ethane, as evidenced by the admixture of the corresponding authentic samples. The major pyrolysis product acetyl chloride (**5**) was further identified by hydrolysis and concurrent formation of additional acetic acid (**7**); chloroform and 1,1,2,2-tetrachloroethane were also identified by GLC analysis.

Model Experiments Concerning the Mode of Formation of Acetyl 1,1-Dichloroethyl Peroxide (12) and Diacetyl Peroxide (13). (a) Attempted Reaction of 1,4-Dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (9) with Acetyl Chloride. A solution of 40 mg (0.21 mmol) of **9** and 35 mg (0.45 mmol) of acetyl chloride in 1 g of dichloromethane was kept at ambient temperatures for 2 days and was then heated to 45 °C for 30 min. Neither **12** nor **13** could be detected by NMR analysis.

(b) Attempted Conversion of 1,4-Dimethyl-1,4-dichloro-2,3,5,6-tetroxolane (9) into Diacetyl Peroxide under Mild Conditions. To a solution of 40 mg of **9** in 2 ml of methyl acetate, 3 drops of water were added and the mixture was kept at room temperature for 1 day. NMR analysis showed that **9** was unchanged and no diacetyl peroxide (**13**) was formed.

Acknowledgment. The authors wish to express their gratitude to Professor Dr. H. Beckey and Dr. W. D. Lehmann of the Institut für Physikalische Chemie, Universität Bonn, and to Dr. F. Volk of the Institut für Chemie der Treib- und Explosivstoffe at Berghausen for the field ionization mass spectra. Support of this work by the Deutsche Forschungsgemeinschaft, Bad Godesberg, the Fonds der Chemischen Industrie, Düsseldorf, and the Elektrochemische Werke, München, is gratefully acknowledged.

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(17) Attempted elemental analysis of **9** resulted in the complete shattering of the combustion equipment and insertion of a sample of **9** into the heated port (approximately 250 °C) of a mass spectrometer resulted in a violent explosion.

(18) Attempted injection of **12** into the inlet port of a gas chromatograph resulted in an explosion and the concomitant destruction of the syringe. Elemental analysis of **12** could be carried out without explosion.

(19) There is experimental evidence that the conversion of **8** into **12** may, at least in part, be brought about by reaction of acetyl chloride with the ozonide **8**. Addition of excess CD_3COCl to solutions containing **8** resulted in the formation of a mixture of **12** and of $CH_3CCl_2{-}OO{-}COCD_3$. The latter was isolated by chromatography; its structure was proven by the fact that the field ionization mass spectrum shows the fragments CH_3CCl_2 and CD_3CO, but no CD_3CCl_2 fragment. Treatment of **12** with excess of CD_3COCl did not lead to the formation of $CH_3CCl_2{-}OO{-}C({=}O)CD_3$.

(20) Prevention of ozonide formation in the presence of tetracyano ethylene has been amply demonstrated. The reactions lead to the formation of carbonyl fragments of the corresponding olefinic substrates and to tetracyanoethylene oxide: R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963).

(21) Indeed, addition of concentrated aqueous hydrochloric acid to a mixture containing **8** and unconverted substrate **4** resulted in the rapid disappearance of **8** and the concomitant formation of 2,2,3,3-tetrachlorobutane (**10**).

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Electron Bridges in the Mechanisms of Chromic Acid Oxidation of Alcohols

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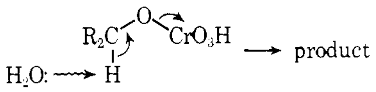
Abstract: The temperature dependence of the kinetic isotope effect criterion (TIC) has been applied in studies of the Cr(VI) oxidation of a variety of alcohols. Cyclohexanol, 1-phenylethanol, and benzhydrol, regarded as normal in their behavior, display TIC parameters which are fully consistent with a pericyclic transition state of H transfer. The highly hindered alcohol di-*tert*-butylcarbinol shows evidence of a large tunneling correction which is also variable and dependent on $[H^+]$. Electron-withdrawing substitution, as in trifluoromethylphenylcarbinol, appears to exert very similar effects. These have been rationalized as an alteration in transition-state structure which allows for H transfer through the associated structure of the solvent and the ligands of the octahedral chromium (chromate ester) complex, whose decomposition is occurring in the rate-determining step of the oxidation process. While pericyclic electron transfer (where hydrogen is performing the role of the electron bridge) has not been previously identified in familiar redox systems, the transfer of electrons through a bridging structure of water molecules is not unprecedented[12-14] as an inner sphere "coordination mechanism".

