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THE RELEVANCE OF OXIDATION RATES OF ALCOHOLS TO STERIC INHIBITION OF IONISATION IN THE ACETOLYSIS OF p-TOLUENESULPHONATES

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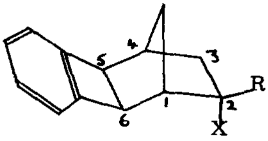
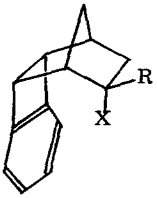
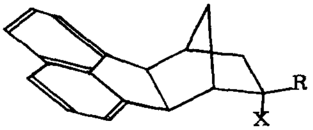
Frequent use has been made of the chromic acid oxidation rates of alcohols as a measure of non-bonded interactions since, in most cases, the rate determining step has been assumed to be the decomposition of the intermediate chromate ester with the transition state resembling the carbonyl product[1,2]. Further, these results have been used to estimate the ground state steric interactions of a number of toluene-p-sulphonates used in solvolysis reactions[3,4]. Our recent studies clearly indicate that caution should be exercised in the use of oxidation studies in this way for alcohols which have large ground state interactions. The rates and α deuterium isotope effects for the oxidation of 1a ⟶ 4a by chromic acid in aqueous acetic acid have been measured and compared to the rates of acetolysis of the corresponding toluene-p-sulphonates[5].



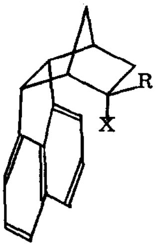
1a-c



2a-c



3a-c



4a-c

5a-c, endo-2-norbornyl; 6, exo-2-norbornanol

a) R = H, X = OH; b) R = D, X = OH; c) R = H, X = OTs.

TABLE 1. Rates of acetolysis at 100.0°C.

Compound	$k \times 10^7 sec^{-1}$	relative rate
1	683.0	1.000*
2	25.0	0.037*
3c	517.0	1.000†
4c	9.4	0.014†
5c	6330.0	1.000

* factor of 9.25 allowed for inductive effects. Ref. 6.

† " " 12.0 " " " "

The acetolysis rate of 4c further illustrates the importance of steric inhibition to ionisation due to the presence of the large endo 5, 6 substituent, Table 1. Comparison of the rate of acetolysis of 3c with that of endo-norbornyl tosylate (5c) allows an estimate of a factor of 12 to be made for the rate deceleration due to the electron withdrawing effect of the 5, 6 naphthalene substituent in both 3c and 4c. Using this factor 4c is observed to solvolyse 71 times slower than 5c. This figure is larger than the factor of 27 obtained for 2c[6], and is expected, since a study of models indicates that the non-bonded interactions increase by a larger amount during the ionisation of 4c than during the ionisation of 2c because of the larger endo 5, 6 substituent in the former. No allowance has been made in this treatment for the higher ground state energy of 4c compared to 5c but no estimate for the ground state energies of 4c or 2c could be obtained due to rearrangements which occur during equilibration of the alcohols and acetates[5]. Brown, however, has suggested that the higher ground state energy of endo-5,6-trimethylene-endo-2-norbornyl-toluene-p-sulphonate compared to endo norbornyl toluene-p-sulphonate would produce a rate factor of 100 in their solvolyses, favouring the former[7]. The acetolysis of 2c and 4c would be expected to be associated with similar, if not larger, ground state differences from 5c and, if allowance is made for this in the observed acetolysis rates, extremely large factors for the steric inhibition to ionisation would be obtained.

