Permanganate oxidation of aromatic alcohols in acid solution[1]

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The mechanism of the permanganate oxidation of di- and tri-arylcarbinols has been studied in aqueous sulfuric acid. With both kinds of alcohols the rate-controlling step in solutions more acidic than H_0 -0.50 was found to be the ionization of the carbinol to give the carbonium ion followed, it is believed, by rapid reaction with permanganate ion to form the ester which decomposes rapidly to products. In the case of the tertiary alcohols the decomposition probably proceeds via a 1,2-aryl shift. The effect of substituents is correlated with σ^+ in both cases, ρ^+ being -1.02 and -1.39 for the secondary and tertiary series. The acidity function which governs both reactions is H_0. Tri(*p*-tolyl)carbinol is exceptional in that its oxidation in solutions more acidic than H_R -2.6 is second-order and is governed by the H_R acidity function.

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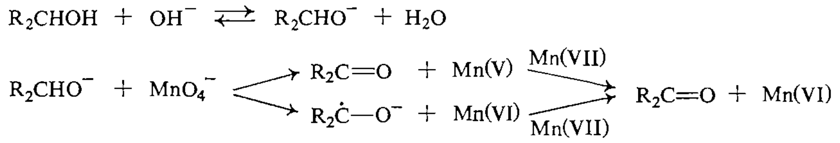
Introduction

The permanganate oxidation of primary and secondary alcohols has previously been studied in basic and weakly acidic solution (1–4). The reaction is strongly accelerated by base and this has been shown to be due to the ready transfer of hydrogen (either as a hydride ion or as a hydrogen atom) from the alkoxide ion to the permanganate ion.



$$R_2CHOH + OH^- \rightleftharpoons R_2CHO^- + H_2O$$

$$R_2CHO^- + MnO_4^- \begin{array}{l} \nearrow R_2C{=}O + Mn(V) \xrightarrow{Mn(VII)} \\ \searrow R_2\dot{C}{-}O^- + Mn(VI) \xrightarrow[Mn(VII)]{} \end{array} R_2C{=}O + Mn(VI)$$

Little is known about the way in which strongly acidic permanganate reacts with alcohols, although it has been shown that aldehyde hydrates (which are gem diols) undergo much more rapid oxidation in acidic than in neutral solution, because of the increased reactivity of the permanganate acid formed in this region (5). Furthermore, virtually nothing is known about the way tertiary alcohols are oxidized by permanganate. These compounds lack a hydrogen atom on the alcoholic carbon and any oxidation must produce carbon–carbon bond cleavage, possibly via aryl migration. It seemed worthwhile to study these reactions and accordingly, a series of diarylcarbinols and triarylcarbinols were prepared and subjected to permanganate oxidation over a wide acidity range. The results have been analyzed in terms of mechanism.

Experimental

Materials

The substituted benzhydrols were prepared by standard methods usually involving the reduction of the corresponding ketone (1). The triarylcarbinols were, with one exception (4-nitrotriphenylcarbinol (6)) prepared by the Grignard procedure. The physical properties of those compounds that have previously been prepared agreed in all cases with the literature values. The following two compounds have not been previously reported.

(1) 3-Trifluoromethyl-4′-methyltriphenylcarbinol: from 4-methylbenzophenone and 3-trifluoromethylphenylmagnesiumbromide. Yield 41%, b.p. 184°/0.8 mm.

Anal. Calcd. C, 73.7; H, 4.97; F, 16.7. Found: C, 73.5; H, 5.11; F, 16.9.

(2) 3-Trifluoromethyltriphenylcarbinol: from benzophenone and 3-trifluoromethylphenylmagnesiumbromide. (We thank Mr. I. Beheshti for the preparation of this compound.) Yield, 61%, b.p. 120°/0.2 mm.

Anal. Calcd. C, 73.17; H, 4.57; F, 17.37. Found: C, 73,14; H, 4.87; F, 17.14.

