the HA-100 spectrometer are asterisked. IR spectra were taken with a Perkin-Elmer Model 257 spectrometer. Mass spectra were run on a single-focusing Hitachi Perkin-Elmer RMV-6 spectrometer. Preparative thin-layer chromatography (PTLC) was carried out on Merck silica gel 60 F_{254} precoated plates. Gas chromatograms were obtained by using a Varian Aerograph Model 920 preparative GLC with peak areas determined by triangulation. Compounds **1a–d**, **2a**, **3a**, **4a–c**, **5a,b**, **6a**, **7a,b**, **8a**, **9**, and **10** are all commercially available from Aldrich. The ^{1}H NMR and IR spectra of these compounds are found in the Aldrich libraries of NMR[27] and IR[28] spectra. An authentic sample of **6b** was graciously supplied by Professor Henry J. Shine of Texas Tech University. The spectral data of the remaining compounds (**2b,c**, **3b**, **4b**, and **8b**) are given below.

Preparation of *N*-Benzylanilines 2b,c. Compounds **2b,c** were synthesized according to literature methods[5] and characterized by their spectral data which follows.

2b: ^{1}H NMR* ($CDCl_3$) δ 2.23 (3 H, s), 3.69 (1 H, br s, NH), 4.27 (2 H, s), 6.53 (2 H, d, $J = 9$ Hz), 6.98 (2 H, d, $J = 9$ Hz), 7.32 (5 H, s); IR (neat) 3390 (s) 3010 (s), 2890 (s), 2840 (s), 1940 (w), 1850 (w), 1600 (s), 1570 (m), 1500 (s), 1480 (s), 1455 (s), 1440 (s), 1390 (m), 1345 (m), 1310 (s), 1285 (s), 1250 (s), 1235 (s), 1170 (s), 1110 (s), 1050 (m), 1015 (m), 980 (w), 900 (w), 795 (s), 730 (s), 685 (s) cm^{-1}; mass spectrum (70 eV), *m/e* 197 (M^+), 120 ($M^+ - C_6H_5$), 106 ($M^+ - C_6H_5CH_2$), 91 ($CH_3C_6H_4^+$), 77 ($C_6H_5^+$).

2c: ^{1}H NMR* ($CDCl_3$) δ 2.33 (3 H, s) 3.80 (1 H, br s, NH) 4.24 (2 H, s) 6.67 (3 H, m) 7.2 (7 H, m); IR ($CHCl_3$) 3400 (m), 3030 (s), 2990 (s), 2910 (m), 1900 (m), 1590 (s), 1490 (s), 1460 (m), 1415 (s), 1370 (w), 1345 (w), 1310 (s), 1235 (s), 1165 (s), 1140 (m), 1095 (m), 1080 (m), 1055 (m), 1010 (m), 980 (m), 915 (w), 860 (m), 79 (s); mass spectrum (70eV), *m/e* 197 (M^+), 105 ($M^+ - NHC_6H_5$), 77 ($C_6H_5^+$).

General Oxidation Procedure. The experimental procedures employed in this paper are typified by the following description of the reaction of potassium superoxide with *N*-benzyl-*p*-toluidine (**2b**). Powdered potassium superoxide (710 mg, 10 mmol) was added at 25 °C to a dry benzene solution (70 mL) containing **2b** (500 mg, 2.5 mmol) and 18-crown-6 polyether (1.36 g, 5.1 mmol) contained in a 250-mL flask equipped with Teflon-coated stirring bar and topped with a drying tube. The resulting mixture was stirred for 72 h, during which time the course of the reaction was followed by TLC. The reaction mixture was then acidified with 10% HCl and extracted three times with 10% $NaHCO_3$ solution to remove inorganic salts, crown ether, and acidic products. The organic layer containing the nonacidic products was dried over $MgSO_4$ and concentrated. The resulting mixture was separated into product components by preparative TLC on silica with 3:1 hexane–acetone solution as the eluent. The combined $NaHCO_3$ extracts were acidified and extracted three times with ether. The combined ether extracts were dried and concentrated, and the product components were likewise separated by preparative TLC as above. The identity of the various fractions was readily determined by comparison of their spectral data (NMR, IR, and MS) and physical properties (melting point and TLC retention time) with those of authentic samples. In addition to the various products listed in Table I, 242 mg (1.2 mmol, 52% conversion) of unreacted substrate was recovered. Several minor unidentified fractions were also present. Each reaction was repeated at least once, and the results were found to be generally reproducible. The runs with the highest product yield were incorporated into Tables I and II.