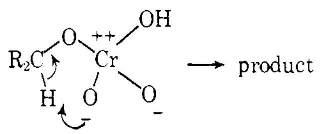
The Cr(VI) oxidation of alcohols is regarded as a two-step reaction; the initial, ordinarily rapid, equilibrium formation of chromate ester is followed by a rate-determining decomposition to product. Three possible modes of hydrogen transfer have been proposed in discussions[1] of the ester decomposition mechanism (see Scheme I). Considerations bearing on possible

Scheme I

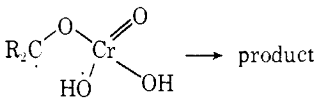
(A) An H transfer to external base without specification of the timing of bond-make and -break



(B) Cyclic H transfer with concerted bond-make and -break



(C) Cyclic H transfer with formation of radical intermediate



distinctions between these mechanistic alternatives have been extensively reviewed.[1-3] A decisive basis for choice has not been reached as yet, nor has it been possible to specify on the basis of kinetic information a unique mechanism appropriate to all secondary alcohol Cr(VI) oxidations operating to the exclusion of all other kinetically admissible possibilities.

The temperature dependence of the primary kinetic isotope effect criterion for transition-state structure, hereafter referred to as TIC, has been treated in earlier communications[4-6] disclosing preliminary evidence supporting the occurrence of more than one mode of H transfer in Cr(VI) oxidation of alcohols. The purpose of this report is to consider the variety of substrate structure and reaction conditions which can influence the mechanistic course of oxidation. At issue also in the ensuing discussions is the mechanism and stereochemistry of electron transfer in redox reactions of transition elements, a subject which has been extensively investigated by Taube and coworkers.[7]

Results and Discussion

Although not widely recognized previously, the magnitude of the primary kinetic deuterium isotope effect in a H-transfer process is controlled by two independent factors: the zero-point energy difference and the tunneling correction. The basis for this statement has been most recently advanced by Bell[8] and abundantly illustrated in a number of kinetic studies of proton-transfer reactions in solution by Caldin and co-workers.[9] Even from a purely qualitative viewpoint it is important to bear in mind that the size of the tunnel correction is related to structural features of the transition state. In fact, the tunnel correction may prove to be the best empirical index available for elucidating these structural features.

Thus, in a symmetrical transition state in which H transfer is effected through synchronous bond-make and -break, and where the C–H vibrational energy decreases almost to extinction as the hydrogen tends to become immobilized in the course of linear transfer between the reaction centers, the tunnel correction will also tend to disappear. In all other cases, the size of the tunnel correction can be correlated with features in the activated complex which allow for a significant energy content of the critical C–H bond. The primary features exerting direct influence are (1) the synchronism of bond-make and -break or what is often referred to as the product-like or reactant-like nature of the transition state and (2) solvation of the transferring hydrogen via electrostatic or dipolar interactions with components of the medium which can thereby determine the "effective mass" of the hydrogen. Secondary factors can be recognized among a variety of steric and electronic influences affecting the vibrational energy of the critical C–H bond.

Most of the above considerations have been applied in these studies aimed at clarifying the salient features of the ester decomposition step. The results are presented in the following sections of this report. They are most conveniently separated and discussed in terms of the several types of substrate alcohol structures which appear to determine which course of Cr(VI) oxidation is experienced.

Ordinary Secondary Alcohols. To evaluate the size of the tunnel correction in a series of substituted alcohols, which are classifiable as unhindered and electronically unbiased, the temperature dependence of the primary kinetic isotope effect must be determined. Application of this criterion (TIC) has already been illustrated[4] for one of these alcohols, cyclohexanol (**1**). Two other secondary alcohols, 1-phenylethanol (**2**) and benzhydrol (**3**), and their deuterated analogues have now been examined in TIC runs with very similar results. The kinetic data gathered in these experiments are compiled in readily available form.[6]

A comparison of the TIC parameters computed from these data is given in Table I. Those of the ordinary alcohols (**1, 2,** and **3**) show direct correspondence with the properties of a symmetrical transition state; the activation energy difference for k_H/k_D is equal to the zero-point energy difference (ca. 1.1 kcal) of respective C–H and C–D bonds, and the frequency factors for the respective oxidations are nearly identical ($A_H/A_D \simeq 1$). Plots of the experimental ln k vs. $1/T$ data clearly demonstrate the coincidence with all the experimental points of a theoretical line drawn on the assumption of only zero-point energy control of the relative rates k_H/k_D. That is to say, the experimental data confirm that the tunnel correction is zero to all intents and purposes in the oxidation of cyclohexanol[4] as well as the ordinary alcohols **2** and **3.**