Reaction Products

The following benzhydrols were oxidized (listed in the order in which they appear in Fig. 8, left to right: 4,4′-dimethoxy, 2,4,6,2′,4′,6′-hexamethyl (σ^+ value calculated from pK_{R^+} of the diarylcarbinol (9), 4-methoxyl 4,4′-dimethyl, 4-methyl, unsubstituted, 4-chloro, 4,4′-dichloro, 4-carboxy. Isolation experiments

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were performed in the cases of benzhydrol and 4-methoxybenzhydrol. The former gave a 99.2% yield of benzophenone, m.p. 49°, 2,4-dinitrophenylhydrazone, m.p. 238°. The latter gave a 98.1% yield of crystalline 4-methoxybenzophenone, m.p. 62°. The reaction products of all the other alcohols contained strong carbonyl peaks in their infrared spectra.

The following triphenylcarbinols were oxidized (listed in the order which they appear in Fig. 9, left to right): 3,3′,3′′-trichloro, 4,4′,4′′-trichloro, 4,4′-dichloro, 3-trifluoromethyl-4′-methyl, 4-chloro, unsubstituted, 4-fluoro, 4-methyl, 4,4′-dimethyl, 4,4′,4′′-trimethyl. The ketonic products have been identified in the case of triphenylcarbinol and two of its derivatives (Table II). Triphenylcarbinol was shown to produce benzophenone and carbon dioxide when an excess of permanganate was employed. The carbon dioxide was swept out of the reaction mixture and trapped in barium hydroxide solution. The increase in weight of this system corresponded to the production of 6 moles of carbon dioxide. We conclude that phenol is the other product of reaction and that it has been completely degraded by the acidic permanganate, the known fate of phenol under these conditions (4).

Kinetics

The kinetics of the reaction were followed by two procedures; titration of unreacted permanganate and observation of the disappearance of the 526 mμ permanganate peak in the visible spectrum, essentially as previously described (1, 5, 7).

A spectrophotometric method was used to follow the rate of ionization of 4-methoxybenzhydrol by observing the increase in absorption of the corresponding carbonium ion at 466 mμ. Because of the low solubility of the carbinol in water, 70% methanol (by volume) in water was taken as the reaction medium. In a typical experiment 2 ml of 18.0 *M* sulfuric acid was taken in a 10 ml volumetric flask and made up to the mark with the aqueous methanol; 2.5 ml of this solution was taken in a cell and placed in the thermostatted cell compartment of a Cary 16 spectrophotometer. Next 50 μl of a 2.5 *M* solution of 4-methoxybenzhydrol were injected to the cell from a syringe. The increase in optical density at 466 mμ showed the extent of ionization. The values for the acidity functions, H_0 and H_R, for the solutions were determined by the standard Hammett indicator technique (8). The results are given in Table I.

TABLE I

H_0 and H_R values for 70 vol% aqueous methanol

$M(H_2SO_4)$	H_0*	H_R†	(H_R)‡
1.80	−0.15 (−0.14)	−0.58	−0.63
2.16	−0.38	−0.98	−0.89
2.31	−0.50	−1.25	−1.02
2.88	−0.64	−1.65	−1.78
3.60	−0.82	−1.94	−2.01

*4-Chloro-2-nitroaniline was used as indicator except for the value in parentheses which was obtained using 2-nitroaniline (8).
†4,4′-Dimethoxytriphenylchloromethane was used as indicator (9).
‡Calculated from the final absorbance of the 4-methoxybenzhydryl cation (9).

Results and Discussion

The stoichiometry of both reactions, the oxidation to the ketone in the case of the secondary alcohols, and the oxidative cleavage in the case of the tertiary alcohols, requires a 3:2 molar ratio of alcohol to permanganate

$$3Ar_2CHOH + 2MnO_4^- + 2H^+ \rightarrow 3Ar_2C{=}O + 2MnO_2 + 4H_2O$$

$$3Ar_3COH + 2MnO_4^- + 2H^+ \rightarrow 3Ar_2C{=}O + 3ArOH + 2MnO_2 + H_2O$$

Although the permanganate–alcohol reaction in basic and in mildly acidic solution is cleanly second-order (1), the reaction that becomes dominant as more acidic conditions are reached ($H_0 < -0.50$) is first-order in alcohol and zero-order in permanganate. Figure 1 shows a typical first-order plot for the oxidation of benzhydrol. Doubling the permanganate concentration has no effect on the rate at which it is consumed.

