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Bond Length and Reactivity. Variable Length of the C–O Single Bond

Frank H. Allen and Anthony J. Kirby*

Contribution from the University Chemical Laboratory, Cambridge CB2 1EW, England.
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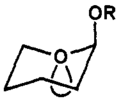
Abstract: An analysis of C–O bond lengths of 2367 ethers and esters taken from the crystallographic literature reveals substantial and systematic variations. The length of the bond in the system R_1–OR_2 increases with increasing electron withdrawal in the group OR_2 and also as the group R_1 changes from methyl through primary, secondary, and tertiary alkyl. The observations are consistent with varying contributions to the ground state from the valence bond tautomer $R_1{}^{+}\,{}^{-}OR_2$, and there is good evidence that charge separation accompanies bond lengthening. A knowledge of the length of the bond in the ground state is considered desirable and may be essential for any detailed mechanistic investigation of a reaction involving the ionic cleavage of a bond to oxygen.

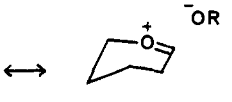
A fundamental problem for the mechanistic chemist is understanding how bonds are made and broken. Kinetic studies give information on differences between ground and transition states and may attempt to locate the transition state on an appropriate scale between the ground state and product. Not unnaturally the emphasis, particularly in work on ionic reactions, is generally on the description of the transition state, in which a given bond is likely to be partially broken, rather than that of the ground state or product, where it is intact. Of course the structures of these, usually stable, molecules must be known, but most workers are content with a knowledge of their gross molecular structure.

We attempt to show, in this and the following papers, that valuable mechanistic information may, in appropriate cases, be derived from a detailed knowledge of the ground state of a reacting system and particularly from the *length* of a bond being broken. The necessary structural information is in most cases readily obtained by modern crystallographic techniques or may be already available in the Cambridge Structural Data Base.[1]

Early work on structural parameters led to the valuable generalization that the length of a given bond, particularly in saturated compounds, is close to constant. Sutton, for example, in his list of selected bond lengths,[2] gives 1.426 ± 0.005 Å as the length of the C–O single bond, and a value of 1.43 Å has been widely assumed. However, many recent structure determinations have given values for C–O bond lengths which fall well outside the quoted range. In particular, our recent work on acetal structures[3,4] has shown that the lengths of the C–O bonds at the acetal centers of a series of tetrahydropyranyl acetals **1** and **3** are not even approximately constant but vary over a range of more than 0.1 Å. More significantly, this variation is systematic and depends on the effective electronegativity of the oxygen atom of the exocyclic OR group: the more electronegative the group, the longer is the C–OR bond and the shorter the endocyclic bond (RO)C–O.



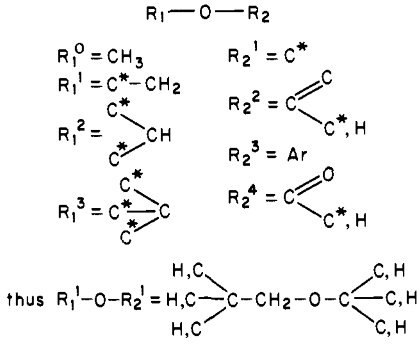
1



2

3

Scheme I



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It might reasonably be supposed that acetals are a special case. We interpret the bond length changes in compound **1** in terms of a stabilizing n–σ^* intraction between the axial lone pair on the ring oxygen and σ^*_{C-OR},[4] represented in valence bond terms as a contribution to the ground-state structure from the ion pair form **2**—which is clearly unique to acetals and related compounds. But we recently found similar (actually 32% smaller) effects on bond lengths in acetals fixed in the equatorial form **3** for which n–σ^* overlap is stereoelectronically unfavorable.[4,5] This can be explained in terms of a σ–σ^* interaction, between σ^*_{C-OR} and the *antiperiplanar* σ-bonding orbital of the remote ring C–O bond. But an interaction of this general sort is clearly not unique to acetals and related compounds. So we have now looked for evidence of systematic variations in C–O bond lengths in simpler compounds and present here an analysis of data taken from the Cambridge Structural Data Base for a large number of ethers and esters.

