Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.7; H, 8.4; mol. wt., 192. Found (major product): C, 68.3; H, 8.1; mol. wt., 195. Found (minor product): C, 68.6; H, 8.3.

The minor product was not investigated further.

The major product gave a positive Jamieson test as did its oxalate (m.p. 135–137° from ethanol).

Anal. Calcd. for $C_{24}H_{34}N_4O_6$: C, 60.7; H, 7.2. Found: C, 60.4; H, 7.2.

This hydrazino alcohol gave a different oxalate (1:1; m.p. 108–109° from ethanol–ether) when it was treated with an excess of oxalic acid in ether.

Anal. Calcd. for $C_{13}H_{18}N_2O_5$: C, 55.3; H, 6.4. Found: C, 55.1; H, 6.4.

A mixture of the solution of I with indene (25.0 g., 0.207 mole) was stirred for 7 hr. at 0°. The white solid that precipitated was removed upon a filter and was washed with cold acetone to give 1,1-dimethyl-2-(1-bromo-2-indanyl)hydrazinium bromide (18.0 g., 56% based on indene used, m.p. 125° dec.).

Anal. Calcd. for $C_{11}H_{16}N_2Br_2$: C, 39.3; H, 4.8; Br, 47.6. Found: C, 39.4; H, 4.8; Br, 47.0.

The two-phase filtrate was extracted with ether (200 ml.) and the ether solution was washed with sodium carbonate solution (5%) and water (extract dried Na_2SO_4). Its distillation gave indene (13.5 g., 54% recovered, b.p. 69–70° at 16 mm., $n^{20}D$ 1.5592).

The aqueous phase was made alkaline with sodium hydroxide solution (20%) and it was stirred overnight. The upper organic phase that had separated was extracted with ether (four 100-ml. portions, dried Na_2SO_4). Evaporation gave 1,1-dimethyl-2-(1-hydroxy-2-indanyl)hydrazine (3.5 g., 19% yield, m.p. 83–85° from ligroin).

Distillation of the ether solution that had been removed in the evaporation gave tetramethyltetrazene (5.43 g., 75% based upon I not used in the formation of other two products, b.p. 48.5–49° at 32 mm., $n^{20}D$ 1.46 49).

The usual solution of I and indene (23.2 g., 0.20 mole) in methanol (250 ml.) was stirred for 5 hr. at 0°. 1,1-Dimethyl-2-(1-bromo-2-indanyl)hydrazinium bromide (7.0 g., 0.021 mole, 52% based on indene used) precipitated. Indene (18.5 g., 0.16 mole, 80% recovery, b.p. 69–70° at 16 mm., $n^{20}D$ 1.5588) was obtained by distillation of a benzene extract of the reaction mixture.

The reaction mixture was made basic and was extracted with ether. Distillation gave tetramethyltetrazene (7.0 g., 0.068 mole, 85% yield).

The 1,1-dimethyl-2-(1-bromo-2-indanyl)hydrazinium bromide (38.0 g., 0.113 mole) in ethanol (95%, 340 ml.) was hydrogenated (Parr, 25°, Adams catalyst, 0.4 g.; hydrogen, 0.16 mole,

absorbed). The reaction mixture was filtered and then evaporated (Rinco). The residue was treated with a sodium hydroxide solution (10 g. in 50 ml. of H_2O; strong amine odor). The mixture was extracted with ether (350 ml., dried Na_2SO_4). Distillation gave an ether solution that was treated with excess oxalic acid to give dimethylammonium oxalate (3.0 g., 0.022 mole, m.p. 148–150° from ethanol,[34] 20%), 2-amino-indane (0.9 g., b.p. 43–46° at 1 mm., $n^{20}D$ 1.5352, 6%; benzoyl derivative, m.p. 152–155°,[36] oxalate m.p. 214–216° dec.), and 1,1-dimethyl-2-(2-indanyl)hydrazine (8.6 g., 0.049 mole, b.p. 65–69° at 1 mm., $n^{20}D$ 1.5310, 43%, postive Jamieson test). This hydrazine gave an oxalate (m.p. 143–146° from ethanol).

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.6; H, 6.8; N, 10.5. Found: C, 58.6; H, 5.4; N, 10.2.

