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(18) Alfred P. Sloan Research Fellow, 1969–1971.

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Transition States in Chromium(VI) Oxidation of Alcohols

Sir:

The structure of the transition state of chromic acid oxidation of alcohols to ketones has long been the subject of controversy.[1] The rapid formation of a chromate ester equilibrium in a two-step reaction mechanism was indicated both by direct[2] and indirect rate evidence.[3] This conclusion was strongly supported by subsequent work by Roček, *et al.*,[4] suggesting that with a highly hindered alcohol the rate-determining event can be diverted to the ester formation step. These and other authors[5,6] favored an acyclic mechanism in which the carbonyl product formation is largely complete (perhaps two-thirds to three-fourths of a carbonyl bond formed)[7a,8c] in the transition state, based on the normally large magnitude of the kinetic deuterium isotope effect and kinetic acceleration reflecting steric hindrance in the alcohol.[7–9] This mechanism has taken root in the literature and has been applied[8,9] as the basis for structural distinctions in alicyclic and bicyclic alcohols correlating with Cr(VI) oxidation rates. However, a mechanism involving a cyclic, concerted transition state for decomposition of the ester intermediate, in which the carbonyl product is just half-developed, has been advocated by Kwart and Francis[10,11] to account for the same type of rate data.

The kinetic deuterium isotope effect has often been applied[1,4] as a valid criterion for mechanistic identification in Cr(VI) oxidations. The recent demonstrations[12–14] that the symmetrical transition state in a variety of cyclic, concerted H-transfer processes could be verified through measurement of k_H/k_D as a function of temperature prompted us to apply this expanded criterion in evaluation of the mechanism of Cr(VI) oxidation of alcohols. Such measurements have now been carried out over a 45–60° range of temperatures using two different substrates, respectively, a typical alcohol (cyclohexanol) and a highly hindered alcohol (di-*tert*-butylcarbinol) exhibiting an essentially zero rate of bimolecular, carboxylic acid esterification.

The data for the unhindered alcohol listed in Table I, part A, and plotted in Figure 1a can be readily fitted to the familiar expression, $k_H/k_D = A_H/A_D \exp(-\Delta E_a/RT)$. They show direct correspondence with the properties of a symmetrical transition state in which the activation energy difference (ΔE_a) for k_H/k_D is equal to the zero-point energy difference for the respective C–H and C–D bonds (*ca.* 1 kcal/mol), and the frequency factors of the respective reactions are nearly identical (*i.e.*, $A_H/A_D \cong 1.0$ and $\Delta(\Delta S^\ddagger) \cong 0$). The graphs in Figure 1 also illustrate the coincidence of the so-called maximum isotope effect line with the experimental rate points for cyclohexanol-d_1 oxidation.[12–15] This theoretical line is calculated on the assumption that the k_H/k_D ratio stems only from the zero-point energy factor, $(\Delta E_0)_D{}^H$.

Rate data of entirely different character were ob-

Table I. Pseudo-First-Order Oxidation of ROH in 50% Aqueous Acetic Acid Solution[a]

(A) Cyclohexanol				(B) Di-*tert*-butylcarbinol			
Proteo		Deuterio		Proteo		Deuterio	
T, °K	10^2k, min^{-1}	*T*, °K	10^2k, min^{-1}	*T*, °K	10^2k, min^{-1}	*T*, °K	10^2k, min^{-1}
294.6	1.39	303.2	0.42	289.4	2.86	298.7	0.56
298.7	1.97	307.4	0.52	293.9	4.75	302.7	0.75
302.2	2.58	312.6	0.89	307.4	13.5	307.4	1.24
306.8	3.64	316.6	1.04	316.2	22.3	316.2	2.69
311.6	5.17	318.5	1.21	317.4	26.6	326.2	5.58
319.8	7.73	322.6	1.59	325.1	42.6	330.9	8.98
315.1	5.69	330.2	2.40	325.8	42.8	335.7	11.6
320.8	8.54	332.7	2.91	326.0	40.1	340.1	20.0
320.4	8.67	338.0	4.14	326.2	44.7	344.4	23.4
319.5	8.04	340.7	5.00	330.9	63.3	350.9	41.4
331.8	15.0	344.2	6.20	331.2	58.3		
340.2	25.2			334.8	76.8		
332.2	14.9			334.9	79.5		
348.7	44.0			339.4	110		
344.7	34.9			340.0	105		
345.7	35.3			344.9	165		
348.7	42.4			344.9	155		
				349.0	204		