The yields of benzene and toluene in these reactions were determined by repeating the reaction on a smaller scale in ethylbenzene as the solvent containing an internal standard. Samples from the reaction mixture prior to workup were injected on a 33 ft × 0.25 in. copper column at 115 °C packed with 10% SE-30 on Chromosorb W AW DMCS.

3b: ^{1}H NMR ($CDCl_3$) δ 2.35 (3 H, s) 7.2, 7.5, and 7.8 (overlapping m, 9 H); mass spectrum (70 eV), *m/e* (relative intensity) 211 (M^+, 46), 120 ($M^+ - C_6H_4CH_3$, 14), 105 ($C_6H_5CO^+$, 100), 92 ($CH_3C_6H_5$, 14), 91 ($CH_3C_6H_4^+$, 12), 77 ($C_6H_5^+$, 57).

4b: ^{1}H NMR ($CDCl_3$) δ 2.43 (3 H,S) 7.23 and 7.7 (overlapping m, 9 H); mass spectrum (70 eV), *m/e* (relative intensity) 211 (M^+, 15), 119 ($CH_3C_6H_4CO^+$, 100), 91 ($CH_3C_6H_4^+$, 46).

8b: ^{1}H NMR ($CDCl_3$) δ 6.2 (1 H, br s, NH), 6.5 (1 H, m, H-4), 7.16 (1 H, d, $J = 3$ Hz, H-3), 7.47 (1 H, br s, H-5) (this spectrum is nearly identical with that of 2-furoic acid hydrazide[27]); mass spectrum (70 eV), *m/e* (relative intensity) 111 (M^+, 99.3), 95 ($M^+ - NH_2$, 100).

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Registry No. **1a**, 120-73-0; **1b**, 73-24-5; **1c**, 525-79-1; **1d**, 1214-39-7; **2a**, 103-32-2; **2b**, 5405-15-2; **2c**, 15818-64-1; **7a**, 100-46-9; **7b**, 617-89-0.

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[27] Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, 1974.

[28] Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 3rd ed.; The Aldrich Chemical Co.: Milwaukee, 1981.

Ferrous Ion Catalyzed Oxidations of 2-Propanol with Peroxyacetic Acid

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The ferrous ion catalyzed oxidations of 2-propanol by peroxyacetic acid are compared with the oxidations of 2-propanol with the Fenton reagent (ferrous ion and hydrogen peroxide). The peroxyacetic acid reactions are considerably faster than the hydrogen peroxide oxidations at similar concentrations of ferrous ion. Further, the peroxyacetic acid oxidations at low ferrous ion concentrations do not yield any detectable amounts of 2,5-hexanediol, a significant byproduct formed in the hydrogen peroxide oxidations when performed with sufficient ferrous ion present to achieve reaction rates comparable to those of the peroxyacetic acid oxidations at the low ferrous ion concentrations. These observations are discussed in terms of the hydrogen atom abstracting species encountered in these oxidation reactions.

The oxidations of secondary alcohols to ketones by organic peroxides has proven fruitful over the past 30 years in terms of providing insight into the behavior of free radicals as reaction intermediates.[2] Such studies have provided information concerning the reduction of the peroxide linkage by an intermediate α-hydroxyalkyl radical by its interaction with the peroxide either by hydrogen

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[1] Taken in part from the thesis submitted to the University of Kansas for the M.S. degree by G.W.H., 1979.