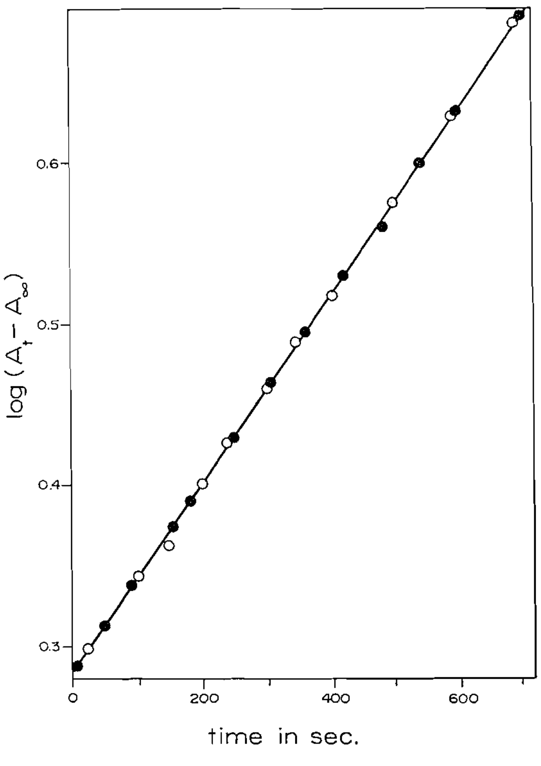


FIG. 1. First-order rate plots of the permanganate oxidation of benzhydrol, $H_0 = -0.69$, $T = 25°$, [benzhydrol] = 3.65×10^{-4}; [MnO_4^-] = 4.87×10^{-4} (open circles), [MnO_4^-] = 2.43×10^{-4} (closed circles); $k_1 = 2.00 \times 10^{-3}$ s^{-1}.

TABLE II

Analysis of permanganate oxidation product of triarylcarbinols

Substituted triphenylcarbinols	Melting point of ketone derivative* (°)		λ_{max} of conc. H_2SO_4 soln. of products (mμ)	Identified benzophenones
	Obs.	Lit. (12)		
4-Me	238	239	344†	Unsubstituted
4-Cl	184	185	299, 367‡	4-Cl

*2,4-Dinitrophenylhydrazone.
†The conjugate acid of benzophenone absorbs at 344 mμ (13).
‡The conjugate acid of 4-chlorobenzophenone absorbs at 300 and 367 mμ (13).

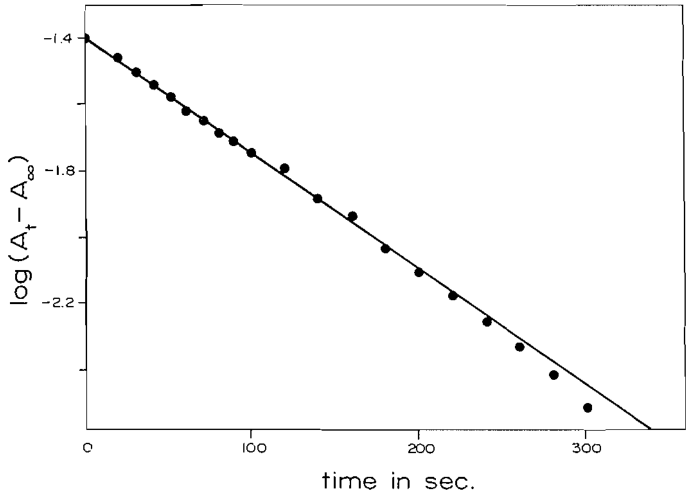


FIG. 2. First-order rate plot of the permanganate oxidation of triphenylcarbinol, $H_0 = -1.50$, $T = 25°$, $k_1 = 1.14 \times 10^{-2}\ s^{-1}$.