These results permit a clear choice among the mechanistic alternatives considered previously[1-3] to be indistinguishable on the basis of other kinetic criteria. Thus, mechanism A in Scheme I, a noncyclic pathway, would be expected to display a tunneling correction, but in hydroxylic solvents this should vary in magnitude due to variation of the effective mass of the transferring hydrogen in the solvating medium. These characteristics of the isotope effect have not been noted in the case of the ordinary alcohols studied. Mechanism C, which is cyclic but nonconcerted, should show the tunneling correction normally associated with reactant-like (exothermic) transition states. On the other hand, mechanism B, a most reasonable, symmetrical transition state corresponding to a minimum tunneling correction, is one which can be identified as a pericyclic electron-transfer mechanism.

Pearson[10] has examined from the viewpoint of perturbation theory the orbital symmetry rules generally operative to various inorganic reactions. The possibility of an electron-transfer process occurring via an orbital symmetry-controlled mechanism has been previously considered only in hydrocarbon oxidations by OsO_4 and MnO_4^-. It must now be recognized that an electron bridge[11] involved in a redox process can comprise a pericyclic construction by means of which linear hydrogen transfer is effected. The identification of such a pericyclic mechanism of electron transfer can be confidently established through application of TIC.

The mechanistic picture in Figure 1 is very informative in that it suggests circumstances which may prevent the realization of the pericyclic process. For example, certain structural features of the carbinol ligand of the central Cr(VI) could conceivably act to restrain the hydrogen from achieving the linear, coaxial relationship accommodating the pericyclic transition state. Under these circumstances an alternative pathway for H transfer must be provided which engenders the possibility of an unsymmetrical electron bridge and, therefore, a measurable tunnel correction. These circumstances have been realized both with certain sterically hindered alcohols and with

Table I. Summary of Kinetic and TIC Parameters Computed from Rate Data[a] on Oxidation of Various Alcohols with Cr(VI)

	Alcohol	$[H^+]$, M	E_a, kcal	$(\Delta S^{\ddagger})$[b]	A[c]	R[d]	$[E_a]_D{}^H$	A_H/A_D	Crossover[e] temp, °C
Cyclohexanol	**1**-H	0.12	12.6 ± 0.1	−27.5 ± 0.5	3.3×10^7	0.999			
	1-D	0.12	13.6 ± 0.1	−28.0 ± 0.6	2.6×10^7	0.999	1.0	1.3	∞
Phenylethanol	**2**-H	0.12	12.7 ± 0.2	−31.9 ± 0.7	2.0×10^6	0.998			
	2-D	0.12	13.8 ± 0.2	−31.9 ± 0.5	2.0×10^6	0.999	1.1	1.0	∞
Benzhydrol	**3**-H	0.12	13.1 ± 0.2	−17.4 ± 0.6	2.9×10^9	0.991			
	3-D	0.12	14.1 ± 0.2	−17.7 ± 0.6	2.4×10^9	0.998	1.0	1.2	∞
Di-*tert*-butylcarbinol	**4**-H	0.12	14.1 ± 0.1	−20.3 ± 0.8	1.2×10^9	0.997			
	4-D	0.12	17.1 ± 0.1	−14.9 ± 0.9	1.8×10^{10}	0.999	3.0	0.067	283
	4-H	3.5	10.4 ± 0.2	−19.0 ± 0.8	1.2×10^9	0.997			
	4-D	3.5	11.6 ± 0.3	−18.3 ± 0.8	1.8×10^9	0.998	1.2	0.67	1340
	4-H	5.9	10.0 ± 0.3	−17.8 ± 1.0	2.2×10^9	0.994			
	4-D	5.9	13.6 ± 0.2	−5.8 ± 0.8	9.4×10^{11}	0.998	3.6	0.0023	25
	5-H	2.3	13.8 ± 0.1	−29.1 ± 0.8	1.5×10^7	0.997			
	5-D	2.3	18.5 ± 0.2	−17.1 ± 1.3	6.3×10^9	0.998	4.7	0.0024	116
Trifluoromethylphenylcarbinol	**5**-H	7.1	10.4 ± 0.2	−25.6 ± 0.5	4.6×10^7	0.998			
	5-D	7.1	12.9 ± 0.2	−20.8 ± 0.6	5.0×10^8	0.998	2.5	0.092	257
	5-H	8.2	10.5 ± 0.2	−23.9 ± 0.6	1.1×10^8	0.998			
	5-D	8.2	13.4 ± 0.2	−17.5 ± 0.7	2.7×10^9	0.998	2.9	0.041	170