Methodology

Our approach, which elicited the variations observed in acetal C–O bond lengths, is to use as a probe a series of OR groups of increasing effective electronegativity at oxygen. We then examine the response of the system to increasing electron demand at the center concerned, primarily in terms of the length of the bond to the OR group. For this sort of investigation data for individual compounds are of strictly limited value, in particular because of the random effects of experimental error and crystal–packing forces. These factors can, however, be minimized in two ways. One is to make accurate structure determinations for a series of related compounds in which a single structural feature is varied, as in our acetal work described in the following paper in this issue. Alternatively, one can survey a much larger number of structures of the same structural type taken from the literature, as in this work.

As in the acetal series, the OR groups of interest, in order of increasing effective electronegativity at oxygen, are O–alkyl, O–aryl, and O–enol (ethers), O–acyl (carboxylic esters), and esters of the oxyacids of phosphorus and sulfur. A preliminary search of the data base revealed only small numbers of derivatives of the inorganic oxyacids so the main search concentrated on the first four classes. We suspected that *C*–OR bond

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[1] (a) Allen, F. H., Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146. (b) Bürgi, H. B.; Dunitz, J. D. *Ibid.* **1983**, *16*, 153. Bürgi and Dunitz discuss two or three other cases where bond length appears to be correlated with reactivity, particularly in substitution and electron-transfer reactions of metal complexes.

[2] Sutton, L. E., Ed. "Tables of Interatomic Distances and Configuration in Molecules and Ions"; The Chemical Society: London, 1965; Special Publication 18.

[3] Jones, P. G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* **1979**, 288.

[4] Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J.; Ramaswamy, P. *J. Am. Chem. Soc.*, in this issue.

[5] Jones, P. G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1365.

0002-7863/84/1506-6197$01.50/0

Table I. Mean Bond Lengths in Ethers and Esters, R_1-O-R_2[a]

R_1	$R_2 = C^*$ C_1-O-C_2		R_2 = Ar C_1-O-C_2		R_2 = H,C^*-C=C C_1-O-C_2		R_2 = H,C^*-C=O[b,c] C_1-O-C_2	
CH_3	**1.418 (2)**	1.427 (2)	**1.424 (1)**	1.370 (1)	**1.434 (2)**	1.354 (2)	**1.450 (1)**	1.330 (1)
			C_2=C	1.390 (1)	C_2=C	1.328 (5)	C_2=O	1.197 (1)
					C_2=C^*	1.499 (4)	C_2-C^*	1.510 (2)
	$N = 234, R < 0.07, n = 83$		$N = 689, R < 0.05, n = 217$		$N = 112, R < 0.07, n = 33$		$N = 574, R < 0.05, n = 63$	
C^*-CH_2	**1.426 (2)**	1.420 (4)	**1.437 (3)**	1.368 (2)	($\sigma > 0.01$ Å)		**1.452 (2)**	1.330 (2)
	C_1-C^*	1.518 (4)	C_1-C^*	1.505 (3)			C_1-C^*	1.503 (7)
			C_2=C	1.390 (2)			C_2=O	1.196 (3)
							C_2-C^*	1.497 (4)
	$N = 121, R < 0.07, n = 66$		$N = 77, R < 0.07, n = 32$		$N = 10, R < 0.10, n = 3$		$N = 357, R < 0.07, n = 30$	
$CH(C^*)_2$	**1.432 (2)**	1.427 (4)	**1.446 (4)**	1.365 (3)	($n = 0$)		**1.460 (2)**	1.334 (2)
	C_1-C^*	1.529 (2)	C_1--C^*	1.532 (6)			C_1-C^*	1.526 (2)
			C_1=C	1.388 (3)			C_2=O	1.198 (2)
							C_2-C^*	1.493 (2)
	$N = 175, R < 0.07, n = 66$		$N = 13, R < 0.07, n = 7$		$N = 8, R < 0.10, n = 0$		$N = 602, R < 0.07, n = 68$	
$C(C^*)_3$	**1.450 (2)**	1.427 (3)	**1.478 (4)**	1.369 (3)	**1.463 (7)**	1.351 (6)	**1.475 (2)**	1.334 (5)
	C_1-C^*	1.533 (4)	C_1-C^*	1.524 (4)	($\sigma > 0.01$ Å)		C_1-C^*	1.530 (4)
			C_1=C	1.392 (2)			C_2=O	1.203 (3)
							C_2-C^*	1.503 (8)
	$N = 75, R < 0.07, n = 23$		$N = 39, R < 0.10, n = 25$		$N = 6, R < 0.10, n = 4$		$N = 73, R < 0.10, n = 9$	