Most of the tertiary alcohols also gave good first-order plots up to about 50–60% reaction, after which serious deviations began to appear, presumably because of degradation of the phenolic products (Fig. 2). In the case of tri(*p*-tolyl)carbinol a second-order reaction reappeared at higher acidities ($H_R < -2.6$).

The effect of acidity on the rate of the permanganate oxidation of benzhydrol and triphenylcarbinol is shown in Figs. 3 and 4. In both cases, reasonably linear plots are obtained when the logarithm of the first-order rate constant is plotted against H_0 (8) and the slopes are found to be close to unity. When the acidity function H_R is used (9), somewhat less linear plots are obtained and, more significantly, the slopes are found to deviate greatly from unity (0.58 for benzhydrol and 0.45 for triphenylcarbinol). Only for tri(*p*-tolyl)carbinol did H_R appear to govern the rate of the oxidation reaction. Between H_R values of -2.5 and -3.6, a straight line of unit slope was obtained when the logarithm of the second-order rate constant for the oxidation of this alcohol is plotted against H_R (Fig. 5).

Rate-controlling Step

The first-order dependence of the rate on the concentration of alcohol, the zero-order dependence on permanganate, and the first-order dependence on the acidity means that the rate can be expressed by the equation

$$\text{rate} = k[\text{alcohol}]h_0 \qquad \text{where } h_0 = -\text{antilog}\, H_0$$

This suggests that the rate-controlling step is the ionization of the alcohol to give the carbonium ion

$$ROH + H^+ \rightleftarrows ROH_2^+ \qquad \text{fast}$$
$$ROH_2^+ \rightarrow R^+ + H_2O \qquad \text{slow}$$
$$R^+ + MnO_4^- \rightarrow \text{products} \qquad \text{fast}$$

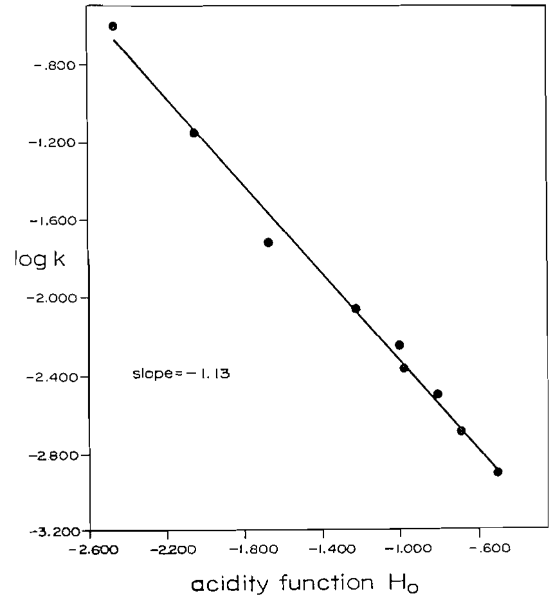


FIG. 3. Variation of the rate of permanganate oxidation of benzhydrol as a function of H_0; correlation coefficient, 0.996.

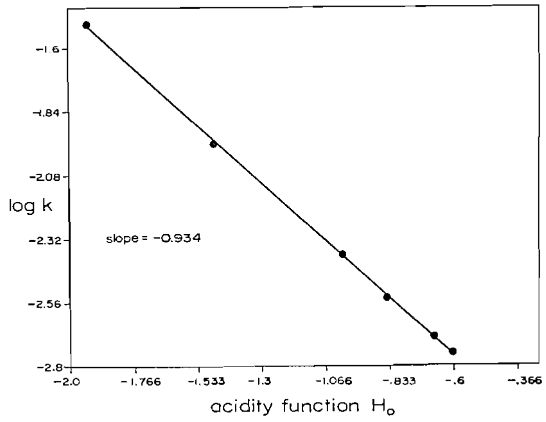


FIG. 4. Variation of the rate of permanganate oxidation of triphenylcarbinol as a function of H_0; correlation coefficient, 0.999.

