_6$ |
|---|---|---|---|---|
| 1.96 | 3.92 | 3.92 | 2.03 | 0.26[b] |
| | 2.94 | 3.92 | 1.88 | 0.21[b] |
| | 1.96 | 3.92 | 2.24 | 0.24[b] |
| | 3.92 | 3.92 | 2.15 | 0.26 |
| | 3.92 | 3.92 | 2.10 | 0.26 |
| | 3.92 | 1.96 | 1.90 | 0.34 |
| | 3.92 | 0.118 | 1.60 | 0.33 |
| | 36.5 | 0.472 | 2.60 | 0.26 |
| | 18.3 | 0.944 | 1.96 | 0.28 |
| | 7.81 | 1.56 | 1.85 | 0.28 |
| 0.491 | 3.92 | 3.92 | 5.75 | 0.23 |
| 0.392 | 3.92 | 3.92 | 4.52 | 0.21 |
| 7.16 | 3.92 | 3.92 | 0.575 | 0.24 |
| 1.96 | 3.65 | 4.68 | 11.7 | 0.20[c] |
| | 3.65 | 4.68 | 0.45 | 0.17[d] |
| | 36.5 | 4.57 | 0.134 | 0.20[e] |
| | 3.92 | 3.92 | 3.26 | 0.51[f] |
| | 3.92 | 3.92 | 2.22 | 0.19[g] |

[a] Unless indicated, all experiments at 30° with $ClO_4^-$ salts in $HClO_4$, ionic strength adjusted to 0.435 with $NaClO_4$. All units in liters, moles, and seconds. [b] Nitrate anion. [c] 39.5°. [d] 20.5°. [e] 13°. [f] $CD_3COCD_3$ in place of acetone. [g] 1.09 × $10^{-4}$ *M* $Cu^{2+}$ added.

Table I summarizes data for $H_2O_2$ consumption taken over a wider variety of conditions. Each value was taken from a plot similar to Figure 1. All were satisfactorily linear, and the data show consistent values of $k_1$ and $k_3/k_6$ for a 100-fold change in initial ratios of $H_2O_2$ to iron with other variables held constant (standard deviations for both $k_1$ and $k_3/k_6$ are 4–5% of measured values). Experiments at varying acidities show $k_1 \sim 1/[H^+]$, but $k_3/k_6$ independent of $[H^+]$ as predicted. Similarly, changes in temperature affect chiefly $k_1$, the slow step, and have little effect on $k_3/k_6$ which measures the ratio of rates of two fast, low-activation energy

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(5) Deviations from second-order kinetics at low $H_2O_2/Fe^{3+}$ ratios are at least partially accounted for by both schemes; in the chain process by incursion of the step $HO\cdot + Fe^{2+} \rightarrow HO^- + Fe^{3+}$.

(6) In the chain process $k_1$ and $k_4$ are complex, and presumably involve prior equilibria, *e.g.*

$$Fe^{3+} + H_2O_2 \rightleftharpoons H^+ + FeOOH^{2+} \longrightarrow Fe^{2+} + HO_2\cdot$$

$$HO_2\cdot \rightleftharpoons H^+ + O_2\cdot^- \xrightarrow{Fe^{3+}} O_2 + Fe^{2+}$$

and rates of both should be proportional to $1/[H^+]$.

(7) S. B. Brown, P. Jones, and A. Suggett, *Progr. Inorg. Chem.*, **13**, 159 (1970).

(8) J. M. Flicstein and M. L. Kremer, *J. Catal.*, **8**, 145 (1967).

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

(10) G. M. El-Taliawi, Ph.D. Dissertation, Columbia University, 1972.

(11) C. Walling and G. M. El-Taliawi, *J. Amer. Chem. Soc.*, **95**, 844 (1973).

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

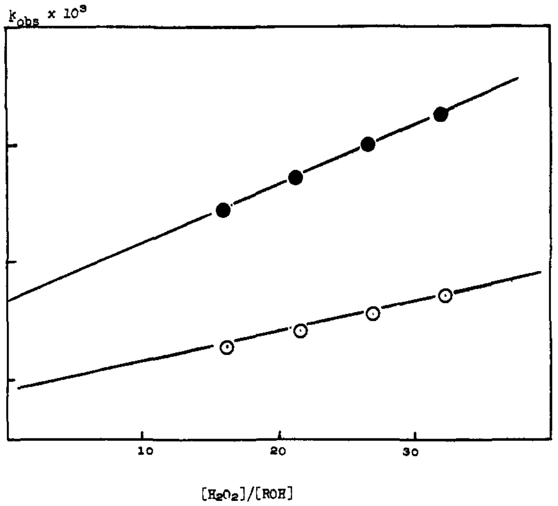


Figure 2. Effect of *tert*-butyl alcohol on $Fe^{3+}$-catalyzed decomposition of $H_2O_2$: (●) $H_2O_2$ consumption; (○) $O_2$ evolution. Conditions the same as Figure 1.