[a] Each group contains up to five bond lengths. The top pair in each case refer to the C-O bonds of the R_1-O (bold type) and O-R_2 fragments; the lower set give bond lengths, if any, within the fragments R_1 and R_2 and are specified in each case. Of the numbers at the bottom of each section, N gives the number of compounds with the given structure retrieved by the connectivity search, while n gives the size of the subset of these for which H atoms were located by the crystal structure analysis *and* for which the crystallographic R factor is below the limit specified. Details are given in the text. [b] Schweizer and Dunitz (Schweizer, W. B.; Dunitz, J. D. *Helv. Chim. Acta* 1982, *65*, 1547) have published an analysis of the structural characteristics of the ester group, including data parallel to those in the final column of Table I. In all cases the mean C-O bond lengths obtained by Schweizer and Dunitz differ by less than the sum of the standard deviations from those given in Table I. [c] Note that the O-C_2 bond lengths are constant within each column. The observed shortening of O-C_2 as R_2 becomes first sp^2 then more strongly mesomerically electron withdrawing is normal for ethers and esters.

lengths would also depend on the degree of substitution at *C* so we further subdivided the data into methyl and primary, secondary, and tertiary alkyl derivatives. The detailed procedure was as follows.

The January 1982 version of the Cambridge Structural Data Base (28 978 compounds) was used, together with associated computer programs[6] for substructure search, data retrieval, and numeric analysis. All searches were performed on a subset of the data base corresponding to those compounds (16 325) which are normally regarded as organic (data-base classes[6] 1–61, 63, 64, 70).

The substructure R_1–O–R_2 was located for four values of R_1 (Me and primary, secondary, and tertiary alkyl) and four values of R_2 (C_{sp^3}, C=C, Ar, C=O) as shown in Scheme I. The R_1 substituent was formalized as shown, where C* indicates a sp^3-hybridized carbon *having only C or H substituents*. The R_2 substructures are also shown in Scheme I. The use of C* atoms avoids additional electron-donating or withdrawing substituents which might perturb the geometry of the C–O bond (see below). The program CONNSER[6] was amended to locate atoms coded C* in its searches of the chemical connectivity segment of the data base. Sixteen separate searches were carried out, and the number of hits (N(h)) for each R_1, R_2 combination is shown in Table I. The numeric crystallographic data were retrieved for each of the 16 subsets.

The numeric analysis program GEOM78[6] permits the systematic tabulation of molecular geometry for a user-defined chemical fragment. In this case the coded fragment is located by a comparison with the molecular connectivity established via the crystallographic analysis. This differs from the chemical connectivity in that (i) explicit bond types are not available, although they can generally be assigned on a geometric basis, and (ii) H counts are only available when these atoms have been located (however inaccurately) by the crystal structure analysis. The present study demands a knowledge of H counts in order to differentiate substructures unambiguously. Hence, in defining fragments for geometric analysis the H atoms were included explicitly [e.g., $R_1{}^1$–O–$R_2{}^1$ (Scheme I) is defined as **4**], and only those structures having H-atom coordinates were included in the calculations. The data sets were further restricted by setting an upper limit to the crystallographic R factor, as indicated in Table I.

