

Communications

Primary Deuterium Isotope Effects in the Oxidation of Benzyl- α -*d* Alcohol by Transition Elements and Related Reagents: Mechanisms of Electron Transfer

Summary: The vast disparity in the temperature dependencies of k_H/k_D observed in the oxidation of benzyl alcohol by manganese dioxide and nickel peroxide on the one hand and for Ce(IV) and DDQ on the other seems to be correlatable with differences in their respective cyclic transition states involving coupled-hydrogen and electron-transfer processes.

Sir: As a result of measurements of the temperature dependence of the kinetic deuterium isotope effect, the normal mechanism of Cr(VI) oxidation of alcohols is interpreted to involve a broad reaction barrier in a cyclic concerted transition state of linear hydrogen transfer.^{1,2,3} This occurs in a pericyclic mode (Figure 1) wherein the proton- and electron-transfer processes are coupled.⁴ A number of related oxidations of alcohols by higher valence transition elements are not as well understood.⁵ MnO₂ and NiO₂ are typical of such reagents, widely used in preparative organic chemistry, which have also received considerable attention mechanistically,⁶⁻⁹ but the mechanistic generalities which relate these periodic neighbors to Cr(VI) have not been hitherto perceived. We present here results of kinetic isotope effect studies which seem to provide increased understanding of the common features among these alcohol oxidation processes.

As has been pointed out in earlier studies¹⁻³ of the Cr(VI) oxidation reaction of alcohols, only the temperature dependence of k_H/k_D affords a basis for assessing the structural features of the activated complex in hydrogen-transfer processes.¹⁰ This has now been realized by oxidizing benzyl- α -*d*₁ alcohol (1) to the aldehyde over a broad range of accurately controlled temperatures with four reagents: MnO₂, NiO₂,⁷ Ce(IV),¹¹ and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).¹² Estimation of the C₆H₅CHO/C₆H₅CDO product ratios was carried out by means of the mass spectrometric technique previously developed¹³ for the high precision measurements required in applying these data as a mechanistic criterion. The conditions of the experiments were: MnO₂ and NiO₂ dispersed in a heptane solution of 1 (heterogeneous), Ce(IV) in an aqueous solution of 1 (homogeneous), and the quinone DDQ in a benzene solution of 1 (homogeneous). All runs were carried out in fully degassed, sealed tubes.

The results are summarized in Tables I and II. The principal observations are the striking temperature-dependent k_H/k_D values measured for the MnO₂ and NiO₂ systems and the equally striking temperature-independent isotope effects measured for the Ce(IV) and DDQ systems. For MnO₂ and NiO₂ (Table I) the activation parameters $[\Delta E_a]_D^H$ and A_H/A_D are of magnitudes which indicate tunneling in a reaction of

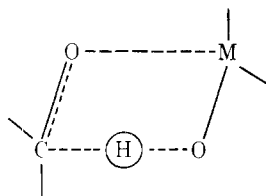


Figure 1. Linear H transfer in transition element oxidation of alcohols, where M = a transition element with tetragonal, tetrahedral, or octahedral coordination sphere.

Table I. Temperature Dependence of k_H/k_D in Oxidation of C₆H₅CHDOH

| by MnO ₂ k_H/k_D | T, K | by NiO ₂ k_H/k_D |
|----------------------------------|------|----------------------------------|
| 12.67 | 298 | 10.16 |
| 11.10 | 308 | 7.41 |
| 9.59 | 318 | 6.07 |
| 8.29 | 328 | 5.00 |
| 7.42 | 338 | 4.12 |
| 6.57 | 348 | 3.49 |
| 5.93 | 358 | 3.05 |

| by MnO ₂ | by NiO ₂ | |
|--|---------------------|-------|
| Computed Quantities | | |
| $[\Delta E_a]_D^H$, kcal/mol | 2.72 | 3.92 |
| A_H/A_D | 0.130 | 0.012 |
| Classical Barrier Height Calculated ^{10d} | | |
| E_H^{class} , kcal/mol | 15.5 | 14.6 |
| E_D^{class} , kcal/mol | 16.4 | 14.8 |
| A (barrier width), Å | 0.75 | 0.62 |