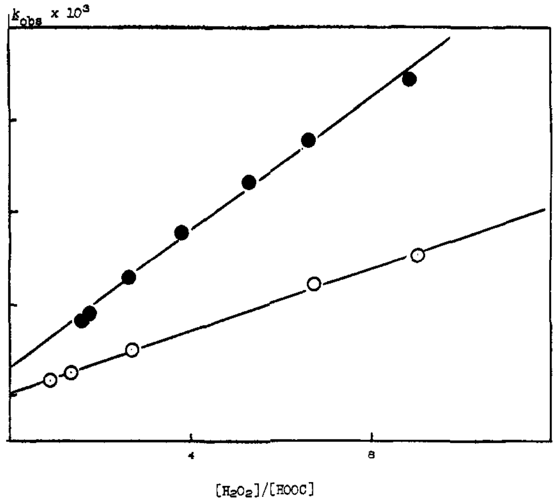


Figure 3. Effect of acetic acid on the $Fe^{3+}$-catalyzed decomposition of $H_2O_2$: (●) $H_2O_2$ consumption; (○) $O_2$ evolution. Conditions the same as Figure 1.

processes. From our data over a 27° temperature range, $E_1 = 30$ kcal/mol and $A_1 = 8.43 \times 10^{18}$ sec$^{-1}$.

Experiments with perdeuterioacetone and added $Cu^{2+}$ also give results consistent with our scheme. The former show an isotope effect $k_H/k_D \cong 2$ on $k_3/k_6$ and little effect on $k_1$. In the case of added copper, it should be pointed out[3] that $Cu^{2+}$ alone is only a weak catalyst for peroxide decomposition, but has a strong synergistic effect on the $Fe^{3+}$ catalyzed reaction in the absence of organic substrate. In the radical chain formulation this is accounted for[3] by the replacement of (4) by a more rapid sequence

$$HO_2\cdot + Cu^{2+} \longrightarrow H^+ + O_2 + Cu^+ \xrightarrow{Fe^{3+}} Cu^{2+} + Fe^{2+} \quad (12)$$

However, in the rate expression for the retarded reaction (eq 10), $k_4$ no longer appears, so copper should have no effect. This is precisely what we observe, although the amount employed increases $k_{obsd}$ for the *unretarded* reaction severalfold.

Finally, our average value of $k_3/k_6$ (0.24) may be compared with quite independent measurements derived from radiation chemistry. Here the agreement is quite satisfactory, but discussion is deferred to a later section, where data on several substrates are compared.

We have also examined the products formed in the retarded reaction. Contrary to Kremer's inference,[8] acetone is oxidized, and we have identified hydroxyacetone and acetic acid among the products. The presumed initial product, hydroperoxyacetone, evidently reacts further, which is not surprising since it should be more readily attacked by hydroxyl radicals than acetone itself, and could also undergo both $Fe^{2+}$ initiated decomposition and an acid-catalyzed cleavage to acetic acid analogous to the known base-catalyzed reactions of similar compounds.[13]

$$RCOCH_2OOH \longrightarrow RCOOH + CH_2O \quad (13)$$

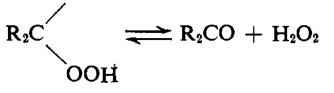
***tert*-Butyl Alcohol.** From our measurements,[11] *tert*-butyl alcohol is 5.5 times as reactive as acetone toward hydroxyl radicals generated from $Fe^{2+}$–$H_2O_2$. It should thus be a stronger retarder of $H_2O_2$ decomposition at low concentration, but should yield the same limiting rate as the ratio $[H_2O_2]/[RH]$ is increased. Typical results are shown in Figure 2, and averaged results of two sets of measurements give $k_1 = 1.34 \times 10^{-3}$ and $k_1k_3/k_6 = 9.7 \times 10^{-5}$. Again added $Cu^{2+}$ had no effect on the retarded rates. Product studies show extensive substrate oxidation. Acetone and 2-methylpropane-1,2-diol were identified as products, and an organic peroxide (presumably 1-hydroperoxy-2-methyl-2-propanol) detected by thin layer chromatography.

