Oxygen Substituent Effects on Alkene Addition Equilibria

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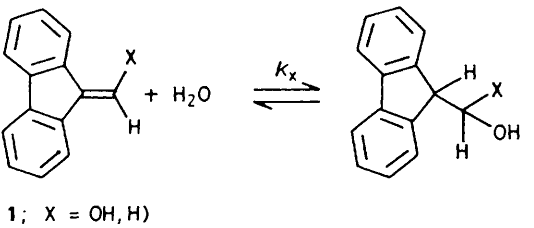
Comparisons of equilibrium constants for the hydration of alkenes to form alcohols and of enols to form *gem* diols show that an oxygen substituent favours hydration as a result of the stabilising geminal interaction of carbon–oxygen bonds in the diol; oxygen substituent effects on other H–X addition equilibria (*e.g.* $HNMe_2$, HSEt) measure the strength of 'geminal' C–O/C–X interactions.

Geminal oxygen atoms experience a strong mutual stabilising interaction. This is well known from quantum calculations of torisonal barriers[1] and 'bond separation'[2] energies as well as the impossibility of expressing heats and free energies of formation of acetals and orthoesters in terms of additive carbon–oxygen bond contributions.[3] Yet, as Hine has remarked, the effect has had much less influence upon the outlook of organic chemists than the energetically weaker interaction (3.5 compared with 10 kcal mol^{-1}; 1 cal = 4.184 J) between conjugated carbon–carbon double bonds.[3] Much attention has been given to the anomeric effect,[1] which presumably stems from the stereochemical dependence of the interaction, and Kirby has drawn attention to striking variations in geminal carbon–oxygen bond lengths.[4] However, no simple experimental manifestation of the full strength of the interaction appears to have been reported.†

While studying the keto–enol–hydrate equilibria of 9-formylfluorene we noticed that at equilibrium 25% of the enol (**1**; X = OH) is converted into the hydrate, whereas for the structurally related alkene lacking an enolic OH, dibenzofulvene (**1**; X = H), no hydration is detected (equation 1).[5,6] At first, this seemed surprising because an oxygen substituent strongly stabilises a double bond. Hydration of the enol is nonetheless favoured because the oxygen–double bond interaction of the enol reactant is more than outweighed by the oxygen–oxygen interaction of its hydration product.



(1)

(**1**; X = OH, H)

$K_{OH} = 0.35, K_H < 0.02$

This oxygen substituent effect can be expressed quantitatively by combining recent measurements of the enol contents of acetaldehyde, isobutyraldehyde, and acetone[7] with the extents of hydration of their keto groups to obtain equilibrium constants for hydration of the enols (equation 2). These may

$$H_2O + CH_2{=}CHOH \overset{K_E}{\rightleftharpoons} H_2O + CH_3CHO \overset{K_h}{\rightleftharpoons} CH_3CH(OH)_2 \quad (2)$$

be compared with values for hydration of the corresponding alkenes available from direct experimental measurements or accurately calculable from thermodynamic data.[9] Values of log *K* for both sets of reactions are listed in Table 1, and it can be seen that in each case addition of H_2O to the enol is more favourable than to the alkene, *e.g.* log K = 6.2 for vinyl alcohol (acetaldehyde enol) and 4.4 for ethylene.

The stabilisation arising from this oxygen–oxygen interaction may be demonstrated in several ways. For example, the equilibrium constant for addition of H_2O to vinyl alcohol to form the vicinal diol (ethylene glycol) is 7×10^6 times less favourable than that for formation of the gem diol. It is also apparent from comparing oxygen substituent effects, log (K_{OH}/K_H), for addition of water to a double bond with the corresponding effects for addition of hydrogen (hydrogenation), which are also shown in Table 1. For ethylene and vinyl alcohol, log (K_{OH}/K_H) is 1.8 for hydration compared with −3.8 for hydrogenation. For hydrogenation there is no geminal stabilisation of the enol adduct and the addition is less favourable by a factor of 4×10^5.

Oxygen substituents affect other addition equilibria and values of log (K_{OH}/K_H) for addition of various HX, including alcohols, amines, and thiols, to ethylene and vinyl alcohol are

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† The lower reactivity towards displacement or elimination of F^- from a CF_3 than a CH_2F group is probably a result of the corresponding geminal fluorine interaction.