To confirm further the identity of this hydrazine its oxalate was dissolved in hydrochloric acid, and it was oxidized with potassium iodate solution. The residue from evaporation of an ether extract of this reaction mixture gave the 2,4-dinitrophenylhydrazone of 2-indanone (m.p. 194–196° dec. from 95% ethanol).[37]

The Reaction of I with Acetaldehyde.—A reaction mixture containing I and acetaldehyde (8.8 g., 0.20 mole) was stirred for 4 hr. at 0°. It was then made basic with sodium hydroxide solution, and it was extracted with ether (four 100-ml. portions). The ether solution (dried Na_2SO_4) was distilled to give tetramethyltetrazene (2.8 g., 0.024 mole, 24%; infrared identical with that of known). The ether distillate was treated with oxalic acid, and 1,1-dimethylhydrazinium oxalate (1.0 g., 0.006 mole, m.p. 142–143° from ethanol, positive Jamieson test) was obtained.

The distillate (300 ml.) from steam distillation of the basic aqueous solution until volatile base ceased to codistil contained 1,1-dimethylhydrazine (8.3 g., 0.138 mole, 72%; by titration of aliquot portions with standard potassium iodate solution in acid).

The aqueous solution remaining in the distilling flask was made acidic with sulfuric acid. It was then distilled until no more acid codistilled. Titration of the distillate with standard sodium hydroxide solution showed that it contained acetic acid (7.2 g., 0.12 mole, 60% yield). The distillate was then made basic and evaporated to dryness. The residual salt was treated in ethanol–water with p-nitrobenzyl chloride, and p-nitrobenzyl acetate (m.p. 76–77° from 95% ethanol) was obtained.

The same products as well as acetaldehyde and 1-butanol were obtained in the reaction of I with an equimolar amount of butyl vinyl ether. Apparently, in the acidic reaction mixture this ether was hydrolyzed to give the butanol and acetaldehyde that was then in part oxidized to acetic acid.

(36) J. Kenner and A. M. Mathews, *J. Chem. Soc.*, **105**, 747 (1914).

(37) M. Mousseron, R. Jaquiet, and H. Christol, *Compt. rend.*, **236**, 929 (1953).

Transition State Characterization for the Permanganate Oxidation of Fluoral Hydrate

BY JOSEPH L. KURZ[1]

Rate data for the four kinetically distinct mechanisms for permanganate oxidation of fluoral hydrate have been analyzed to assign upper and lower limits to bond breaking and bond making in the four transition states. For the first time in this type of analysis, both upper and lower limits have been assigned for a single transition state. The data are shown to be interpreted easily by this approach if the reactions are assumed to proceed with hydride transfer from fluoral hydrate to permanganate in the rate-determining step. The data are shown to be inconsistent with this analysis if a hydrogen atom transfer mechanism is assumed.

It recently has been shown[2] that rate data for corresponding catalyzed and uncatalyzed reactions may be analyzed to obtain the thermodynamic parameters for the virtual dissociation of the catalyst from the transition state of the catalyzed reaction to yield the transition state of the uncatalyzed reaction. Such parameters may then be used to characterize the structures of the two transitions states.

A set of related reactions which are particularly well suited to such an analysis is found in the oxidation of fluoral hydrate to trifluoroacetic acid by permanganate.[3] For this reaction, the rates of four kinetically distinct processes have been determined. The kinetic terms differ only in the extent of protonation of the reactants, so that three successive pK_a's can be calculated corresponding to virtual equilibria between the four transition states. For reaction in aqueous solution

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(2) J. L. Kurz, *J. Am. Chem. Soc.*, **85**, 987 (1963).

(3) R. Stewart and M. M. Mocek, *Can. J. Chem.*, **41**, 1160 (1963).

at 25°, the rate constants which were measured[3] may be defined by the rate laws

$$R = [MnO_4{}^-][CF_3CH(OH)_2](k_0 + k'[H^+] + k''[OH^-]),$$
$$\text{pH} < 10$$

$$R = [MnO_4{}^-][CF_3CH(OH)O^-](k_a + k_b[OH^-]), \text{pH} > 12$$

The $k'[H^+]$ term is attributed to a reaction between neutral fluoral hydrate and permanganic acid, the k_0 term to reaction between neutral fluoral hydrate and permanganate ion, the $k''[OH^-]$ term (and the related k_a term) tor eaction between fluoral hydrate monoanion, $CF_3CH(OH)O^-$, and permanganate ion, and the $k_b[OH^-]$ term to the corresponding reaction of fluoral hydrate dianion, $CF_3CH(O^-)_2$. From these specific rates, the three successive acid dissociation constants for the transition state may be calculated by the previously derived[2] equations for specific acid and specific base catalysis

$$pK_1{}^{\neq} = \log (k'/k_0) = 0.4$$
$$pK_2{}^{\neq} = \log (k_0/k'') + pK_w = 5.4$$
$$pK_3{}^{\neq} = \log (k_a/k_b) + pK_w = 11.8$$