[a] Computed from data tabulated in ref 6; in aqueous acetic acid media, at constant ($NaClO_4$ or $LiClO_4$) ionic strength (0.20), $Cr(VI)_0 = 8.9 \times 10^{-4}$ M, with $HClO_4$ as source of $[H^+]$. [b] The entropy of activation in entropy units. [c] In units of l./(mol s). [d] Correlation coëfficient. [e] Defined as the temperature at which $k_H/k_D = 1.0$ in a mechanism of H transfer involving tunneling.

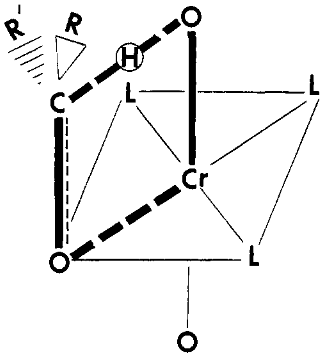


Figure 1. The normal pericyclic transition state of hydrogen transfer; critical bonds are represented by heavy lines.

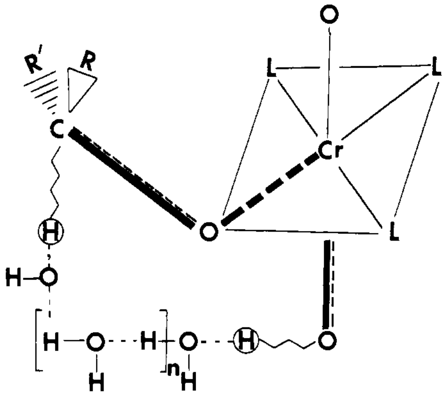


Figure 2. The tunneling transition state of hydrogen transfer; wavy lines indicate unsymmetrical transfer of hydrogen.

relatively acidic carbinols made so by a large degree of electronegative substitution at the carbinyl center.

Effect of Acidifying Substituents. When the methyl group in 1-phenylethanol is replaced by a highly electron-withdrawing trifluoromethyl group, as in trifluoromethylphenylcarbinol (**5**), the effect on the TIC parameters, as seen in Table I, can be correlated with the incidence of a large tunneling correction. The symmetry which characterized the pericyclic transition states of oxidation of **1**, **2**, and **3** has been vitiated by the trifluoromethyl substituent which can be assumed to have greatly acidified the C–H bond to be transferred in the rate-determining step. $[E_a]_D{}^H$ is increased from the normal value (1.1 kcal/mol) of the symmetrical transition state for oxidation of the nonfluorinated analogue **2** to almost 5 kcal/mol at 2.3 M $[H^+]$, and A_H/A_D is decreased by a factor of nearly 400.

Figure 1, which takes into account the octahedral structure of the coordinated Cr(VI), is proposed to represent the pericyclic transition-state geometry by which the ordinary alcohols like **2** undergo oxidation. The carbinyl C–H bond in **2**, lacking in polarity, finds the hydrogen relatively unsolvated in the aqueous acetic acid medium. This condition allows for ready fulfillment of the required coaxial relationship with a neighboring oxygen ligand of the central Cr(VI). However, these circumstance are drastically altered by replacing R or R′ with strongly electronegative substituents exerting a strongly acidifying influence on the carbinyl hydrogen. Consequently, a steep increase in the degree of hydroxylic (electrostatic) solvation of this hydrogen is experienced. An increase in the degree of associative organization of the hydroxylic solvent medium can also be presumed to attend this substitution. The type of solvent packing that results has the twin effect of preventing the formation of the planar, pericyclic relationship in Figure 1 while fostering a nonplanar chain structure of hydroxylic molecules capable of transferring a hydrogen via the familiar Grotthus mechanism.[5] Quantum-mechanical tunneling is a conceivable concomitant of the circumstances depicted in Figure 2.