[2] P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, 69, 2299 (1947); M. S. Kharasch, J. R. Rowe, and W. H. Urry, *J. Org. Chem.*, 16, 905 (1951).

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Table I. Ferrous Ion Catalyzed Reactions of 2-Propanol with Peroxyacetic Acid

time, h	mol %			
	AcOOH	CH_3COCH_3 [a]	H_2O_2	AcOH
		Run 1 [b]		
0.75	64	54	4	
1.50	44	60		
2.40	39	69		
3.60	33	75	4	
14.5	17	92	4	
22.0	3	102	4	97
		Run 2 [c]		
1	66	36	3	
2.1	55	64	3	
3.6	37	70	3	
6.4	30	79	3	
19.0	20	91	3	
41.9	10	96	3	97.6

[a] Mole percent of reagent based on initial amount of peroxyacetic acid present. [b] 30 °C, $[Fe^{2+}] = 5.7 \times 10^{-5}$ M, initial [2-propanol] = 12.8 M; initial [AcOOH] = 0.20 M. [c] 30 °C, $[Fe^{2+}] = 5.3 \times 10^{-5}$ M; initial [2-propanol] = 12.8 M; initial [AcOOH] = 0.20 M.

Table II. Ferrous Ion Catalyzed Oxidation of 2-Propanol at 30 °C with Hydrogen Peroxide

time, h	mol % [a]	
	H_2O_2	CH_3COCH_3
	Run 1 [b]	
12.8	94	8
28	83	16
106	62	29
189	46	49
324	30	58
372	25	64
	Run 2 [c]	
4	98	3
9	94	7
24	77	18
333	26	71

[a] Mole percent of reagent based on initial amount of hydrogen peroxide present. [b] $[Fe^{2+}] = 6.1 \times 10^{-5}$ M; initial [2-propanol] = 1.25 M; initial $[H_2O_2]$ = 0.20 M. [c] $[Fe^{2+}] = 1.32 \times 10^{-4}$ M; initial [2-propanol] = 1.25 M; initial $[H_2O_2]$ = 0.2 M.

atom transfer reactions as observed in dialkyl peroxides[3,4] or by electron-transfer processes in reactions with acyl peroxides and peresters.[4] While oxidation of alcohols by hydrogen peroxide catalyzed by ferrous ions (Fenton's reagent) have also been carefully investigated,[5] metal ion catalyzed oxidations of alcohols to the carbonyl oxidation state with alkyl hydroperoxides[6] and peroxycarboxylic acids[7] have received considerably less attention. The present work describes the ferrous ion oxidation of 2-propanol with peroxyacetic acid. For comparison purposes, we have also reexamined certain aspects of the Fenton reagent oxidations of this same alcohol.

Results

The reactions of peroxyacetic acid with 2-propanol catalyzed by small amounts of ferrous ion were examined both in terms of the products produced and the rate of the reaction. The peroxyacetic acid used in these studies was prepared in our laboratory by the sulfuric acid catalyzed reaction of glacial acetic acid with hydrogen peroxide. The distilled reagent was subjected to quantitative analysis (see Experimental Section) before use in each case and consisted of about 70% peroxyacetic acid, 20% acetic acid, 0.2–3% hydrogen peroxide, and the remainder water. Reactions of this material with 2-propanol yielded acetic acid and acetone as the reaction products,

$$CH_3CO_3H + (CH_3)_2CHOH \rightarrow (CH_3)_2C{=}O + CH_3CO_2H + H_2O \quad (1)$$

the quantitative analysis of the former achieved by potentiometric titration with NaOH and that of the latter by gas chromatographic analysis of the reaction mixture. The absolute quantitative data obtained (Table I) by these procedures generally showed a somewhat greater than stoichiometric amount of acetone produced than peroxyacetic acid consumed. This discrepancy most likely reflects the inadequacies of the gas chromatographic procedure employed to determine the amount of acetone. Oxidations of 2-propanol with H_2O_2 at similar concentrations of ferrous ion were comparatively very slow (Table II), many days being required for the same extent of reaction observed in the peroxyacetic acid oxidations after a few hours.