Although the rate-controlling step above involves the formation of a carbonium ion, it is not surprising that the operative acidity function is H_0 rather than H_R. The latter governs the *equilibrium* of the alcohol–carbonium ion reaction and differs in form from H_0 by containing a water activity term. It seems unlikely that the activity of water in the medium will alter the *rate* at which a water molecule is expelled although it will clearly affect the equilibrium position of the system. In this connection Rocek (10) has shown that the rate of carbonium ion formation from 1-methylcyclohexanol is governed by H_0. Further information on this point was obtained by measuring the rate of ionization of *p*-methoxybenzhydrol under conditions that were as close as possible to those used for the oxidation process. Unfortunately the high concentration of alcohol required to measure the rate and degree of ionization of this alcohol at acidities so far from its pK_{R^+} value, precluded the use of a purely aqueous system. The rates of ionization of 4-methoxybenzhydrol were accordingly determined in 70 vol% aqueous methanol containing sulfuric acid ranging from 1.8 to 3.6 *M*. The reaction was found to be of first-order in carbinol concentration. The following first-order rate expression was used to obtain the rate constants

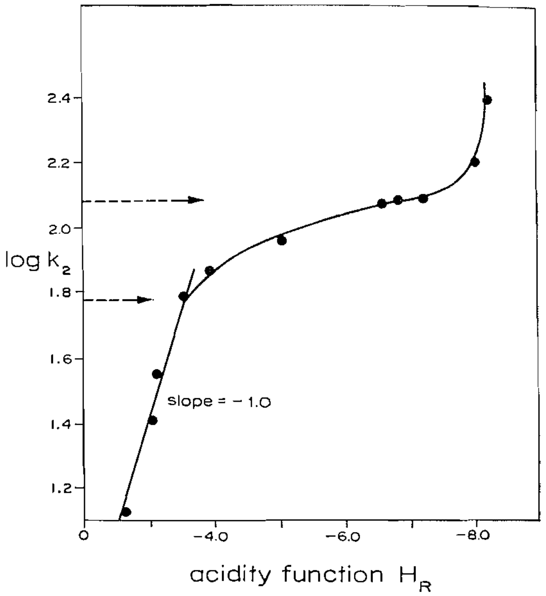


FIG. 5. Variation of the rate of permanganate oxidation of tri(*p*-tolyl) carbinol with H_R.

$$kt = 2.303 \log \frac{A_\infty}{A_\infty - A_t}$$

where A_∞ = absorbance at infinite time, and A_t = absorbance at time t, at the wavelength maximum for the carbonium ion, 466 mμ. Log $(A_\infty - A_t)$ was plotted against time and the rate constants calculated from the slopes of the lines. A typical rate plot is shown in Fig. 6.