Table II. Temperature Dependence of the Isotope Effect in the Oxidation of C₆H₅CHDOH (1)

| by Ce(IV) ^a | | by DDQ ^b | |
|------------------------|-----------|---------------------|-----------|
| T, K | k_H/k_D | T, K | k_H/k_D |
| 298 | 2.39 | 343 | 3.92 |
| 303 | 2.36 | 363 | 3.96 |
| 323 | 2.37 | 383 | 3.93 |
| 323 | 2.36 | 403 | 3.94 |
| 333 | 2.38 | 423 | 3.93 |
| 343 | 2.37 | 443 | 3.95 |
| 373 | 2.37 | 463 | 3.92 |
| av 2.37 ± 0.01 | | av 3.94 ± 0.01 | |

^a A reaction sample was charged with 2 cm³ of 0.5 M aqueous ceric ammonium nitrate and 70 μL of 1. ^b A reaction sample was charged with 5 cm³ of dry benzene, 150 μL of 1, and 0.363 g of DDQ.

linear H transfer, preceded on the very extensive theoretical developments of Bell and Caldin and their co-workers.¹⁴ The reaction barrier widths have been calculated on the assumption of a parabolic shape by a procedure discussed previously.^{10d} These distances provide a measure of the separation of the ligand centers in the coordination complex, 0.75 Å for the MnO₂ complex with 1 and 0.62 Å for the NiO₂, i.e., these data imply tunneling across a barrier of even narrower width for NiO₂ than for MnO₂.

In the case of MnO₂, free-radical intermediates have been involved in interpretations of a number of kinetic data.⁸ Furthermore, the finding of a large kinetic deuterium isotope effect^{9a} measured at a single temperature^{9b} ($k_H/k_D \approx 18.2$) was presumed to result from combined primary and secondary isotope effects and was regarded as indicative of a reversible adsorption of the reagent alcohol on the surface of the MnO₂. Alternative mechanisms involving seemingly reasonable cyclic transition states were considered to be excluded on the basis of the proposed intermediacy of free radicals in such oxidations.⁹ In our view, the marked tunneling, which is symptomatic of the narrow reaction barriers in the oxidation of 1

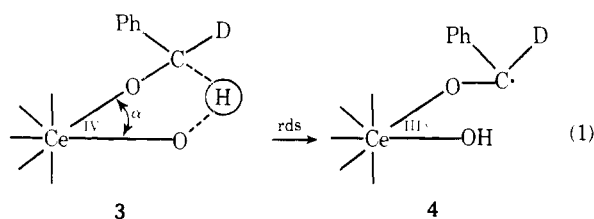
by MnO_2 and NiO_2 , suggests that the putative transition states (if the curvature of the barrier top was much lower) would be comprised of five-membered, cyclic arrangements of reaction centers with linear transfer of the hydrogen between the carbon and oxygen (see Figure 1). Oxidations of many normal alcohols like **1** by Cr(VI) , the neighboring element in the periodic system, have been proposed¹⁻³ to occur via such a pericyclic process; $[\Delta E_a]_D^H = [\Delta E_0]_D^H \approx 1.1$ kcal/mol and $A_H/A_D \approx 1.0$. With crowded, highly strained alcohols like di-*tert*-butylcarbinol, however, a shift in mechanism is experienced when the steric requirements for this concerted process of linear H transfer (Figure 1) cannot be fulfilled.³

A reasonable assumption would be that the steric requirements for a concerted process with Mn(IV) and Ni(IV) could be difficult to realize because of the limitation of effecting zero-point energy determined H transfer between the carbon and oxygen centers in these transition metal complexes which are spaced too closely in the lattice structure. In other words, the width of the activation barrier, which is equivalent to the spacing of the carbon and oxygen centers to be bridged in the H-transfer event, is far too narrow in these transition element oxidation reactions to permit the normal, zero-point energy-determined passage over the activation barrier shown¹⁰ for many other pericyclic H-transfer reactions.

The conclusion we draw from comparison of Cr(VI) , Mn(IV) , and Ni(IV) oxidations of normal alcohols is that the coupled electron- and hydrogen-transfer events in oxidations by transition elements tend to occur within the planar structure of a five-membered cyclic arrangement of reaction centers (Figure 1). Mechanistic preferences appear to be determined by factors which control the distance of separation of the reaction centers involved in the H-transfer step.