**Acetic Acid.** From our analysis, acetic acid should be a relatively weak retarder of $H_2O_2$ decomposition since its reactivity toward hydroxyl radicals is only 0.275 that of acetone.[11] Results, Figure 3, show this to be the case and give $k_1 = 1.5 \times 10^{-3}$ and $k_1k_3/k_6 = 1.8 \times 10^{-3}$. Product studies indicated almost complete degradation to $CO_2$, since no methanol, formaldehyde, formic acid, oxalic acid, or glycolic acid could be detected among the products.

**Other Substrates.** Although we find that all organic substrates which we have investigated retard the $Fe^{3+}$ catalyzed decomposition of $H_2O_2$, all do not obey the simple scheme which we have applied to the cases discussed so far. Indeed it would be surprising if they did in view of the great number of possible reactions we have excluded from our analysis. Methanol (and other alcohols with available α hydrogens) provides an example. Here two complications could, *a priori*, arise: competition with (9) by the fast oxidation of α-hydroxy radicals by $Fe^{3+}$ [9]

$$R_2\dot{C}OH + Fe^{3+} \longrightarrow R_2CO + Fe^{2+} \quad (14)$$

and (for those radicals which do react with $O_2$) regeneration of $H_2O_2$ *via* the facile equilibrium


$$R_2C(OH)(OOH) \rightleftharpoons R_2CO + H_2O_2 \quad (15)$$

Reaction 14, since it introduces an alternative chain propagation step, should increase $k_{obsd}$ above its predicted value, while (15) by regenerating starting material should decrease $k_{obsd}$. Some actual methanol results are shown in Figure 4. The plots are linear and

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(13) R. van Helden and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, 80, 57 (1961).

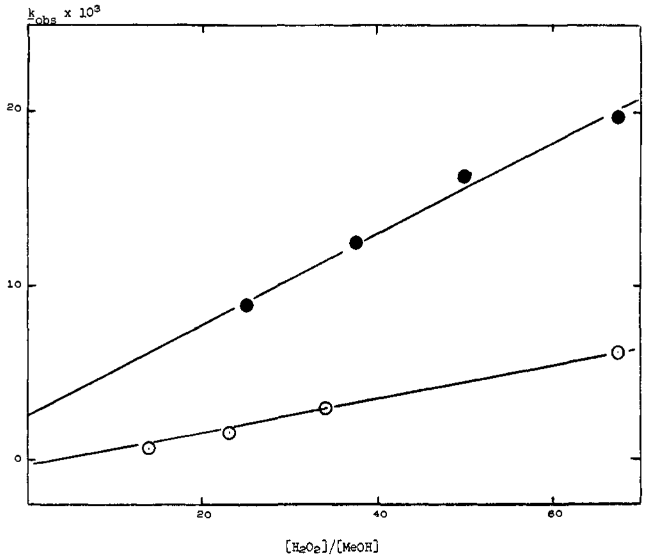

Figure 4. Effect of methanol on the $Fe^{3+}$-catalyzed decomposition of $H_2O_2$: (●) $H_2O_2$ consumption; (○) $O_2$ evolution. Conditions the same as Figure 1.

show approximately the correct intercepts and 2:1 ratio of slopes, but slopes are considerable larger than calculated,[14] methanol is a poorer retarder than expected, presumably because of the importance of (14), and isopropyl alcohol gives qualitatively similar results.

## Discussion

We have seen that the retardation of $H_2O_2$ decomposition by several organic substrates shows a dependence on $H_2O_2$/substrate ratios consistent with our kinetic scheme, and that, in the case of acetone, results vary as predicted over considerable changes in concentration, pH, and temperature. A further test of our model is in the consistency of results obtained with different substrates for which our model is obeyed. Our results are summarized in Table II where we see that, in spite of a 20-fold change in $k_3/k_6$, $k_1$ remains substantially constant as it must for the scheme to be valid.[15]

**Table II.** Summary of Rate Constants

| Substrate | $10^3k_1$ | $k_3/k_6$ | Lit.$^a$ | $k_6$ rel | Lit.$^a$ | $Fe^{2+}$–$H_2O_2$$^b$ |
|---|---|---|---|---|---|---|
| Acetone | 2.0 | 0.27 | 0.53 | (1.0) | (1.0) | (1.0) |
| *tert*-Butyl alcohol | 1.34 | 0.048 | 0.096 | 5.6 | 5.5 | 5.5 |
| Acetic acid | 1.5 | 0.9 | 0.38 | 0.30 | 0.72 | 0.275 |

$^a$ Calculated from ref 16. $^b$ From ref 9 and 11.