The large primary kinetic deuterium isotope effect observed[3] in the oxidation suggests that the C–H bond is being broken in the transition state. The structure which is common to all four transition states may thus be written as

$$\begin{array}{c} \text{OH} \ (2) \\ | \\ CF_3 - C \cdots H \cdots OMnO_3H \ (1) \\ | \\ OH \ (3) \end{array}$$
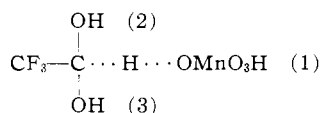
The degree of protonation of the transition state for each individual reaction corresponds to the degree of protonation of the reactants. The proton to whose ionization each $pK_a{}^{\neq}$ refers is thus indicated by the parenthetical numbers.

The extent to which a reacting bond has been formed in the transition state can be estimated from the $pK_a{}^{\neq}$ for an acidic group on the moiety to which the reacting bond is being made.[2] The value of $pK_a{}^{\neq}$ must lie between the values of pK_a for the reactants (zero bond formation) and for the products (complete bond formation). Its position between these extremes is a measure of the extent to which the bond has been formed. Analogous considerations will hold for a bond being cleaved in the transition state. However, since the strength of the reacting bond will be, in general, different in the two transition states to which $pK_a{}^{\neq}$ refers, the value calculated for the extent of bonding will refer to an average structure and will be an upper limit for one transition state and a lower limit for the other.

Hydride Ion Transfer.—Structural parameters calculated for the transition states from the $pK_a{}^{\neq}$ values will depend on the assumed mechanism, since that will determine the structures and hence the pK_a's of the products. The experimental data originally were interpreted to be in better accord with a hydride transfer mechanism than with one involving hydrogen atom transfer in the rate-determining step.[3] The amounts of bond formation and cleavage present in the transition states will therefore first be estimated assuming hydride transfer.

The value calculated for $pK_1{}^{\neq}$ refers to the ionization of a proton from the permanganate moiety in the

average transition state for the reactions corresponding to the rate constants k' and k_0. The value of pK_a for zero bond formation between the hydride ion and the permanganate moiety is simply that of unperturbed $HMnO_4$. Unfortunately, two different values for this constant have been reported in the recent literature: -2.3[4] and -5.1.[2] These values were measured, respectively, in perchloric acid and in sulfuric acid. Since the kinetic data used here were obtained from measurements on sulfuric acid solutions, the latter value (-5.1) is probably the one appropriate to these calculations. Owing to the uncertainty, however, both are carried through the argument. The pK_a for complete bond formation (i.e., 100% hydride transfer) would be that for $H_2MnO_4{}^-$. This may be approximated by using the value for $H_2VO_4{}^-$ which has been reported[4] to be 9.0. As a first approximation, the experimentally determined value, $pK_1{}^{\neq} = 0.4$, is thus seen to correspond to either 24 or 39% bond *making* between the hydride and the permanganate moiety depending on whether -2.3 or -5.1 is used as pK_a ($HMnO_4$). However, this estimation implicitly assumes that the dissociation of the proton from the $HMnO_4$ moiety in the transition state is unaffected by the developing positive charge on the carbon atom from which the hydride ion is departing. Assuming the transition state structure shown above, the carbon bearing the partial positive charge is the fourth atom in the chain away from the oxygen bearing the ionizing proton. The effect of a positive charge at this distance on the value of $pK_1{}^{\neq}$ may be estimated from the observation that $pK_1 = 3.6$ for β-alanine,[5] which is 1.2 pK units less than pK_a for acetic acid. If the partial charge on the carbon is taken as 0.4 protonic charge, its expected effect on $pK_1{}^{\neq}$ would therefore be to lower that quantity of 0.5 pK unit. Application of this correction leads to corrected estimates of 28 and 43% bond *making* in the average transition state corresponding to $pK_1{}^{\neq}$, the two values arising from the use of -2.3 and -5.1, respectively, for pK_a ($HMnO_4$).