It must be recognized that the Figure 1 reaction process comprises a familiar representation, typical of redox mechanisms, in which a group is acting as an electron bridge between oxidizing and reducing centers and resembling, in this respect, an "inner sphere" coordination mechanism.[11,7] However, such a process of pericyclic nature in which hydrogen may be regarded as the bridging species has not been recognized pre-

Table II. Calculated Room-Temperature Isotope Effects for Cr(VI) Oxidation of Certain Alcohols

Alcohol	[H$^+$], M	$(k_H/k_D)_{25°C}$
1	0.12	6.9
2	0.12	6.6
3	0.12	6.4
4	0.12	10.6
4	3.5	5.3
4	5.9	1.0
5	2.3	6.6
5	7.1	6.4
5	8.2	5.0

viously. The representation of Figure 2 as an atom-transfer process is precedented for the case of hydrogen transfer in the work of Dodson and Davidson,[12] Stranks and others,[13] where one or more hydrogen-bridged water molecules can intervene between the reactant centers. Distinctive evidence that electron transfer can occur through an extended bridge of atoms and details on how the nature of the bridge controls the redox rate come from the exhaustive studies of Taube and co-workers.[14] The feasibility of transferring electrons over considerable distances through a suitably organized water structure has been the subject of both speculation[15] and mechanistic hypothesis.[16]

Stewart and Lee[17] have previously noted the effects of aromatic substitution on k_H/k_D at a single temperature (25 °C) in a series of trifluoromethylphenylcarbinols and have shown that such values of k_H/k_D are a function of substitution. Application of the TIC now brings to light the influence of acidifying substitution on the tunneling factor controlling the full magnitude of the isotope effect. Solvation effects of this nature in proton-transfer transition states have been identified[9] as the factor that often reduces the size of the tunnel correction through solvation increases in the effective mass of the proton. In the present instance, however, it can be seen that solvation can develop into a factor which *increases* the tunnel correction through deviation of the transition-state symmetry (from pericyclic). This point will receive further consideration in a later section concerned with the effect of medium acidity.

Sterically Hindered Alcohols. It has frequently been shown that large tunnel corrections are to be found for sterically hindered systems, and this has been attributed[18] to a higher and steeper energy barrier. This has been interpreted as the result of exclusion of solvent molecules by the hindering group, thus producing a low effective mass for the transferring proton. Indeed, when the highly hindered substrate di-*tert*-butylcarbinol (**4**) is subjected to the TIC trials, the results show a very large increase in the tunnel correction (see Table I), $[E_a]_D{}^H = 3$ and $A_H/A_D = 0.07$. This is taken to indicate a sharp departure from the symmetrical transition state exhibited by ordinary alcohols.

However, since an increase in solvation of the carbonyl hydrogen occasioned by the substitution of acidifying groups has been noted to produce a mechanistic deviation characterized by a large increase in the tunnel correction, a similar consequence induced by the substitution of bulky, hindering groups in the environment of the carbinyl hydrogen cannot correspond to a change in solvation or a significant change in the effective mass of the transferring hydrogen. The simplest, most direct and, therefore, the most attractive conclusion as to the effect of steric hindrance producing an increased tunneling correction (here) is that the bulky groups prevent fulfilment of the geometric requirements of the normally planar, pericyclic transition state. Contrary to the usual situation, the hindering groups enforce a mechanism of hydrogen transfer to a second ligand of the Cr(VI) in Figure 2 via the organized solvent structure linked to the reactant centers through electrostatic solvation of the carbonyl hydrogen. Despite the bulk of the *tert*-butyl substituents, a linear, coaxial movement in the direction of the surrounding solvent structure, with which the carbinyl hydrogen is electrostatically interacted, is apparently much more feasible than toward a neighboring ligand of the central Cr(VI). This may very well be of ground-state origin, not unlike the effect of bulky α-alkyl substitution destroying favor for the eclipsed conformation of the α hydrogen and the carbonyl group in aliphatic aldehydes, possibly by making the gauche rotamer relatively more stable.[19]

Influence of Medium Acidity. Previous notice has been taken of the fact that the magnitude of the tunnel correction is a relatively sensitive function of the acidity of the medium. It suggests that a partitioning between pericyclic (Figure 1) and solvent transfer (Figure 2) mechanisms occurs generally. The composition of the hydroxylic medium is known to regulate the rapidly exchangeable ligand structure of the coordination sphere of Cr(VI), as well as its own association structure. The tunnel correction depends on both of these considerations in ways which affect the choice of mechanism and thus the pathway of H transfer. Consequently, the ability to predict the values of the parameters $[E_a]_D{}^H$ and A_H/A_D as a function of [H$^+$] may not be easily realized until the influence exerted by [H$^+$] on these mechanism-governing factors can be treated quantitatively or at least understood.