Table 1. Equilibrium constants for addition of H_2O and H_2 to alkenes and enols in aqueous solution at 25 °C.[a]

	$\log K_X$[b]		$\log(K_{OH}/K_H)$	
	X = H	X = OH	$+H_2O$[c]	$+H_2$[d]
$CH_2{=}CH{-}X$	4.44	6.21	1.77	−3.77
$CH_2{=}C(Me){-}X$	3.60[e]	5.37	1.77	−1.25
$Me_2C{=}CH{-}X$	0.26[f]	3.35	3.09	−2.10

[a] Thermodynamic data here and in Table 2 are mainly from compilations cited in references in J. P. Guthrie, *Acc. Chem. Res.*, 1983, **16**, 122. [b] Log K for hydration of C=C double bond; standard state for water is the pure liquid, $K_X = [R_2CHCR'(OH)X]/[R_2C{=}CR'X]$. [c] OH substituent effect on hydration. [d] OH substituent effect on hydrogenation. [e] $\Delta G°_f(aq) = -44.38$ kcal/mol at 298.15 K for isopropyl alcohol based on J. H. S. Green, *Trans. Faraday Soc.*, 1963, **59**, 1559 and ref. 10. [f] $\Delta G°_f(aq) = -40.07$ kcal/mol at 298.15 K for isobutyl alcohol, H. A. Skinner and A. Snelson, *Trans. Faraday Soc.*, 1960, **56**, 1776; J. A. V. Butler, C. N. Ramchandani, and D. W. Thomson, *J. Chem. Soc.*, 1935, 280; J. I. Counsell, E. B. Lee, and J. F. Martin, *J. Chem. Soc. (A)*, 1968, 1819.

listed in Table 2. The magnitude of $\log(K_{OH}/K_H)$ reflects the stabilising effect of the C–O/C–X interaction.

For additions of HX to alkenes and enols, addition of H_2 is conveniently taken as a reference reaction. Then, oxygen substituent effects become logs of equilibrium constants (K_{gem}) for the 'bond separation' reactions of geminally substituted ethanes (equation 3), as shown in equation (4) (where the superscripts H_2 and HX denote addends and $pK_{gem} = -\log K_{gem}$). $\Delta G°$ for reaction (3) (1.36 pK_{gem} at 25 °C) is a bond separation energy and measures the strength of a C–O/C–X (and C–H/C–H) relative to C–H/C–X and C–H/C–O bond interaction.

$$CH_3CH(OH)X + CH_3CH_3 \rightleftharpoons CH_3CH_2X + CH_3CH_2OH \qquad (3)$$

$$K_{gem} = \frac{[CH_3CH_2X][CH_3CH_2OH]}{[MeCH(OH)X][CH_3CH_3]}$$

$$\log(K_{OH}/K_H)^{HX} - \log(K_{OH}/K_H)^{H_2} = pK_{gem} \qquad (4)$$

Values of pK_{gem} from reaction (3) for OH and X substituted ethanes are listed in Table 2. Also listed are values for substituted methanes from reaction (5), which can be estimated from equilibria for addition to formaldehyde. The two sets of values differ systematically, probably as a result of steric interactions at the tertiary carbon atom of the $CH_3CH(OH)X$, but otherwise depend similarly upon X. Positive values of pK_{gem} imply a stabilising C–O/C–X interaction and negative values destabilisation. Perhaps most interesting are the weak interaction implied for oxygen with sulphur and the destabilisation of oxygen by cyanide. The interactions presumably result from an interplay of dipole and orbital effects (*e.g.* n–σ*).[1] Separation of these will be necessary to achieve an adequate understanding of substituent effects in saturated organic molecules.

$$CH_2(OH)X + CH_4 \rightleftharpoons CH_3OH + CH_3X \qquad (5)$$

Table 2. Hydroxy substituent effects $[\log(K_{OH}/K_H)]$ for addition of HX and H_2 to ethylene, and C–OH/C–X bond separation constants (pK_{gem}) for substituted ethanes and methanes (in aqueous solution at 25 °C).

			pK_{gem}	
HX	$\log K_H$[a]	$\log(K_{OH}/K_H)$[b]	$CH_3CH(OH)X$[c]	$CH_2(OH)X$[d]
HO^-	2.54	4.08	7.85	9.98
EtOH	3.82	2.05	5.82	7.57
MeOH	4.42	1.82	5.59	7.61
H_2O	4.44	1.75	5.52	7.65
$MeNH_2$	7.38	0.08	3.85	6.64
Me_2NH	7.59	0.37	4.14	6.14
$Me_2NH_2^+$	—	—	—	4.28
CH_4	9.49	−1.26	2.51	3.90
MeCHO	8.77	−2.10	1.67	—
EtSH	7.73	−3.13	0.64	3.18
H_2	20.32	−3.77	0	0
HCN	10.02	−9.79	−6.02	−3.54

[a] $K_H = [CH_3CH_2X]/[CH_2{=}CH_2][HX]$. [b] $K_{OH} = [CH_3CH(OH)X]/[CH_2{=}CHOH][H{-}X]$. [c] K_{gem} as in equation (3). [d] $K_{gem} = [CH_3OH][CH_3X]/[CH_2(OH)X][CH_4]$. Values calculated from equilibrium constants for addition to formaldehyde and values of $\Delta G°_f$ for CH_2O, CH_4, CH_3OCH_3, CH_3X, and HX.

Received, 24th November 1986; Com. 1672

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