A similar computation may be made based on $pK_2{}^{\neq}$. Here the ionizing proton is on the fluoral hydrate moiety. For 0% bond breaking, pK_a (0%) = pK_a ($CF_3CH(OH)_2$) = 10.2.[3] For 100% bond breaking, pK_a (100%) = pK_a ($CF_3C^+(OH)_2$). This latter species is the conjugate acid of trifluoroacetic acid. Its pK_a may be approximated from the known[6] value, $pK_a = -0.3$, for trifluoroacetic acid by assuming that ΔpK_a between the carboxylic acid and its corresponding conjugate acid is the same for trifluoroacetic acid as for acetic acid.[7] For the latter, $pK_a(CH_3C^+(OH)_2) = -6.1$,[8] which makes $\Delta pK_a = 10.9$ and $pK_a(CF_3C^+(OH)_2) = -11.2$. These values lead to a first approximation of 22% bond *breaking*. It is then necessary to correct for the perturbing negative charge on the permanganate

(4) N. Bailey, A. Carrington, K. A. K. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 290 (1960).

(5) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London, 1959, p. 517.

(6) O. Redlich and G. C. Hood, *Discussions Faraday Soc.*, **24**, 87 (1957).

(7) This procedure may give too high a value for $pK_a(CF_3C^+(OH)_2)$, since $\rho(ArC^-(OH)_2) = 1.09$, which is higher than $\rho(ArCO_2H)$ (R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960)). Assuming that a similar effect exists for aliphatic acids, ΔpK_a should be increased by electron-withdrawing groups. If the aliphatic ρ^* changes by the same factor as ρ, this error would be 0.5 pK unit. Since this rather uncertain correction is small compared to the range of pK values under consideration ($+10.2$ to -11.2), it is not included.

(8) A. R. Goldfarb, A. Mele, and N. Gutstein, *ibid.*, **77**, 6194 (1955).

moiety. Although no data are available for a model system involving a transition metal oxyanion, data are available[9] for the effect of the $-SeO_2^-$ substituent on the pK_a's of carboxylic acids. In the acid $HO_2CCH_2CH_2$-SeO_2^-, the Se atom is separated from the ionizing proton by about the same distance which separates the Mn atom from the ionizing proton in the transition state under consideration. This model acid is 1.2 pK units more basic than acetic acid. The $-OMnO_3$ group in the transition state bears its original negative charge plus a partial charge from the hydride ion being transferred, which may be estimated to be 0.2 electronic charge from the first approximation to the extent of hydride transfer. The total effect of the charge residing on the permanganate moiety would thus be expected to be a lowering of $pK_2^{\ddagger}$ by 1.4 pK units. Inclusion of this correction leads to a second estimate of 29% bond *breaking* in the average transition state corresponding to $pK_2^{\ddagger}$.

For the transition state corresponding to $pK_3^{\ddagger}$, pK_a (0%) = $pK_a(CF_3CH(OH)O^-)$. This second ionization constant for fluoral hydrate may be estimated from the first by using carbonic acid as a model. After correcting $pK_1(H_2CO_3)$ for the H_2CO_3/CO_2 equilibrium,[10] ΔpK for carbonic acid is found to be 6.4. The difference in symmetry of the acids which are being compared requires a small correction for a statistical factor which would tend to make the magnitude of ΔpK for fluoral hydrate larger than that for carbonic acid by the additive term $\log {}^4/_3$. The estimated value of $pK_2 - pK_1$ for fluoral hydrate is thus 6.5, so that $pK_2 = 16.7$.

In this use of carbonic acid as a model for an acid having both hydroxyls attached to a single tetrahedral carbon, it is implicitly assumed that resonance effects involving the carbonyl in carbonic acid make the same contribution to the acidity in both the first and second ionizations. It can be shown that errors arising from this assumption are probably small by attempting a direct calculation of the desired ΔpK. Tanford[11] has developed an empirical modification of the Westheimer–Kirkwood[12] model for the interaction of electrostatic charges on organic ions which allows the values of ΔpK for dibasic acids to be calculated directly from molecular dimensions. For example, satisfactory agreement between predicted and observed ΔpK_a's was found for diammonium ions, $H_3N^+(CH_2)_nNH_3^+$, with $n \geqslant 2$. An analogous calculation for $R_2C(OH)_2$ gives $\Delta pK = 7.5$, one pK unit higher than that estimated from carbonic acid. Tanford's calculated value for the diamine with $n = 2$ was high by 0.4 pK unit, in contrast to his values for $n = 3, 4, 5$ which were low by 0.1 pK unit. It thus seems probable that the model gives high values when the two acidic groups are very close together, so that the value calculated for R_2C-$(OH)_2$ may be counted as a satisfactory confirmation of the estimate based on carbonic acid.