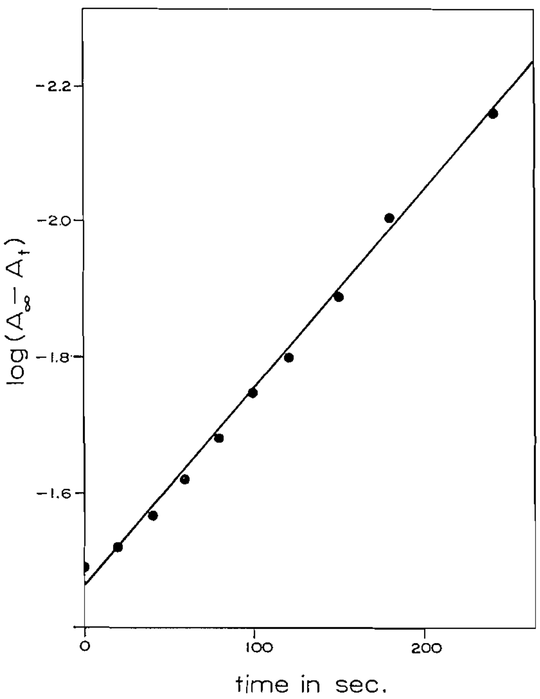


FIG. 6. Rate of ionization of *p*-methoxybenzhydrol in 70 vol% aqueous methanol containing sulfuric acid, 25°. $H_0 = -0.38$, $[H_2SO_4] = 2.16$, [*p*-methoxybenzhydrol] = 6.0. $k_1 = 5.99 \times 10^{-3}\ s^{-1}$.

In Fig. 7 the logarithm of the ionization rate for *p*-methoxybenzhydrol in 70 vol% aqueous methanol is plotted against the acidity function H_0. A straight line of slope −1.00 with a correlation coefficient of 0.998 is obtained by this means whereas the use of the function H_R gives a considerably less satisfactory relation (slope = −0.48, correlation coefficient 0.990). The rate of ionization of 4-methoxybenzhydrol is close to this compound's rate of oxidation by permanganate when these measurements are made in solutions of the same acidity. For an H_0 of −0.81 the two rates are $1.55 \times 10^{-2}\ s^{-1}$ for the ionization (in 70 vol% aqueous methanol) and $1.79 \times 10^{-2}\ s^{-1}$ for the oxidation (in water).

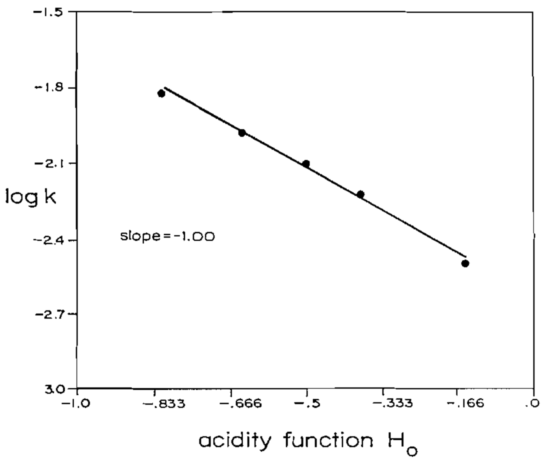


FIG. 7. The variation of the rate of ionization of *p*-methoxybenzhydrol with H_0; correlation coefficient, 0.998.

The isotope effect for the permanganate oxidation of $(C_6H_5)_2CDOH$ at 25° is 7.3 at pH 7.00 (where the reaction is second-order) (1), but is only 1.08 in the region between $H_0 = -0.50$ and -1.22 (where the reaction is first-order). This, too, is consistent with the ionization reaction being the rate-controlling step of the oxidation.

Overall Reaction Path

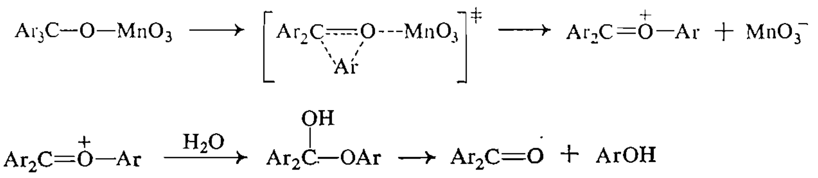
The following path accounts for the oxidation of secondary aromatic alcohols by permanganate in aqueous sulfuric acid

$$Ar_2CHOH + H^+ \rightarrow Ar_2CH^+ + H_2O \quad \text{slow}$$

$$Ar_2CH^+ + MnO_4^- \rightarrow \text{products} \quad \text{fast}$$

A permanganate ester, $Ar_2CH—O—MnO_3$, is likely the first intermediate formed in the fast steps that lead to product.