The lack of inductive effects on the ratio of chromic acid oxidation of the alcohols[3]

TABLE 2. Rates of chromic acid oxidation of alcohols at 25.0°C in 35% aqueous acetic acid with 0.1M perchloric acid.*

Compound (R = H)	$k_2 \times 10^3$ $l. mole^{-1} sec^{-1}$	Relative rate	Compound (R = D)	$k_2 \times 10^3$ $l. mole^{-1} sec^{-1}$	$^{kH}/_{kD}$
1a	13.07	6.82	1b	2.23	5.85
2a	105.80	55.10	2b	17.47	6.05
3a	15.18	7.90	3b	2.62	5.80
4a	85.75	44.80	4b	23.20	3.70
5a	15.08	7.85	5b	2.52	5.97
6	1.92	1.00			

* Concentrations were 0.435×10^{-3}M potassium dichromate, 1.305×10^{-3}M alcohol.

is apparent by comparison of 1a, 3a and endo-norbornanol (5a), Table 2. These three alcohols oxidise between six and eight times faster than 6 , and this is attributed to the relief of non-bonded interactions[8] between the endo 5, 6 hydrogens and the endo OH groups. 2a and 4a oxidise 55 and 45 times faster than 6a respectively even though larger steric inhibition was found in the acetolysis of 4c. Clearly, no quantitative measurement can be obtained for the non-bonded interactions of 4a from its oxidation rate although the gross effect observed is still a marked acceleration compared to 5a.

Oxidation by chromic acid is considered to take place by decomposition of an initially formed chromate ester[1] ,

$$R_2CHOH + HCr^{VI}O_4 \rightleftharpoons R_2CHOCr^{VI}O_3H$$

$$R_2CHOCr^{VI}O_3H + B \longrightarrow R_2C = O + Cr^{IV}O_3H_2$$

Both Cr^{IV} and Cr^{V} are involved in the oxidation sequence, but recently Wiberg has produced evidence that Cr^{V} oxidation proceeds similarly to Cr^{VI} [9] . The titrimetric technique used in our studies[10], however, take account of the disappearance of all oxidising species. Normally the decomposition of chromate ester is assumed to be the rate limiting step and a primary α deuterium isotope effect of about 7 would be expected.

Eschenmoser has found that, under certain conditions, the highly hindered alcohol 3β, 28-diacetoxy-6β-hydroxy-18β-olean-12-ene oxidises with rate limiting chromate ester formation, shown by an isotope effect of 1[11]. Our isotopic studies, Table 2, indicate that 1a, 2a, 3a and 5a oxidise by rate limiting chromate ester decomposition. The isotope effect of 3.7 observed in the oxidation of 4a suggests that both ester formation and decomposition are partially rate limiting, which would explain the slower rate of oxidation of 4a compared with that of 3a. This work emphasises that in the correlation of oxidation rates with non-bonded interactions the α-deuterium isotope effects should be considered.

Satisfactory analyses and spectral data were obtained for all new compounds.

REFERENCES

1. K.B.Wiberg, "Oxidation in Organic Chemistry" Part A, Academic Press Inc. New York, 1965.
2. A.K. Awarthy, J.Rocek and R.M.Moriarty, J.Am.Chem.Soc., 89, 5400 (1967).
3. R.Baker and J.Hudec, Tetrahedron Letters, 4715 (1968).
4. I.Rothberg and R.V.Russo, J.Org.Chem., 2003 (1967); I.Rothberg, Chem.Comm., 268 (1968).
5. 3a and 4a were prepared from the exo and endo adducts formed in the Diels-Alder addition of acenaphthylene to cyclopentadiene, R.Baker and T.J.Mason, J.Chem.Soc. (C), in press. The deuterated alcohols 1b → 5b were prepared by lithium aluminium deuteride reduction of the corresponding ketones.
6. R.Baker and J.Hudec, Chem.Comm., 929 (1967).
7. H.C.Brown, Chem. and Eng. News, 45, 87 (1967).
8. E.L.Eliel, N.L.Allinger, S.J.Angyal and G.A.Morrison, "Conformational Analysis", Interscience Publishers Inc., New York, 1966, pp.81-84, 271.
9. K.B.Wiberg and H.Schafer, J.Am.Chem.Soc., 91, 933 (1969).
10. R.S.Stewart and D.G.Lee, Can.J.Chem., 42, 439 (1964).
11. J.Rocek, F.H.Westheimer, A.Eschenmoser, L.Moldovanyi and J.S.Schreiber, Helv.Chim.Acta, 45, 2554 (1962).