A tendency toward smaller isotope effects with increasing acidity has been noted by Kaplan[20a] for tritium isotope effects in Cr(VI) oxidation of 2-propanol. A similar observation of this general trend was made by Lee and Stewart[20b] studying trifluoromethyl-substituted 2-propanols. These workers found abnormally high k_H/k_D values at moderate acid concentrations at ambient temperatures. At very high H_0 values these decline toward a zero isotope effect. The increase in rate paralleling the decline in k_H/k_D crested in the vicinity of $H_0 = -4$. At even higher acidities the rate gradually declined as k_H/k_D approached unity. This inflection point in the rate was interpreted to signal the incursion of a new mechanism in which chromate ester formation became the rate-determining step; the slow step in the oxidation was assumed to become esterification, since at the higher acidities both the alcohol and Cr(VI) moieties which form the ester may be converted to their positively charged, less reactive, conjugate acid forms.

However, these observations can be accommodated without the assumption of such a profound shift in mechanism. An alternative interpretation may, in fact, be tested and established through application of the TIC. Thus, the size of k_H/k_D at 25 °C (Table II) for alcohols studied for this purpose shows a similar sensitivity to acid strength which is to a first approximation independent of structure. However, it can also be seen that, while ordinary alcohols (**1**, **2**, and **3**) have nearly identical isotope effects at the same temperature and medium composition, abnormal alcohol (**4** and **5**) characterized by transition states with tunneling corrections show TIC parameters which vary in a decidedly nonlinear manner with acidity of the medium (see Table I).

These data make it apparent that the disappearance of the isotope effect ($k_H/k_D \simeq 1$) at sufficiently high acidity is not necessarily due to a fundamental shift in the rate-determining step, but rather to a change in transition-state symmetry and partitioning between symmetric and nonsymmetric activation steps. Variation in the values of $[E_a]_D{}^H$ and A_H/A_D with [H$^+$] change can conceivably lead to k_H/k_D values approaching unity or even less than 1.0 at ambient temperatures,[5] where single values of the isotope effect have been commonly compared[1-3] as a basis for mechanistic decision. A case in point has been realized with the data in Table II describing the variation of k_H/k_D with temperature and perchloric acid concentration at fixed ionic strength. An increase in [H$^+$], under otherwise closely similar conditions, from 0.12 to 5.9 M perchloric acid results in a decline of k_H/k_D from 10.6 to 1.0 at 25 °C for di-*tert*-butylcarbinol oxidation. Moreover, the data demonstrate (see Table I) conclusively that this is the result of an attendant change in TIC parameters and, therefore, a change in the partitioning between unsymmetrical (tunneling) and symmetrical transition states of H transfer.

The role of acid as a regulator of such partitioning may be traced to both the effect of the proton on the properties of the highly associated aqueous medium and of the conjugate anion as a (possible) ligand in the coordination sphere of Cr(VI). At sufficiently high levels of [H^+], where most of the hydroxylic components of the medium tend to become protonated, the partitioning may actually favor the symmetrical transition state. At even higher [H^+], however, the altered character of the association structure and the resultant increased efficiency of H transfer via the proton jump mechanism[5] appears to shift favor in the direction of the unsymmetrical transition state.

The role of the acid anion participating in the regulation of the TIC parameters is apparently very complex. Preliminary results show, for instance, that a change from $HClO_4$ to H_2SO_4 as the acid component of the medium has a profound influence on the TIC parameters of both hindered alcohols and those with highly electron-withdrawing substituents.[21]

In sum, it must be emphasized that all substrates possessing a critical degree of steric hindrance or electronegative substitution in Cr(VI) oxidation are inclined to react via transition states characterized by an extensive tunnel correction. The acid components (both H^+ and A^-) of the reaction medium are clearly capable of regulating the partitioning between unsymmetric and symmetric pathways and, therefore, both the size of the tunnel correction and k_H/k_D. In a given instance, the existence of steric hindrance or electronic substituent factors may be sufficient to create the impression of a zero isotope effect, when, in fact, application of the temperature dependence of the isotope effect criterion (TIC) would reveal the dominance of the tunneling correction in determining k_H/k_D. A case in point may be the alcohol DAHO,[22a] which has been alleged to oxidize via a rate-determining esterification mechanism on the basis of a $k_H/k_D \simeq 1$ at ambient temperatures. It is unfortunate that this uncertain allegation continues to be applied[22b] as the basis for interpretation of the results of selective Cr(VI) oxidations of alcohols of crucial importance.