Table III lists further observations made for the peroxyacetic acid and hydrogen peroxide oxidation reactions of 2-propanol. Although acetone was observed in each case, the discrepencies in the amounts of acetone actually observed reflect both the problems encountered in its gas chromatographic analysis and the fact that under these reaction conditions (pH $\simeq$1) some of the acetone may have undergone condensation. At higher concentrations of ferrous ion (0.17 M), the hydrogen peroxide oxidations of 2-propanol were completed in comparatively short times (~1 h). Although high yields of acetone were observed (70–75% based on initial H_2O_2 concentration), the reaction products also showed the presence of 2,5-hexanediol (ca. 3–5% based on initial H_2O_2 concentration) and trace amounts of 1,2-propanediol. These observations are consistent with those reported by Walling and Kato.[5c] Our gas chromatographic technique for the analysis of 2,5-hexanediol allowed for detection of this material in quantities as low as 0.1 mol % of the initial peroxide concentrations. It is pertinent that in the oxidations of 2-propanol with both peroxyacetic acid and hydrogen peroxide at low ferrous ion concentrations no 2,5-hexanediol could be detected in any of our reactions. However, we did observe this product in peroxyacetic acid oxidations of 2-propanol when the ferrous ion concentrations was 0.1 M. In these very rapid reactions, acetic acid was produced in stoichiometric amounts relative to the peroxyacetic acid consumed and the yields of acetone approached 70% on the basis of the initial peroxide concentration. It should also be pointed out that while cobaltous ion catalyzed the oxidations of 2-propanol with peroxyacetic acid at both low and high concentration levels, no detectable amounts of 2,5-hexanediol were observed in either case.

Discussion

The most striking features of our observations are that (1) the peroxyacetic acid oxidations of 2-propanol proceed rapidly at even low concentration levels of the metal ion catalysts in contrast to the hydrogen peroxide oxidations,

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(6) R. Hiatt, K. C. Irwin, and C. W. Gould, *J. Org. Chem.*, **33**, 1490 (1968).

(7) Celanese Corp. of America, British Patent 900 831, July 11, 1962; *Chem. Abstr.* **58**, 452a (1963).

Table III. Metal Ion Catalyzed Oxidations of 2-Propanol at 30 °C

oxidant (concn)[b]	[2-propanol]	metal ion (concn)	time, h	peroxide reacted	mol %[a]		
					acetone	AcOH	diol
AcOOH (0.2)	1.25	Fe^{2+} (5.7 × 10^{-5})	120	99	43	94	0
AcOOH (0.2)	1.25	Fe^{2+} (5.1 × 10^{-5})	62.7	82	53	95	0
AcOOH (0.25)	1.25	Fe^{2+} (0.1)	~1	100	*c*	*c*	3-5[d]
AcOOH (0.25)	1.25	Fe^{2+} (0.1)	~1	100	68	97	3-5[d]
AcOOH (0.25)	1.25	Co^{2+} (5.9 × 10^{-5})	6.2	*c*	90	*c*	0
H_2O_2 (0.25)	1.25	Fe^{2+} (0.1)	~1	100	72		3-5[d]
H_2O_2 (0.25)	1.25	Fe^{2+} (0.18)	~1	100	70		3-5[d]

[a] Mole percent of reagent based on initial amount of peroxide. [b] Concentrations in moles per liter. [c] Not determined. [d] 2,5-hexanediol with trace amounts of 1,2-propanediol.