For complete hydride transfer in the transition state for $pK_3^{\ddagger}$, pK_a (100%) = $pK_a(CF_3CO_2H)$ = -0.3.[6] This value, together with the estimate for $pK(0\%)$ and the experimental'y determined value of $pK_3^{\ddagger}$, gives an ap-

proximate estimate of 29% C–H bond cleavage. The correction term for the effect of the negative charge present on the $-OMnO_3$ group can be estimated to be 1.6 pK units by the method described for $pK_2^{\ddagger}$. This leads to a corrected value of 38% bond *breaking* in the average transition state corresponding to $pK_3^{\ddagger}$.

The greater extent of bond breaking calculated from $pK_3^{\ddagger}$ as compared to that from $pK_2^{\ddagger}$ is in accord with the Swain–Thornton rule,[13] which states that an electron-attracting substituent in a transition state will shorten the nearest reacting bond and lengthen the next most distant one. The additional proton in the transition state for $pK_2^{\ddagger}$ may be considered as an electron-attracting substituent introduced into the transition state for $pK_3^{\ddagger}$. By similar arguments, the Swain–Thornton rule may be used to assign the bonding parameters calculated for the three *average* transition states as upper and lower limits on bonding in the four individual transition states for the observed reactions. The results are shown in Table I.

TABLE I

REACTING BONDS IN THE FOUR TRANSITION STATES
(ASSUMING HYDRIDE TRANSFER)

Stoichiometry	Bonding
$CF_3CH(OH)_2 + HMnO_4$	% H–O bond making > 28% $(43\%)^a$
$CF_3CH(OH)_2 + MnO_4^-$	$28\%(43\%)^a$ > % H–O bond making
$CF_3CH(OH)_2 + MnO_4^-$	29% > % C–H bond breaking
$CF_3CH(OH)O^- + MnO_4^-$	38% > % C–H bond breaking > 29%
$CF_3CH(O^-)_2 + MnO_4^-$	% C–H bond breaking > 38%

[a] The value of 28% results from the use of $pK_a(HMnO_4) = -2.3$; the value of 43% results from the use of $pK_a(HMnO_4) = -5.1$.

The data in Table I yield a measure of the extent to which bonding in an individual transition state can differ from the value calculated for the corresponding average transition state. The existence of rate constants for the reaction of fluoral hydrate in all three of its degrees of ionization has permitted the assignment of both upper and lower limits to the extent of carbon–hydrogen bond cleavage in the transition state for oxidation of the monoanionic form by permanganate ion. The length of the range within which this value may fall is 9% of the total distance along the reaction coordinate, which corresponds to an average deviation of less than 5% for this transition state from its two bounds. This is the first reaction for which both upper and lower limits have been calculated for a single transition state.

If one assumes that the total amount of bonding to a hydride ion in a transition state cannot exceed one single bond, then the data for the transition state for the reaction of neutral fluoral hydrate with permanganate ion can be used to test the consistency of the estimates of bonding based on $pK_1^{\ddagger}$ and on $pK_2^{\ddagger}$. The upper bound of 29% bond breaking calculated from $pK_2^{\ddagger}$ would require that H–O bond making be no more than 29%. This value may be compared to the estimates for the upper limit on H–O bond formation which were calculated from $pK_1^{\ddagger}$. They were 28 and 43%, depending on which of the two literature values for pK_a (H-MnO_4), -2.3 and -5.1, respectively, was used.

Hydrogen Atom Transfer.—If the mechanism of the rate-determining step is assumed to be hydrogen atom

(9) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 102.

(10) Reference 9, p. 31.

(11) C. Tanford, *J. Am. Chem. Soc.*, **79**, 5348 (1957).

(12) F. H. Westheimer and J. G. Kirkwood, *J. Chem. Phys.*, **6**, 513 (1930).

(13) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962); *Tetrahedron Letters*, **6**, 211 (1961).

transfer, the values calculated for the three $pK_a^{\ddagger}$'s are not easily reconciled with estimates of the pK_a's for the initial and final states of the reactants. The pK_a's for the initial states are unchanged from those estimated for the hydride transfer mechanism, but those for the final states are different.

For $pK_1^{\ddagger}$, the final state of the proton-bearing permanganate moiety would be H_2MnO_4. The pK_a for this species has not been measured directly, but should be close to that for H_2CrO_4, which has been reported[4] to be -1.0. The experimentally determined value of $pK_1^{\ddagger}$ $(+0.4)$ thus lies completely outside of the range bounded by the pK_a's of the initial and final states. It is unlikely that changes in internal charge distributions accompanying the formation of a transition state for simple hydrogen atom transfer could be sufficient to account for such a deviation.