	(A) Cyclohexanol		(B) Di-*tert*-butylcarbinol	
	Proteo	Deuterio	Proteo	Deuterio
E_a	12.6 ± 0.1	13.6 ± 0.1	14.1 ± 0.1	17.1 × 0.1
$-\Delta S^\ddagger$	27.5 ± 0.5	28.0 ± 0.7	20.3 ± 0.8	14.9 ± 0.9
A	3.27×10^7	2.44×10^7	1.22×10^9	18.4×10^9
R^b	0.999	0.999	0.997	0.999

[a] At constant ionic strength ($NaClO_4$ = 0.20 *M*); acidity, H_0 = 0.658; h_0 = 0.220; $[Cr(VI)]_0 = 8.93 \times 10^{-4}$ *M*; rate = $k[ROH] \cdot [Cr(VI)]h_0$. [b] The correlation coefficient.

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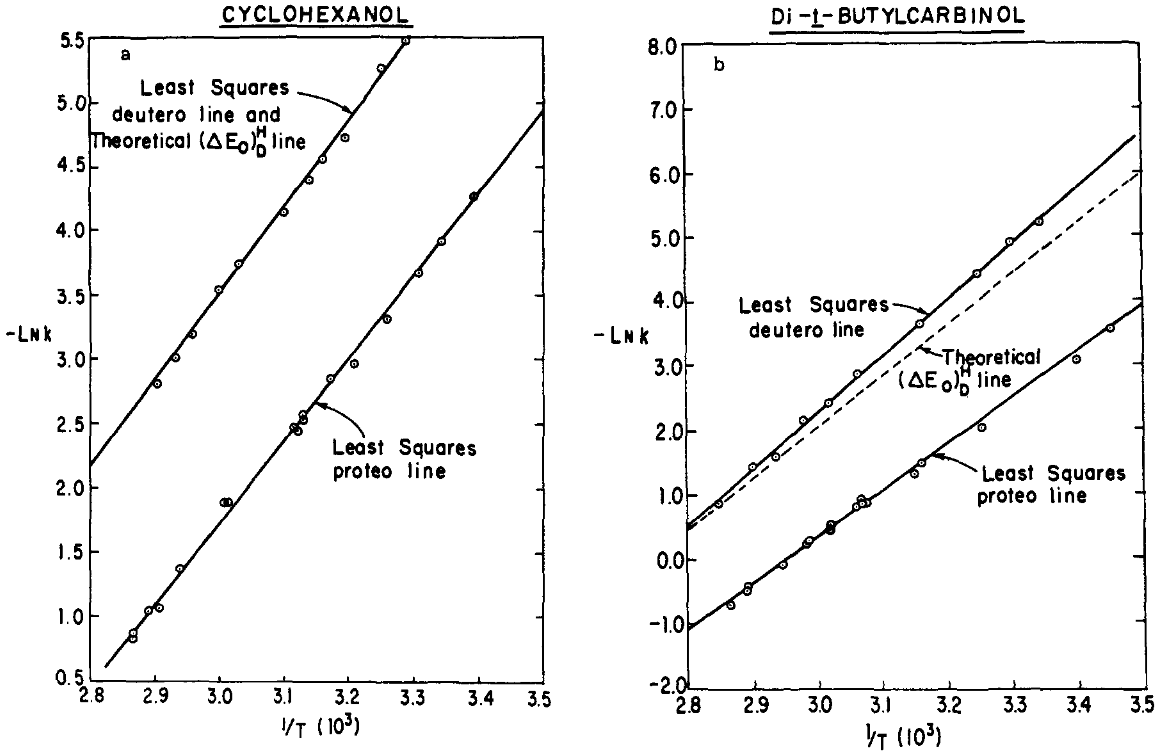