Experimental Section

General. All melting points were determined using a Mel-Temp melting point apparatus and are uncorrected, as are all boiling points. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer using polystyrene film for calibration. Nuclear magnetic resonance spectra were recorded on either a Perkin-Elmer R-12A or a Varian Associates A-60A spectrometer using tetramethylsilane as a reference.

For all reactions involving lithium aluminum deuteride, the ether solvent used was first distilled over lithium aluminum hydride. In all products prepared by the lithium aluminum deuteride reduction of ketones, no more than 1% CHOH was detected by the NMR.

Preparation of Reagents Used in Kinetic Studies.[23] **Cyclohexanol-*1-d*** was prepared from purified cyclohexanone by reduction with lithium aluminum deuteride (Stohler); **di-*tert*-butylketimine,** from pivalonitrile (Aldrich) by methods previously described [24,25] (the product physical and chemical properties were in complete accord with those listed in the literature); **di-*tert*-butyl ketone,** from the ketimine by the previously described[24] method of hydrolysis; **di-*tert*-butylcarbinol,** from the ketone by lithium aluminum hydride reduction in ether solution (the properties of this product were in complete agreement with those described in the literature);[26] and **di-*tert*-butylcarbinol-*1-d*** by the analogous procedure using lithium aluminum deuteride (Stohler).

α,α,α-Trifluoroacetophenone was prepared by the method of Levine.[27,28] The identity of the product was confirmed by NMR (CCl_4): δ 7.5 (m, 3), 8.0 (m, 2); ir (neat) 1720 (C=O), 1150 (C-F), 745 and 710 cm^{-1} (monosubstituted benzene). **Trifluoromethylphenylcarbinol** was prepared by reduction with lithium aluminum hydride in accordance with literature direction.[29] The properties were in agreement with literature values. **1-Phenylethanol-*1-d*,** which was obtained by reduction of acetophenone with lithium aluminum deuteride, was identical in properties with those reported.[30] **Benzhydrol-*1-d*,** obtained by reduction of purified benzophenone with lithium aluminum deuteride, possessed properties identical in all respects with those listed in the literature.[31]

Kinetic Methods. Cary Model 16. The apparatus used for measurements consisted of a Cary Model 16 visible/ultraviolet spectrophotometer equipped with a thermostated cell compartment, a Lauda Model K-4/R heating/refrigeration constant-temperature bath, a Leeds and Northrup Microvolt meter, and a Varian Associates Model G2000 strip chart recorder.

In general, the procedure utilized was to place the reagents (i.e., chromic acid, perchlorate salts, acid, and solvent) in the proportions desired, in a 100-ml volumetric flask. The perchlorate salts were added to maintain constant ionic strength. From this flask were pipeted 3-ml aliquots into a 1-cm square quartz cuvette, which was placed in the thermostated cell compartment and allowed to equilibrate with the compartment temperature.

In order to monitor the difference in temperature between the constant temperature bath and the oxidizing solution, the Leeds and Northrup microvolt meter was utilized. With this apparatus, two iron–constantan thermocouples were connected in opposition, so that the meter measured the difference in voltage between the two. One thermocouple was immersed in the constant-temperature bath.

The cuvette was fitted with a Teflon stopper, through which a 3-cm length of glass capillary sealed at one end was inserted so that the capillary was immersed in the solution to a depth of approximately 1 cm. The capillary was filled with silicon oil and the second thermocouple from the volt meter inserted into the oil. In this way, the actual temperature of the oxidizing solution could be monitored within approximately ±0.2 °C.

When the temperature had reached equilibrium (as evidenced by no further motion of the microvolt meter), reaction was commenced by the addition of 50 μl of appropriate alcohol solution by means of a syringe equipped with a Teflon plunger. The syringe tip was fitted with a small Teflon paddle which was agitated following the addition of the alcohol, thus enabling alcohol addition to occur rapidly and assure complete mixing by the circular motion of the paddle blade.

The rate of reaction was measured by following the loss of Cr(VI), which absorbs at 350 nm. The usual Beer–Lambert relationship between optical density and concentration of Cr(VI) was checked and found to hold in the concentration ranges studied. The optical densities of the solutions at 100% reaction were found to be zero. This information, coupled with the good first-order rate plots obtained, was the basis for the assumption that the absorption of the products was negligible in all cases.