A survey of each of the 16 fragments was made to establish a preliminary mean value for the R_1–O distance. Outliers, which differed widely from this mean (D), were excluded by using a tolerance (t) such that bonds only contributed to the final mean if their lengths were in the range ($D \pm t$ where t = 0.04 Å throughout this work. The outliers result either from systematic errors in a given structure analysis or from abnormal bonding effects; since both represent deviations from the norms which are of interest for this study their exclusion is justified. In substructures involving $R_2' = C^*$ closure of the ether linkage to form an epoxide ring was avoided by omitting any structure when C(R_1) and C(R_2) were bonded.

Error estimates for mean bond lengths (D) are given by $\sigma(D) = [\sum_n(D - d_n)^2/n(n-1)]^{1/2}$ for n independent observations d_i ($i = 1, n$). The expression $\sigma(\text{sample}) = (n\sigma(D))^{1/2}$ may be used to estimate the spread within any sample. Values of D in Table I are cited as $D(\sigma)$. The number of contributors, n, is given as the last entry in each section.

Discussion

Well-defined and systematic variations in the length of the C–O bond of interest (shown in boldface type) are clearly apparent from the data in Table I. For a given type of alkyl group R_1 the C_1–OR_2 bond is clearly longer for derivatives with more electron-withdrawing substituents R_2, even though hybridization changes might be expected to *reduce* the covalent radius of the oxygen atom. (The bond angles C_1OC_2 open out from ~112° to close to 120°, and the O–C_2 bond is substantially shortened on going from left to right across Table I.) The only exception is the longer C–O bond for aryl ethers compared with esters in the final row, just where the data become sparse and most sensitive to special cases. Similar changes are also observed as the degree of substitution of R_1 is increased over the series methyl < primary < secondary < tertiary. Note especially the contrast in every case (all three complete columns of Table I) between the changing length of C_1–O and the constant length (precisely that given by Sutton[2]) of the O–C_2 bond, for systems with a common oxygen atom.

In Figure 1 the data for the length of the C_1–O bond are plotted against the effective electronegativity of the oxygen atom of the OR_2 group, as measured by the approximate pK_a of R_2OH. When similar data for several (structurally homogeneous) series of acetals and glucosides are plotted in this way,[5] rather good straight lines are obtained. The plots shown in Figure 1 suggest that similar linear relationships may correlate the same variables for ethers and esters. It is perhaps surprising that three of the lines drawn

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[6] Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2331.

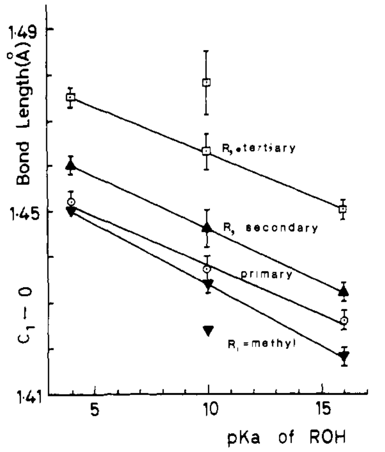


Figure 1. Plot of C_1-O bond lengths from Table I vs. the approximate pK_a of R_2OH. (We have used approximate pK_a's of 16, 10, and 4 for alcohols, phenols (and enols), and carboxylic acids, respectively.) Lines are drawn through data sets for R_1 = methyl (▼), primary (○), secondary (▲), and tertiary (□).

to correlate the data have similar slopes and certainly surprising that the slope of the line correlating the data for primary alkyl derivatives should differ from all the others: but the data are not of a quality to justify detailed attempts at interpretation. They do, however, cover a rather wide range of R_2OH and clearly have some predictive value. Furthermore, as in the acetal case,[5] a linear relationship between the length of the bond C_1-OR_2 and the pK_a of R_2OH is equivalent to a linear relationship with the free energy of activation for reactions in which the C_1-OR_2 bond is cleaved, because Brønsted-type relationships generally correlate the logarithms of rate constants and the pK_a's of the leaving groups in series of this sort. This link between bond length and reactivity is dealt with explicitly for the acetal system in the final paper of this series in this issue.[7] Here we discuss briefly the character of the C-O bond in the light of our results.