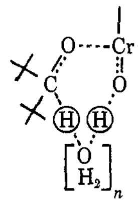
Figure 1. Deuterium isotope effect on the activation parameters of unhindered (a) and hindered (b) secondary alcohols in chromic acid oxidation.

tained for the hindered alcohol oxidation, as presented in Table IB and plotted in Figure 1b. Here ΔE_a ($\cong$3.1 kcal/mol) is nearly three times as great as the theoretical value of $(\Delta E_0)_D{}^H$ for a symmetrical transition state, and A_H/A_D (0.066) is only *ca.* 0.1 as great. These results are evidently consistent with a transition state of quantum-mechanical tunneling in H transfer.[16] Apparently the factor of steric hindrance in the di-*tert*-butylcarbinol has prevented the attainment of a planar symmetrical transition state configuration. Under these circumstances the hydroxylic solvent is required to complete the H transfer. The steric factor has raised the activation demand for ester decomposition, and H tunneling has occurred before the relatively thin "natural" barrier could be surmounted.

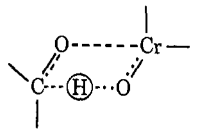
A clear assumption underlies all previous comparisons of the rates of hindered and unhindered substrate alcohols, especially those having an epimeric relationship; conclusions concerning the degree of carbonyl development require that the alcohols being compared must be reacting by identical mechanisms. The results discussed above, however, emphatically recognize that hindered and unhindered alcohols can react by entirely different pathways. They tend to bring into question all quantitative rate comparisons[7-9] and calculations based on the assumption of a commonly structured, product-like transition state for Cr(VI) oxidation of alcohols.

These results also bear directly on the consideration of whether the linear H-transfer event occurs in a cyclic (intramolecular) or acyclic (bimolecular) fashion in normal alcohols. A very cogent summary of the evidence against the occurrence of concerted, one-step, bimolecular processes of H transfer has recently been presented by Bordwell.[17] To the best of our knowledge, moreover, the only truly symmetrical processes involving linear H transfer[18] which have thus far been identified[12-14] by well-established criteria are intrinsically concerted, sigmatropic reactions characterized by cyclic transition states.[19]

The most attractive interpretation is that there are two extreme transition states for the electron transfer process involved in chromate ester decomposition; a planar cyclic symmetrical structure corresponding to a pericyclic[20] process (**2b**) for normal esters, and a nonplanar, unsymmetrical process (**2a**) to accommodate the steric requirements of highly hindered examples. The principal arguments advanced[4] against the process visualized in **2b** are now resolved by these findings



2a
unsymmetrical
transition state



2b
planar pericyclic
transition state

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based on the full kinetic isotopic criterion, *i.e.*, the variation of k_H/k_D with temperature.[18]

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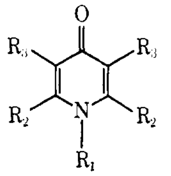
Photochemical Rearrangement of 4-Pyridones

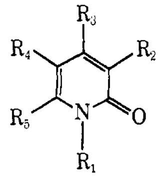
Sir:

The photochemistry of 2-pyridones has been extensively studied and the 4 + 4 adducts[1] or bicyclic isomer[2,3] was obtained. On the other hand, relatively little attention has been given to the photochemical reaction of the isomeric 4-pyridones. Sugiyama and his group reported that irradiation of Ic resulted in the recovery of the starting material.[4] We wish to report a novel photorearrangement of hindered 4-pyridones (Ia and Ib) leading to their isomers, 2-pyridones (IIa and IIb).