Our values of $k_3/k_6$ may next be compared with the extensive, if scattered, values available from radiation chemistry. Here a recent critical summary has been prepared by Dorfman and Adams,[16] updating and revising an earlier compilation by Anbar and Netta.[17] Dorfman and Adams give $k_3(H_2O_2) = 4.5 \times 10^7$; $k_6$(acetone) = 6.6–12 × $10^7$, av 8.5 × $10^7$; $k_6$(*tert*-butyl alcohol) = 4.2–5.2 × $10^8$, av 4.7 × $10^8$; $k_6$(acetic acid) = 0.9–2.3 × $10^7$, av 1.7 × $10^7$. Ratios of $k_3/k_6$ using average values are listed in Table II, and are in the correct order but differ by as much as a factor of 2. A somewhat better check is obtained by comparing relative values of $k_6$, and better still using relative values of $k_6$ derived from our own experiments on $Fe^{2+}$–$H_2O_2$ systems, all of which have been determined relative to the same process, the $Fe^{2+}$–HO· reaction

$$Fe^{2+} + HO\cdot \longrightarrow Fe^{3+} + HO^- \qquad (16)$$

In view of the spread in radiation results, we feel that the agreements shown in the table are adequate to support our general model. To accommodate our results to a "complex" mechanism would require that all our correlations were simply coincidence, and further it would be remarkable if a variety of organic substrates all led to the same extrapolated rates (our $k_1$'s) when the intermediates became completely "complexed."[18]

If our scheme is accepted, we obtain an average value of $k_1 = 2 \times 10^{-3}$ l./(mol sec) in 0.02 *N* perchloric acid at 30°. However, this value is actually inversely proportional to [$H^+$], most plausibly because it involves the sequence

$$H_2O_2 + Fe^{3+} \overset{K}{\rightleftharpoons} FeOOH^{2+} + H^+ \qquad (17)$$

$$FeOOH^{2+} \xrightarrow{k_{18}} Fe^{2+} + HO_2\cdot \qquad (18)$$

The value of *K* has been reported by Evans, George, and Uri as 3.65 × $10^{-3}$ at 20°.[19] Ignoring the effect of a 10° change in temperature on *K*, $k_{18} \cong 1.1 \times 10^{-2}$ $sec^{-1}$.

Although our results support the scheme of Barb, *et al.*, for the $Fe^{3+}$–$H_2O_2$ reaction, our value of $k_1$ indicates that some of their numerical values for rate constants must be in error. They calculated $k_4/k_5$ (their $k_4/k_3$) from measurements on the $Fe^{2+}$–$H_2O_2$ system on the basis of small deviations from pseudo-first-order kinetics at high $H_2O_2/Fe^{2+}$ ratios, obtaining 0.26 in 0.02 *M* acid.[20] From this $k_1$ may be calculated *via* eq 6 as 4.5 × $10^{-5}$. We reverse the procedure and taking $k_{obsd} = 1.2 \times 10^{-1}$ for the unretarded reaction, $k_1 = 2 \times 10^{-3}$ and $k_2 = 76.5$[21] obtain, *via* eq 6, $k_4/k_5 = 0.024$. As Barb, *et al.*, point out, their values indicate that the decomposition occurs *via* very long chains, with chain lengths of ~$10^3$. On the other hand, our value of $k_1$ gives a chain length of 30 (the ratio of rates for the unretarded and completely retarded reaction), a result much more consistent with the much shorter chains reported by Behar and Stein[22] for the photoinduced process. This conclusion provides further support to our formulation since it removes an inconsistency which has been used as an argument against the Barb, *et al.*, scheme.[7,22] Our value of $k_4/k_5$ is also in better agreement with values (0.3 at pH 2.7 and 0.11

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(14) Since, from our data,[11] methanol is 12.4 times as reactive as acetone toward HO·, $k_3/k_6$ should be 0.022, but Figure 4 gives 0.08.