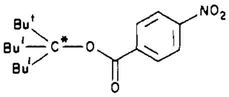
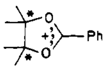
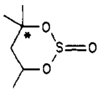
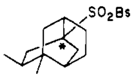
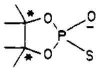
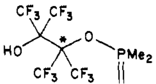
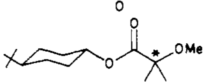
By introducing electron withdrawal into the group R_2 we are making the oxygen atom of the OR_2 group effectively more electronegative and thus increasing the polarity, or ionic character, of the C_1-O bond. It is not self-evident that this will lead to a lengthening of the bond, and indeed increasing ionic character has traditionally been associated with stronger and thus shorter bonds.[8] But clearly in the case of C-O, and probably for carbon-heteroatom bonds in general, increasing ionic character weakens and lengthens the bond (as argued by a number of authors over the years[9,10]). To take an extreme case, the C-X distance in *tert*-butyl halides is substantially longer than in the corresponding methyl compounds,[11,12] and heterolytic cleavage is of course well-known to be much easier in the tertiary halides. The effects on bond length summarized in Table I can be explained in terms of a variable contribution from the ionic valence bond tautomer (**5**) to the ground state. The greater the effective

$$R_1\text{-}OR_2 \leftrightarrow R_1{}^{+}\,{}^{-}OR_2$$

5

electronegativity of the oxygen atom of the OR_2 group, and the greater the stability of the carbocation R_1^+, the greater will be the contribution of structure (**5**) and hence the longer, and more susceptible to heterolytic cleavage, will be the R_1-OR_2 bond. (In symmetrical compounds there will of course be an equal contribution from $R_1O^- R_2^+$, but we are concerned here specifically with the effects of electronic asymmetry, and the greater the contribution from **5**, the smaller also will be the contribution from the other valence bond tautomer.)

Table II. C-O Bond Lengths in Tertiary Esters of Strong Acids

	ester	C*-O bond length, Å	ref
6		1.496 (5)	14
7		1.516 (10)	15
8		1.501 (3)	16
9		1.489 (5)	17
10		1.491 (5) 1.479 (5)	18
11		1.397 (4)	19
12		1.395 (6)	22

An alternative explanation for the increased length of bonds from a given atom to secondary and tertiary centers might be nonbonded (steric) interactions between the increasing number of substituents at the ends of the bond. We present circumstantial evidence to show that this cannot explain the major part of the observed variation in the length of the C-O bond.

Steric effects can of course affect bond lengths.[13] An extreme case in one of the data sets summarized in Table I is tri-*tert*-butylmethyl *p*-nitrobenzoate (**6**, Table II), in which steric compression may be presumed to reinforce electronic effects, to produce the extremely long C*-O bond length of 1.496 Å. On the other hand, steric effects are minimal, for a tertiary system, but electronic effects are much larger (the "leaving group" OR_2 is a neutral ester oxygen) in the dioxocarbenium ion **7**, and this compound has the longest C-O bond that we can find. Very long bonds are found also in tertiary esters of the strong oxyacids of sulfur (**8**, **9**) and phosphorus (**10**). Since the thiophosphate group of **10** is ionized, the R_3C-OP bond of a neutral phosphorus oxyacid ester (K_a of "R_2OH" some 10^5 times greater) might be expected to be longer still, in the region of 1.50 Å. So it is highly significant that the C*-O bond of the phosphinate **11** is actually one of the *shortest* known, at 1.397 Å. Compound **11** is still the ester of a tertiary alcohol and a strong acid, and steric effects across the *C-O bond must be at least as large as in other tertiary alkyl esters. So the striking reduction in the length of the *C-O bond must be an electronic effect.