Irradiation[5] of Ia[6] in acetonitrile, followed by column chromatography of the reaction mixture on silica gel, resulted in the isolation of IIa[7] (mp 179.5–181.0°; ir 1630 cm^{-1} (C═O); nmr (CCl_4) δ 1.62 (s, 3 H), 2.06 (s, 3 H), 3.51 (s, 3 H), 7.1–7.4 (m, 10 H); mass spectrum (70 eV) at *m/e* (relative intensity) 289 (M^+ 78), 288 (100), 261 (44), 260 (39), 115 (27), 77 (39), 56 (37)) and IIc[7] (mp 203.0–203.5°; ir 1625 cm^{-1} (C═O); nmr (CCl_4) δ 1.72 (s, 3 H), 1.97 (s, 3 H), 3.10 (s, 3 H), 7.1–7.5 (m, 10 H); mass spectrum (70 eV) at *m/e* (relative intensity) 289 (M^+ 98), 288 (100), 261 (26), 260 (31), 115 (36), 105 (20), 77 (72), 51 (28)) in 35 and 2.5% yields, respectively. Photolysis[5] of Ib in acetonitrile gave IIb[7] in 31% yield (mp 159.5–160.5°; ir 1635 cm^{-1} (C═O); nmr (CCl_4) δ 1.32 (t, 3 H, J = 6.0 Hz), 1.61 (s, 3 H), 2.11 (s, 3 H), 4.16 (q, 2 H, J = 5.5 Hz), 7.1–7.5 (m, 10 H); mass spectrum (70 eV) at *m/e* (relative intensity) 303 (M^+ 99), 302 (71), 275 (50), 274 (100), 246 (12), 230 (10), 203 (14), 202 (17), 189 (11), 115 (12), 77 (10)). Irradiation[5] of Id[6] or Ie[6] in acetonitrile did not affect the starting materials.



Ia, $R_1 = R_2 = Me$; $R_3 = Ph$
b, $R_1 = Et$; $R_2 = Me$; $R_3 = Ph$
c, $R_1 = Me$; $R_2 = Ph$; $R_3 = H$
d, $R_1 = n\text{-}Pr$; $R_2 = Me$; $R_3 = Ph$
e, $R_1 = Me$; $R_2 = R_3 = Ph$



IIa, $R_1 = R_3 = R_5 = Me$; $R_2 = R_4 = Ph$
b, $R_1 = Et$; $R_3 = R_5 = Me$; $R_2 = R_4 = Ph$
c, $R_1 = R_3 = R_4 = Me$; $R_2 = R_5 = Ph$
d, $R_1 = R_4 = R_5 = Me$; $R_2 = R_3 = Ph$

In the mass spectra of photoproducts the presence of the intense peak corresponding to the expulsion of carbon monoxide from the parent peak (*m/e* 261 for IIa and IIc and 275 for IIb) clearly indicates that the photoproducts have the structure of 2-pyridone.[8] IIc was identical (melting point, ir and nmr spectra) with an authentic sample prepared from the condensation of 3,6-diphenyl-4,5-dimethyl-2-pyrone[9] with methylamine. The appearance of an intense peak at *m/e* 56 in the mass spectrum of IIa suggests the presence of a methyl group at C-6 in II.[10] The change of the nmr signals of the *C*-methyl protons by addition of Eu(fod)$_3$ suggests[11] that the other methyl group should be at C-4 or C-5, not at C-3. Confirmation of the structure of IIa was obtained by comparison with the melting point and the nmr spectrum of an authentic sample prepared by N-methylation of 4,6-dimethyl-3,5-diphenyl-2-pyridone.[12,13]

The accelerating effect of the phenyl groups on the photochemical rearrangement of the hindered 4-pyridones to 2-pyridones is reminiscent of similar substituent effects on the photoisomerization of the hindered 4-pyrones to 2-pyrones[9] and the photoconversion of the hindered 4-thiopyrones to cyclopentadienones.[15] A striking difference in the behavior of the hindered 4-pyridones upon ultraviolet irradiation from that of the hindered 4-pyrones is the position of the substituents in the photoproducts. Photolysis of Ia or Ib gave IIa or IIb, respectively, as the major product, whereas

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(6) The hindered 4-pyridones,[7] Ia (mp 278.5–279.0°), Ib (mp 242.5–243.5°), Id (mp 231.0–232.0°), and Ie (mp 317.0–318°), were obtained by heating a mixture of the corresponding 4-pyrones and alkylamines in a sealed tube.

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