Durrum Model 110 Stopped-Flow Spectrophotometer. In those instances where the measurement of a comparatively rapid reaction was desired, a Durrum Model 110 stopped-flow instrument equipped with a Neslab Model RTE-8 constant temperature bath was employed. The operation of this instrument is relatively straight forward.[32] The procedure consisted essentially of preparation of an alcohol solution and an oxidizing solution of identical solvent composition in order to avoid any evolution of heat due to solvent interactions during the mixing process. The alcohol and chromic acid solutions contained twice the desired alcohol and Cr(VI) concentrations, since a 1:2 dilution effect was realized on mixing.

The rate of reaction was monitored as the loss of Cr(VI) absorbing at 350 nm vs. time and was displayed on a Hewlett-Packard Model 1207B storage oscilloscope furnished with the instrument. Replicate runs were carried out at each temperature and a Polaroid® picture taken of the display on the scope screen.

Acidity Measurements. In cases where measurement of the acidity (H_0) of the solution was desired, the indicator method of Wiberg and Evans[33] was employed using *p*-nitroaniline as the indicator. Generally, the values measured by this method were in good agreement with those reported by Rochester.[34]

Product Analysis. Where side reaction could occur in addition to the normal oxidation reaction, product analysis was carried out on a larger scale reaction sample. These reactions were carried out at both extremes of temperature in all cases.

The procedure consisted of mixing 30 ml of oxidizing solution with

9.5 ml (20–50-fold excess) of alcohol solution and thermostating for the period of time required for the disappearance of the yellow color of Cr(VI). Sodium hydroxide (100 ml, 2.5 M) was then added with cooling to the mixture to neutralize the acetic acid. Completeness of neutralization was monitored with pH paper. The resulting aqueous solution was twice extracted with 100 ml of ether, and the combined ether extracts were washed with water and dried ($MgSO_4$) and evaporated to a volume of ca. 0.5 ml. The mixture was then analyzed on a Hewlett-Packard Model 700 gas chromatograph equipped with dual flame ionization detectors. In each case, only the alcohol starting material and normal oxidation product were detected.

Determination of Activation Parameters. Once the rate constants at various temperatures had been determined, Arrhenius plots of the natural logarithm of the rate constant against the reciprocal of the absolute temperature were made. To aid in the accurate plotting of these data and their linear regression analysis, the University of Delaware Burroughs B-6700 computer was utilized. The appropriate program was written by Dr. John J. Stanulonis of these laboratories and made available to us. The program permitted the determination of the least-squares slope of the plot and its intercept, as well as statistical information which indicated the reliability of the data. The statistical equations were those suggested by Bauer.[35]

From the slope of the Arrhenius plot, the energy of activation may be determined, using the relationship

$$\ln k = \ln A - E_a/RT$$

Plotting ln k vs. $1/T$ resulted in a straight line whose slope is to be equated with $-E_a/R$.

The entropy of activation is calculated from the relationship[36]

$$\Delta S^{\ddagger} = R(\ln A - \ln T - 24.76)$$

where A is the Arrhenius intercept and T is the absolute temperature.

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The Solvatochromic Comparison Method. 2. The α-Scale of Solvent Hydrogen-Bond Donor (HBD) Acidities

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Received July 7, 1975

Abstract: The solvatochromic comparison method is used to evaluate hydrogen-bonding contributions in HBD (hydrogen-bond donor) solvents to several commonly used dye indicator solvent polarity scales (Dimroth's E_{T30}, Brooker's χ_R, Kosower's Z). Hydrogen-bonding effects on other spectral properties, equilibria, and reaction rates are determined, and the results are used to construct an α-scale of solvent HBD acidities.

In part I of this series,[2] information obtained through solvatochromic comparisons was used in constructing a β-scale of solvent hydrogen-bond acceptor (HBA)[3] basicities. This β-scale was to serve, together with an α-scale of solvent hydrogen-bond donor (HBD)[3] acidities, toward correlation of solvent effects on many reaction rates, equilibria, and spectroscopic properties, XYZ, through equations of the form

$$XYZ = XYZ_0 + \text{solvent polarity-polarizability effect} + a\alpha + b\beta \quad (1)$$

where a and b represent the susceptibilities of XYZ to changing solvent HBD[3] acidity and HBA basicity, respectively. In the present paper we shall use the same solvatochromic comparison method toward the formulation of the α-scale of solvent HBD