A striking reduction in the length of this bond is exactly what is expected, if the lengthening of the *C-O bond in secondary and tertiary esters is itself predominantly an electronic effect. The contribution to the ground-state structure from the valence bond tautomer **5** depends on the stabilities of both R_2O^- and R_1^+, and in the case of **11** *C of R_1 is heavily substituted with strongly electron-withdrawing CF_3 groups, which will inhibit the buildup of positive charge at the central *C.

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(7) Jones, P. G.; Kirby, A. J. *J. Am. Chem. Soc.*, last paper in this series in this issue.

(8) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; Chapter 3. Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

(9) Walsh, A. D. *Trans. Faraday Soc.* **1947**, *43*, 60.

(10) Gutmann, V. *Pure Appl. Chem.* **1979**, *51*, 2197.

(11) Hasse, J.; Kamphusmann, H.-D.; Zeil, W. *Z. Phys. Chem.* (*Frankfurt am Main*) **1967**, *55*, 225.

(12) Lide, D. R.; Jen, M. *J. Chem. Phys.* **1971**, *38*, 1504.

(13) Bartell, L. S. *Tetrahedron* **1978**, *34*, 2891.

(14) Cheng, P.-T.; Nyburg, S. C. *Acta Crystallogr., Sect B* **1978**, *B34*, 3001.

(15) Caira, M. R.; deWet, J. F. *Acta Crystallogr., Sect B* **1981**, *B37*, 709.

(16) Petit, G.; Lenstra, A. T. H.; Van de Mieroop, W.; Giese H. J.; Hellier, D. G. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 202.

(17) Barnett, B. L.; Yordy, J. D. *J. Cryst. Mol. Struct.* **1975**, *5*, 113.

(18) Wieczorek, M. W.; Karolak-Wojciechowska, J.; Mikołajczyk, M.; Witczak, M.; Sheldrick, W. S. *Acta Crystallogr., Sect B* **1978**, *B34*, 3414.

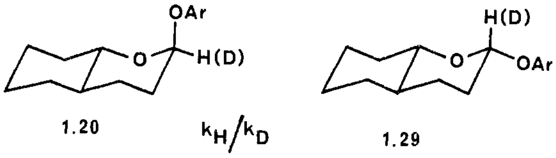
(19) Schomburg, D.; Stelzer, O.; Weferling, N.; Schmutzler, R.; Sheldrick, W. S. *Chem. Ber.* **1980**, *113*, 1566.

Ester **11** is an extreme, but not isolated, example of this effect, where the very long *C–O bond length expected for the ester of a strong acid and a tertiary alcohol is not observed when strongly electron-withdrawing substituents (CF_3, C=O, O) are present at C* or on the adjacent carbon atom.[20,21-22] A similar effect no doubt accounts for the very short *C–OMe bond in the methyl ether (**12**, Table II). We also describe in the following paper in this issue a detailed examination of a comparable series of acetals and glucosides, where the four substituent OH groups of the glucosides similarly inhibit the lengthening of the bond from the anomeric center to good leaving groups, OR_2.

We conclude that systems R_1–OR_2 respond to increasing electron withdrawal in the group OR_2 by electronic reorganization in the direction of the valence bond tautomer (**5**), resulting in the observed increase in the length of the R_1–OR_2 bond and charge separation in the sense $R_1{}^{+}\,{}^{-}OR_2$. This must mean that a substantial part of the high reactivity toward heterolysis of tertiary alkyl compounds with good leaving groups derives from the substantial amount of bond breaking apparent in the ground state, compared with less reactive compounds. (Estimates of the variation of bond energy with bond length in systems of this sort are of the order of 2–300 kcal mol^{-1} Å^{-1},[3,7,23] while bond length differences across a series may easily amount to 0.06 Å (Table I) or more.)