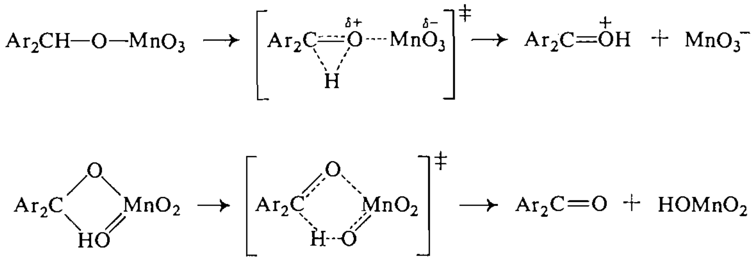
The tertiary alcohols follow a similar course with the decomposition of the permanganate ester probably involving rearrangement of an aryl group, followed by hydrolysis



$$Ar_3C—O—MnO_3 \longrightarrow \left[Ar_2C\overset{}{=\!=}O\text{---}MnO_3\right]^{\ddagger} \longrightarrow Ar_2C{=}\overset{+}{O}—Ar + MnO_3^-$$

$$Ar_2C{=}\overset{+}{O}—Ar \xrightarrow{H_2O} Ar_2\overset{OH}{\overset{|}{C}}—OAr \longrightarrow Ar_2C{=}O + ArOH$$

It is conceivable that the permanganate esters of secondary aromatic alcohols also decompose by a 1,2-rearrangement step in which hydride ion is transferred from carbon to oxygen or in which hydrogen is transferred to the oxygen of the ester via a cyclic 5-membered transition state. Alternatively, the decomposition may proceed by proton loss to a water molecule and expulsion of MnO_3^-. This general question is discussed in greater detail in the accompanying paper on chromium(VI) oxidations. A 1-equivalent step has been considered distinctly possible in the base-promoted permanganate oxidation of alcohols (3, 4) and for the secondary alcohols, at least, it cannot be ruled out for the acid-promoted reaction. Four possibilities, three 2-equivalent and one 1-equivalent routes, are given below. (Since this step follows the rate-controlling step it is difficult to distinguish between these possibilities.)



$$Ar_2CH{-}O{-}MnO_3 + H_2O \longrightarrow Ar_2C{=}O + H_3O^+ + MnO_3^-$$

$$Ar_2CH{-}O{-}MnO_3 \longrightarrow Ar_2CHO\cdot + MnO_3 \xrightarrow{Mn(VII)} Ar_2C{=}O$$

Effect of Substituents

The effect of substituents on the oxidation of the secondary alcohols is shown by the plot in Fig. 8 in which σ^+ substituent constants are used (11). The Hammett rho value of −1.02 and the excellent correlation with σ^+ support the idea that the rate-controlling step is ionization of the carbinol.

The effect of substituents on the rate of oxidation of the tertiary aromatic alcohols is shown in Fig. 9. As in the case of the secondary alcohols an excellent correlation is obtained when σ^+ is used. The rho value of −1.39 is also consistent with an ionization process, the larger value probably reflecting a higher degree of bond-breaking in the transition state.

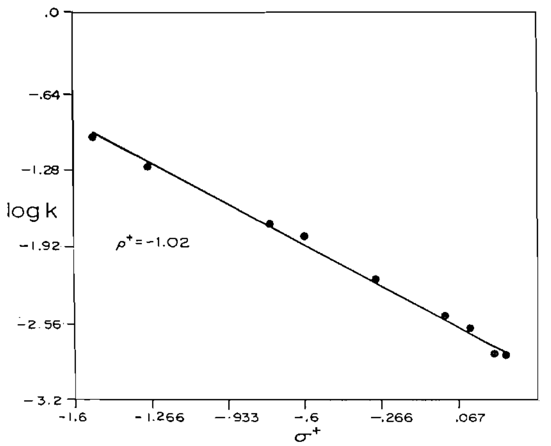


FIG. 8. The effect of substituents on the rate of the permanganate oxidation of diarylcarbinols, $H_0 = -0.81$; correlation coefficient, 0.998.