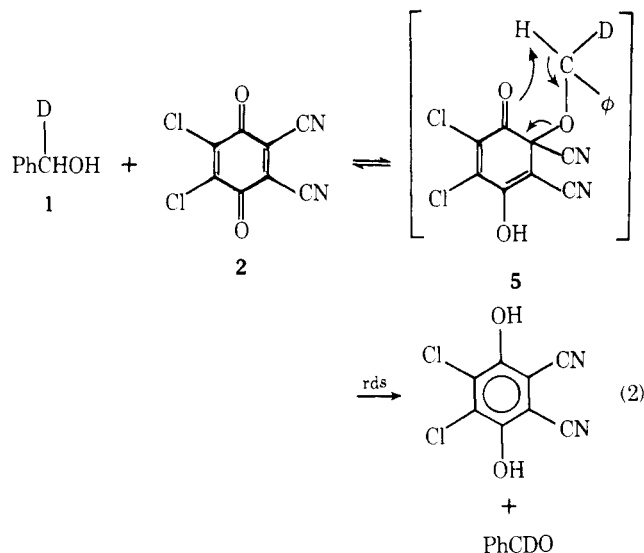
To what extent if any do these deductions apply to other alcohol oxidation processes, namely, the larger (nontransition element) ion Ce(IV) and the purely organic oxidant 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)? The results (Table II) are strongly reminiscent of the isotope effect in a number of cyclic concerted reactions in which the H transfer is effected in a bent transition-state structure.¹⁵ In the case of amine oxide thermolysis, for example, $k_H/k_D = 2.209 \pm 0.007$ over a 120 °C temperature range.^{16,17} In all these cases the temperature-independent value of k_H/k_D , which is equivalent to A_H/A_D , is greater than the theoretical maxima of 1.2 for zero-point energy controlled mechanisms, and 0.75 for tunneling mechanism of linear H transfer.¹⁸ The temperature independence, therefore, cannot be correlated with a linear H-transfer transition state which is either product-like or reactant-like.¹⁹ We interpret the results of Table II in terms of an activated complex of cyclic structure, but with a nonlinear H-transfer geometry.

The origins for the proposed bent transition state in Ce(IV) oxidations can be traced to the structure of the complex formed with the substrate ligand, which has been established²⁰ to attain rapid equilibrium on admixture of the reagents in hydroxylic solution. The large lanthanide group metal ions such as Ce(IV) tend to form multicoordinate (greater than octahedral) complexes with many ligands moving rapidly in and out of the coordination sphere.²¹ Thus, the projected angle (α in **3**, eq 1) subtended by the ligands at the central Ce(IV) would be much smaller than in tetrahedral or octahedral

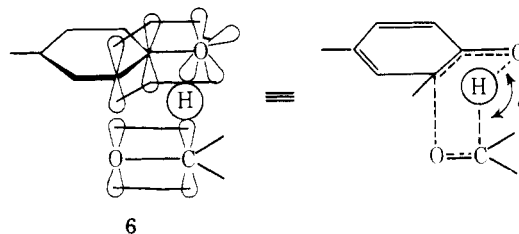


complexes of transition metal ions.

In the oxidation of **1** by DDQ, here also we ascribe the constancy of k_H/k_D over a 120 °C temperature range to a bent transition state of hydrogen transfer. The adduct **5** formed initially by the bimolecular reaction of the alcohol substrate and the DDQ reagent (eq 2) corresponds to the rapid, equi-



librium complex formation prevailing in the metal ion oxidations. The rate-determining step in this process is the hydrogen transfer taking place within the structure of **5**. An orbital diagram of the bent transition state represented by **6** is



intended to illustrate the structure in which nonlinear tunneling of hydrogen can take place. The occurrence of a bent transition state in this case may be correlated with a conformational factor in which severe nonbonded interactions in the cyclic arrangement of reaction centers are relieved by the puckering accompanying an angular transfer of hydrogen. It has been suggested²² that the observed isotope effect here may be a combination of a kinetic and a stereochemical factor. This view, however, is unacceptable, for if k_H/k_D was the product of two component effects, either or both of which involved linear H transfer, we should still observe the temperature dependence of k_H/k_D which is characteristic of the linear transition-state geometry and which is not realized experimentally.

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