Evidently estimates of the extent of bond breaking in the transition state, which are commonly made on the basis of comparisons of reactivity over a series of compounds, should take into account the varying amounts of "bond breaking" in the ground state. Protonation of oxygen results in an enormous increase in electron demand so that much—perhaps most—of the C–O bond-breaking process in acid-catalyzed reactions of tertiary alcohol derivatives may be expected to take place as part of the preequilibrium proton-transfer step. In fact, in any comparison of transition states for a given reaction of two different compounds, it may be of crucial importance to consider the status of the bond or bonds being broken in the ground state. We showed recently in our work on acetal hydrolysis that the secondary deuterium isotope effect for the spontaneous hydrolysis of axial *p*-nitrophenyl acetal (**13a**) is significantly smaller than that of the equatorial isomer (**13e**).

13a



13e

It was tempting to attribute this difference to a stereoelectronic effect on transition states, though much other evidence[7] suggested that the transition states for the reactions of the two isomers were closely similar. But our X-ray structural work[4] shows clearly that the C–OAr bond of the axial isomer is expected to be substantially the longer (1.448 (4) Å for an analogue of **13a**, Ar = *p*-nitrophenyl, compared with 1.424 (4) Å for **13e**). The original state of the axial isomer is thus closer in geometry to the transition state: compared with the equatorial compound it starts farther along the reaction coordinate for C–OAr cleavage, so that the change in the character of the C–H bond between the ground and transition state is reduced. The effect is indeed stereoelectronic in origin, but it is evidently an effect on ground states.

Our results indicate, further, that it should be possible by accurate crystal structure determinations, using an appropriate series of compounds based on an oxygen probe with increasing electron demand, to explore the early stages of bond breaking in many organic reactions which are initiated by ionization to form a carbocation. (This is an extension of the approach pioneered by Bürgi and Dunitz,[1b] who found that similar changes in the lengths of the Y–M bonds of inorganic systems, YMX_3, are related to bond angle changes in the MX_3 fragment.) In principle it should be possible to observe how the carbon fragment R_1 accomodates the developing positive charge. In the following paper in this issue[4] we describe a detailed examination of bond length and reactivity in acetals and glucosides using this approach. We are currently examining several other series, particularly systems which undergo rearrangement and fragmentation reactions.

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Bond Length and Reactivity. Stereoelectronic Effects on Bonding in Acetals and Glucosides

Andrew J. Briggs,[‡] Robert Glenn,[‡] Peter G. Jones,[†] Anthony J. Kirby,*[‡] and P. Ramaswamy[‡]

Contribution from the University Chemical Laboratory, Cambridge CB2 1EW, England, and the Institut für Anorganische Chemie, D-3400 Göttingen, Federal Republic of Germany.
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Abstract: Accurate X-ray crystal structure determinations for 22 axial and equatorial tetrahydropyranyl acetals and α- and β-glucopyranosides reveal systematic changes in the pattern of bond lengths at the acetal center with changing electron demand in the exocyclic ("leaving") group. Stereoelectronic effects on bonding are analyzed and related to reactivity. Linear correlations between the pK_a of the conjugate acid of the leaving group and hence the free energy of activation for cleavage of the acetal C–O bond and the length of the bond being broken appear to be the rule rather than the exception over the range of leaving group studied.

Our recent work[1-5] on the dependence of reactivity on conformation in acetal hydrolysis has shown that the cleavage of acetals is subject to stereoelectronic control.[6,7] C–O cleavage occurs readily only when a nonbonding electron pair (lone pair) on the remaining oxygen atom of the O–C–O group is *antiperiplanar* to the bond being broken either in the ground state or in some reasonably readily accessible higher energy conformation.

[‡] University Chemical Laboratory.

[†] Institut für Anorganische Chemie.

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