which are slow at these low concentration levels, and (2) the formation of the byproduct 2,5-hexanediol is observed only at comparatively high concentration levels of ferrous ion for both peroxyacetic acid and hydrogen peroxide oxidations of 2-propanol. The facility with which the peroxyacetic acid oxidation occurs suggests a long kinetic chain length for the reactions in contrast to a considerably shorter kinetic chain length for the hydrogen peroxide oxidations. A mechanism for the ferrous ion catalyzed peroxyacetic acid oxidation of 2-propanol that is consistent with these observations is shown in eq 2–4. The key step

$$Fe^{2+} + AcOOH \rightarrow Fe^{3+} + AcO^- + HO\cdot \quad (2)$$

$$HO\cdot + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH \quad (3)$$

$$(CH_3)_2\dot{C}OH + Fe^{3+} \rightarrow (CH_3)_2C{=}O + H^+ + Fe^{2+} \quad (4)$$

in this mechanism is the reduction of peroxyacetic acid by the ferrous ion to yield the acetate ion and an hydroxy radical, a reaction that would be expected to occur not only in the manner shown owing to the stability of the acetate ion but also far more readily than the corresponding reduction of hydrogen peroxide by ferrous ion. That this is the case is evidenced not only by a difference in the rate of oxidation of 2-propanol by peroxyacetic acid and hydrogen peroxide but also by the fact that the peroxyacetic acid oxidations occur in the presence of hydrogen peroxide without any significant reaction of the hydrogen peroxide. Such a result is not surprising in terms of the reduction potentials reported for peroxyacetic acid ($E_{1/2}$ = +0.20 relative to a standard calomel electrode)[8] and hydrogen peroxide ($E_{1/2}$ = −0.88 to −1.03).[9] Thus, for a similar chain process for the oxidation of 2-propanol by hydrogen peroxide, the reduction of the hydrogen peroxide would be

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + HO^- \quad (5)$$

the limiting step. At very low ferrous ion concentrations, it is also possible that the peroxide may be reduced, at least in part, by the α-hydroxyalkyl radical. In the case of the

$$(CH_3)_2\dot{C}OH + AcOOH \rightarrow (CH_3)_2C{=}O + H^+ + AcO^- + HO\cdot \quad (6)$$

peroxyacetic acid reactions, the process would likely be an electron-transfer reaction[4] and be expected to proceed more readily than reduction of hydrogen peroxide by the α-hydroxyalkyl, a process that may possibly involve the slow hydrogen atom transfer to the peroxide linkage.[3]

$$(CH_3)_2\dot{C}OH + H_2O_2 \rightarrow (CH_3)_2C{=}O + H_2O + HO\cdot \quad (7)$$

In any case, these mechanisms all require the formation of the free hydroxyl radical as the species that reacts with the alcohol in a chain-propagating reaction (eq 3) to yield the chain-carrying α-hydroxyalkyl radical. The very long kinetic chain lengths for the peroxyacetic acid oxidations suggest that this hydrogen atom abstraction by the hydroxyl radical is highly specific in that only the α-hydrogen atom of the alcohol undergoes reaction. Abstraction of a β-hydrogen atom would yield the β-hydroxyalkyl radical, a species that would not be expected to react either with the peroxide[2] or with the ferric ion.[5c,10] Rather, as has been demonstrated most effectively by Walling and Kato, under these conditions the β-hydroxyalkyl radicals should be expected to dimerize to yield 2,5-hexanediol, a product not

$$2CH_3CHOHCH_2\cdot \rightarrow CH_3CHOHCH_2CH_2CHOHCH_3 \quad (8)$$

formed in detectable quantities in the peroxyacetic acid oxidation of 2-propanol at low ferrous ion concentrations. It is also significant that this oxidative dimer was not observed in the hydrogen peroxide oxidations at low ferrous ion concentrations. However, at ferrous ion concentrations of the order of 0.1 M, 2,5-hexanediol is observed as a reaction product for both peroxyacetic acid and hydrogen peroxide oxidation of 2-propanol. Although Walling and Kato concluded that the formation of this diol indicated attack at a β-hydrogen of 2-propanol by the hydroxyl radical in their Fenton reagent oxidations of 2-propanol, this conclusion is not consistent with the high specificity displayed by this radical in abstracting only α-hydrogens in the peroxyacetic acid oxidations of 2-propanol at low ferrous ion concentrations.