In the case of tri(*p*-tolyl)carbinol the ionization step at intermediate acidities is faster than the decomposition of the ester as shown by the observations that the reaction is first-order in both alcohol and permanganate and is governed by the H_R acidity function (Fig. 5). The pK_{R^+} of this alcohol is −3.56 (9) and the levelling-off of the rate above $H_R = -4$ doubtless reflects the fact that the ionization equilibrium has moved towards completion, although the curve shown in Fig. 5 does not duplicate exactly the ionization curve expected for this alcohol. The sharp rise in rate beyond an H_R of −7.2 (52% sulfuric acid) is

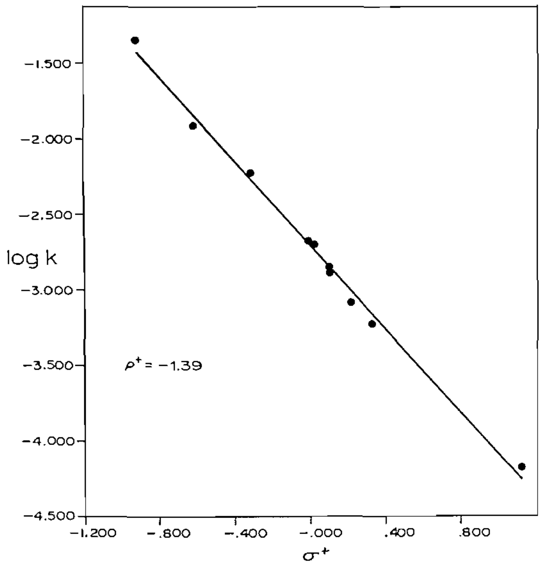


FIG. 9. The effect of substituents on the rate of the permanganate oxidation of triarylcarbinols, $H_0 = -0.65$; correlation coefficient, 0.998.

probably caused by formation of the powerful oxidant, permanganic acid, which is half-ionized in 61% sulfuric acid (5).

In the case of triphenylcarbinol the activation parameters for the oxidation at an H_0 of -1.00 are $\Delta H^\dagger = 17.2$ kcal/mole and $\Delta S^\dagger = 11.7$ e.u. The temperature range over which these measurements were conducted was 15–40°.

Acknowledgments

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1. R. STEWART. J. Amer. Chem. Soc. **79**, 3057 (1957).
2. R. STEWART and R. VAN DER LINDEN. Discuss. Faraday Soc. 211 (1960).
3. R. STEWART. Oxidation mechanisms. W. A. Benjamin, Inc., New York. 1964. Chap. 5.
4. R. STEWART. *In* Oxidation in organic chemistry. K. B. Wiberg, *Editor*. Academic Press, Inc., New York. 1965. Chap. 1.
5. R STEWART and M. M. MOCEK. Can. J. Chem. **41**, 1160 (1963).
6. W. H. STARNES, JR. J. Amer. Chem. Soc. **89**, 3368 (1967); J. Amer. Chem. Soc. **90**, 1807 (1968).
7. M. M. WEI and R. STEWART. J. Amer. Chem. Soc. **88**, 1974 (1966).
8. M. A. PAUL and F. A. LONG. Chem. Rev. **57**, 1 (1957).
9. N. C. DENO, H. E. BERKHEIMER, W. L. EVANS, and H. L. PETERSON. J. Amer. Chem. Soc. **81**, 2344 (1959). N. C. DENO, J. J. JARUZELSKI, and A. SCHRIESHEIM. J. Org. Chem. **19**, 155 (1954).
10. J. ROCEK. Colloq. Czech. Chem. Commun. **25**, 375 (1960).
11. H. C. BROWN and Y. OKAMOTO. J. Amer. Chem Soc. **80**, 4979 (1950).
12. A. I. VOGEL. Practical organic chemistry. Longmans, Green and Co., Ltd., London. 1964.
13. R. STEWART, M. R. GRANGER, R. B. MOODIE, and L. J. MUENSTER. Can. J. Chem. **41**, 1065 (1963).