Turning now to $pK_2^{\ddagger}$, the final state for hydrogen atom transfer from neutral fluoral hydrate would be the conjugate acid of a ketyl, $CF_3C \cdot (OH)_2$. The only ketyl for which an estimate of the acidity of the conjugate acid is available is that derived from benzophenone, $(C_6H_5)_2C \cdot -O^-$. For this example, $pK_a = 9.2$ in 50% isopropyl alcohol.[14] This value is about 6 pK units lower than that expected[15,16] for the corresponding alcohol $(C_6H_5)_2CHOH$. However, much of the decreased basicity of benzophenone ketyl relative to benzhydryl anion probably arises from delocalization of the charge into the aromatic rings, rather than from any inherent stability of the ketyl group *per se*. Aliphatic ketyls would therefore not be expected to differ in basicity from their corresponding alkoxide ions by as large a factor as does benzophenone ketyl.

Thus it should be safe to assume that the acidity increase of 6 pK units accompanying the change from benzhydrol to the conjugate acid of benzophenone ketyl represents an extreme upper limit on analogous changes for aliphatic alcohols such as fluoral hydrate. Since this change corresponds precisely to the assumed rate-determining step for oxidation, the permissible range for $pK_2^{\ddagger}$ predicted on the basis of this mechanism is $4.2 << pK_2 < 10.2$, where 10.2 is the pK_a of the starting alcohol. The observed value of $pK_2^{\ddagger}$ is 5.4, but this must be corrected for the effect of the charge borne by the permanganate moiety using the method outlined for the hydride transfer mechanism. If this charge is assumed to be 1.0 electronic charges, the corrected value of $pK^{\ddagger}$ is 4.2. This value would fall within the permissible range only if the assumption were made that the stabilization of the negative charge in $CF_3C(OH)O^-$ is as great as that in benzophenone

ketyl, and even then would imply that complete C–H bond breaking was present in the transition state.

The argument for $pK_3^{\ddagger}$ may be constructed analogously to that given for $pK_2^{\ddagger}$. The permissible range for $pK_3^{\ddagger}$ is found to be $10.7 << pK_3 < 16.7$. The corrected value calculated for $pK_3^{\ddagger}$ from the kinetic data is 10.6, which again lies outside the range which could be rationalized easily for a hydrogen atom transfer mechanism.

It thus has been shown that the value found for each of the three $pK_a^{\ddagger}$'s makes it improbable that the two specific rates used in the calculation of each $pK_a^{\ddagger}$ both refer to a mechanism in which hydrogen atom transfer is the rate-determining step. However, any single one of the four reactions could be hydrogen atom transfer. So long as at least one of the reactions whose rate is used in the calculation of a particular $pK_a^{\ddagger}$ is assumed to proceed by hydride ion transfer, the range of pK_a values between those estimated for the initial and final states is found to include the observed $pK_a^{\ddagger}$ value. In the set of four reactions under study, a requirement of consistency with the above estimations would therefore allow a maximum of two reactions to proceed by hydrogen atom transfer, and those would have to contain nonadjacent total numbers of protons in the reactants.

It should be pointed out that these arguments against the hydrogen atom transfer mechanism cannot be applied to the oxidation of aromatic alcohols such as benzhydrol. Taking benzhydrol as an example, the rate data for the oxidation of the alcohol and its corresponding alkoxide ion[17] by permanganate imply $pK_a^{\ddagger} = 11.8$ for the average transition state. The substrate $(C_6H_5)_2CHOH$ has a pK_a near 15.[15,16] The product from hydrogen atom transfer, $(C_6H_5)_2C \cdot -OH$, has $pK_a \approx 9$,[14] and the product from hydride ion transfer, $(C_6H_5)_2C^+OH$, would have a still lower pK_a. The experimentally determined value of $pK_a^{\ddagger}$ thus falls within the ranges predicted by both mechanisms, even after correction is made for the effect of the negative charge on the permanganate moiety. Evidence favoring the hydrogen atom transfer mechanism for the oxidation of alcohols containing aryl rings has been summarized recently by Stewart.[18] It may well turn out that aromatic and aliphatic alcohols are oxidized by different mechanisms.

(14) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

(15) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **82**, 795 (1960).

(16) J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).

(17) R. Stewart, *ibid.*, **79**, 3057 (1957).

(18) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1963, pp. 63–70.