The observations that β-hydrogen atom abstraction does occur in both peroxyacetic acid and hydrogen peroxide oxidations of 2-propanol at the higher concentrations of ferrous ion does deserve some comment. If the abstraction of a nonactivated β-hydrogen atom is not ascribed to a hydroxyl radical reaction, the question remains as to what is the highly reactive species responsible for this reaction. The data available from our work do not allow for any fruitful speculation as to the nature of this reactive hydrogen abstracting species other than that it may well involve either ferrous or ferric ions since the β-hydrogen atom abstraction is observed only in those reactions performed at the initial higher ferrous ion concentrations.

The high degree of selectivity in abstracting the α-hydrogen from 2-propanol displayed by the hydroxyl radical in the peroxyacetic acid oxidations of this alcohol is probably not unexpected in terms of both the polar character of the species and the protic medium in which these reactions were performed. The gas-phase kinetic data reported for the hydroxyl radical do not suggest that this species should be highly selective in hydrogen atom

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[9] G. E. O. Proske, *Anal. Chem.*, **24**, 1834 (1952); S. S. Kalbag, K. A. Narayan, S. S. Chang, and F. A. Kummerow, *J. Am. Oil Chem. Soc.*, **32**, 271 (1955); M. F. Romantsev and E. S. Levin, *J. Anal. Chem. USSR (Engl. Transl.)*, **10**, 297 (1939).

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abstraction reactions from alkanes (k_{sec}/k_{pri} = ~10 and k_{tert}/k_{pri} = ~36 at 25 °C).[11] However, a polar factor involving the electron-donor characteristics of the alcohol and electron-acceptor qualities of the hydroxyl radical may markedly lower the activation energy requirement for the abstraction of an α-hydrogen from the alcohol by the hydroxyl radical. The very long kinetic chain lengths observed in reactions involving the *tert*-butoxyl radical with secondary alcohols strongly suggest that this radical displays a high degree of selectivity toward the α-hydrogens of alcohols.[12] It is also possible that the reactivity of the hydroxyl radical in protic solvents is moderated by extensive hydrogen bonding with the solvent and would therefore be expected to display kinetic properties different from those observed in the gas-phase reactions of this species.

Experimental Section

Reagents. Hydrogen peroxide (Fisher, 30% aqueous solution) and acetic acid (Fisher, Anal. Reagent Grade) were used without further purification. Isopropyl alcohol (Mallinckrodt, Anal. Reagent Grade) was refluxed over stannous chloride, distilled from calcium oxide, and stored under nitrogen. Before using, it was subjected to gas chromatographic analysis to assure the absence of any acetone. An authentic sample of 2,5-hexanediol was prepared by sodium borohydride reduction of 2,5-hexanedione (Eastman Kodak). Ferrous ammonium sulfate and ferrous sulfate (Fisher, ACS Certified) were used without further purification.

Peroxyacetic Acid. The peroxyacetic acid used in this work was prepared by careful addition of glacial acetic acid (51 g, 0.85 mol) to a solution of 0.5 mol of hydrogen peroxide (30% solution) in 57 mL of concentrated sulfuric acid. The resulting solution was refluxed at 20 °C at 11 torr for 20 min and then distilled through a 20-cm column packed with glass helices. The first 5 mL of distillate were discarded. The remaining distillate was collected at 22 °C at 11 torr and amounted to 40 mL. Analysis (see below) showed this material to be 71% by weight peroxyacetic acid, 20.2% acetic acid, and 0.22% hydrogen peroxide.[13] The analytical procedure indicated no diacetyl peroxide was present. The remainder (8.38% by weight) was assumed to be water.