(15) Our average value of $k_1$, 2 × $10^{-3}$, was used in calculating $k_3/k_6$'s in Table II, since (*cf.* Table I) individual values scatter considerably.

(16) 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.

(17) M. Anbar and P. Netta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

(18) Flicstein and Kremer's equations[6] are quite different from ours, but their acetone concentrations were too low to lead to "strong" retardation, so the data are not comparable.

(19) M. G. Evans, P. George, and N. Uri, *Trans. Faraday Soc.*, **45**, 230 (1949).

(20) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *ibid.*, **47**, 462 (1951).

(21) T. J. Hardwick, *Can. J. Chem.*, **35**, 428 (1957).

(22) B. Behar and G. Stein, *Science*, **154**, 1012 (1966).

at pH 2.0) reported by Allen, Hogan, and Rothschild from radiation results.[23]

Finally, we should emphasize that our conclusions as to a redox chain process apply only to aquo Fe(III) in acid solution. Complexed Fe(III) in less acid media catalyzes $H_2O_2$ decomposition with rates which vary enormously with the ligands present, and often leads to concurrent oxidation of organic substrates.[7,24] While these reactions have usually been interpreted in terms of "complex" mechanisms, redox chains remain a possibility,[24] and we hope to extend our techniques to such systems in the future.

## Experimental Section

**Materials.** Stock solutions of reagents were prepared from analytical grade perchlorate and nitrate salts, perchloric and nitric acid, 30% $H_2O_2$, distilled under reduced pressure, and commercial organic reagents. All reaction mixtures were adjusted to an ionic strength of 0.435.

**Kinetic Measurements.** Reactions were carried out in magnetically stirred vessels thermostated at 30° or other temperatures, and followed by withdrawing aliquots at intervals, and quenching in dilute $H_2SO_4$ and titrating $H_2O_2$, usually with $KMnO_4$. Preliminary experiments without retarders gave decomposition rates in good agreement with literature results. Gas evolution experiments were carried out in similar vessels, previously saturated with $O_2$, connected to a gas-buret. After equilibration of the other components, $H_2O_2$ was injected into the system through a rubber septum. Ratios of rate constants cited were all obtained from least-squares fits to linear plots such as those shown, using initial values for peroxide decomposition.[25]

**Product analyses** were generally carried out on systems at substrate/$H_2O_2$ ratios of 4. After reaction $Fe^{3+}$ was removed either by treatment with Dowex 50 W-X8 ($H^+$ form) ion exchange resin, or neutralized with NaOH and filtered. Solutions were analyzed by flame ionization glc and products determined by isolation or retention times in comparison with known standards. Hydroxyacetone was further identified by tlc comparison of its 2,4-dinitrophenylhydrazone with authentic materials; organic peroxides were detected by tlc as described by Cartilidge and Tipper.[26]

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# Synthesis of Tritium- and Deuterium-Labeled Apomorphine[1a]

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**Abstract:** Tritium-labeled apomorphine was synthesized from morphine and apomorphine with specific activities of $3.62 \times 10^3$–$1.88 \times 10^5$ dpm/$\mu$g with labeling occurring predominantly on the aromatic rings as demonstrated by pmr and mass spectroscopy studies of apomorphine deuterated under identical conditions. By taking advantage of the large differences in exchange rates of various aromatic hydrogens as shown by pmr studies, one may label exclusively the catechol ring of apomorphine by controlling the reaction conditions.

The action of apomorphine (I) in alleviating the symptoms of parkinsonism[2] may be due to its structural analogy with 3,4-dihydroxyphenylethylamine (II)[3] and phenylethylamine (III). II acts as a dopaminergic neurotransmitter while phenylethylamine displaces neurotransmitters from cellular sites.[4] Some of the beneficial effects of 3,4-dihydroxyphenylalanine, a precursor of II,[5] are suspected to arise from its participation in the synthesis of tetrahydropapaveroline (IV) or the isomeric tetrahydroxynoraporphines (Va and Vb) which are analogs of I.[6] In turn, the structural relationship between I, IV, Va, and Vb suggests that some of the pharmacological properties of I may be due to its *in vivo* hydroxylation in ring A. In I the rings A and D constitute a biphenyl system which has been the subject of hydroxylation studies *in vitro* and *in vivo*.[7]

To test some of the above ideas and to study the distribution of I among animal organs and intracellular organelles, it became necessary to synthesize labeled

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