Differential Peroxide Determination. The hydrogen peroxide, peroxyacetic acid, and acetyl peroxide content of the starting reagent and of the reaction mixtures was determined by the method of Greenspan and MacKellar.[14] This method consisted of determining the hydrogen peroxide content by titration with standardized ceric sulfate solution to a ferroin indicator endpoint. The peroxyacetic acid content of the resulting solution was obtained by determining at room temperature the iodine liberated from a 10% potassium iodide solution added to the mixture. Acetyl peroxide concentration, although not present in our samples, can be determined from the amount of iodine resulting from heating the reaction mixture. All initial peroxide determinations were performed in triplicate. Corresponding blank solutions were also run.

Acetic acid was determined by potentiometric titration with standardized sodium hydroxide.

Oxidations of 2-Propanol with Peroxyacetic Acid and Hydrogen Peroxide. The following general procedure was employed for these oxidation reactions. All reactions involving the higher concentrations of ferrous ion were performed in an aqueous medium required to dissolve the ferrous salts at pH of about 1. The lower concentrations of ferrous ion were attainable in solutions consisting mainly of the alcohol. In all cases, the peroxidic reagent (peroxyacetic acid or 30% hydrogen peroxide) was weighed out into a volumetric flask with the 2-propanol. The ferrous ion was added, either as aqueous solution or weighed out salt, and dissolved in the mixture, which was then diluted to adjust the concentration. At the time intervals indicated (see Tables I–III) aliquots were removed, the peroxide content was measured as described, and the acetone content was determined by gas chromatrographic analysis on a polyglycol column (Dow E600 on Chromasorb W) using benzene or 2-butanone as the internal standard. A sample was also analyzed by gas chromatography on a Carbowax 20M on Chromasorb W for the 2,5-hexanediol. At the end of the reaction, an aliquot of the mixture was subjected to a potentiometric titration with standard sodium hydroxide solution to determine the total amount of acetic acid so that the acetic acid produced in the reaction could be determined.

Registry No. 2-Propanol, 67-63-0; peroxyacetic acid, 79-21-0; hydrogen peroxide, 7722-84-1; ferrous ion, 15438-31-0; 2,5-hexanediol, 2935-44-6; 2-propanone, 67-64-1; hydrogen, 1333-74-0; hydroxyl radical, 3352-57-6; ferrous ammonium sulfate, 10045-89-3; ferrous sulfate, 7720-78-7.

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Interaction of Electron-Deficient 1,2,4-Triazoline-3,5-diones with Electron-Rich Polyalkoxybenzenes

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4-Substituted-1,2,4-triazoline-3,5-diones have been found to form charge-transfer complexes with 1,3,5-trimethoxybenzene, 1,3-dimethoxybenzene, and 1,4-dimethoxybenzene but not with anisole. In the cases of 1,3,5-trimethoxybenzene and 1,3-dimethoxybenzene a reaction occurs to give aromatic substitution; the relative rates are 1,3,5-trimethoxybenzene > 1,3-dimethoxybenzene > 1,4-dimethoxybenzene. The rate of reaction of 4-butyl-1,2,4-triazoline-3,5-dione (*n*-BuTAD) with 1,3,5-trimethoxybenzene (TMB) *increases* with *decreasing* temperature to give apparent activation parameters: $\Delta H^* = -5.9$ kcal/mol, $\Delta S^* = -78$ cal deg^{-1} mol^{-1}. The rate is also dependent on the length of time that solutions of the *n*-BuTAD are exposed to ambient light, suggesting involvement of the urazolyl radical. It is suggested that the overall rate expression is $-[d(n\text{-BuTAD})/dt] = k_1K_{eq}(n\text{-BuTAD})(\text{TMB})(\text{Ur}\cdot)$, where (Ur·) is the urazolyl radical concentration, K_{eq} is the equilibrium constant for charge-transfer complex formation, and k_1 is the rate constant for attack of Ur· on the charge-transfer complex.

In a previous paper, the reactions of 4-phenyl- and 4-alkyl-1,2,4-triazoline-3,5-diones (RTAD's) with vinyl ethers were examined, and evidence was presented that 1,4-dipoles are involved in the reactions.[1] However, changing

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