Primary and Secondary Kinetic Hydrogen Isotope Effects in the Solution and Gas Phase Decomposition of t-Alkoxides

Sani Ibrahim,[a] **C. Ian F. Watt,***[a] **John M. Wilson,***[a] **and Colin Moore**[b]

[a] *Chemistry Department, University of Manchester, Manchester M13 9PL, U.K.*
[b] *Kratos Analytical Ltd., Barton Dock Road, Manchester, U.K.*

Primary and secondary kinetic hydrogen isotope effects (k.i.e.s) in the elimination of toluene from the alkoxide of 1,2,3-triphenylpropan-2-ol have been determined and are consistent with rate limiting proton transfer in gas phase reaction and with rate limiting carbon–carbon bond cleavage in reaction in dimethyl sulphoxide (DMSO) solution.

t-Alkoxides may decompose to one or more enolates by net elimination of hydrocarbon in both solution and gas phases.[1,2] An ionic mechanism is believed to operate in both cases, initiated by collapse of alkoxide to a ketone and carbanion. In the gas phase, subsequent proton transfer occurs within the ketone–carbanion complex to yield products, while solvent has been implicated in the proton transfer events[1,3] in the solution reactions. Such fragmentations are important, not least, in providing an entry to the branch point for the deprotonation and nucleophilic addition pathways in reactions of carbanion with ketones, and allow examination of the effects of structural and solvent variation. We have recently shown that, in dimethyl sulphoxide (DMSO) solution, the alkoxide of 1,2,3-triphenylpropan-2-ol, (**1a**), decomposes yielding toluene and the enolate of 1,2-diphenylethanone (deoxybenzoin) as sole products,[3] and we report here a direct comparison of its gas phase and solution decompositions using the deuteriated derivatives (**1b**), (**1c**), and (**1d**). As a framework for discussion, we adopt the outline mechanism of Scheme 1 which recognises our current inability to separate proton transfer steps and dissociation of any intermediate complexes.

Reactions in DMSO solution (K^+ salts) were conducted under reduced pressure and the toluene collected in a cold trap. Enolates were converted to methyl ethers by addition of dimethyl sulphate to the DMSO solution at completion of the reaction. Products were then analysed for deuterium content by mass spectrometry. The data are collected in Table 1.

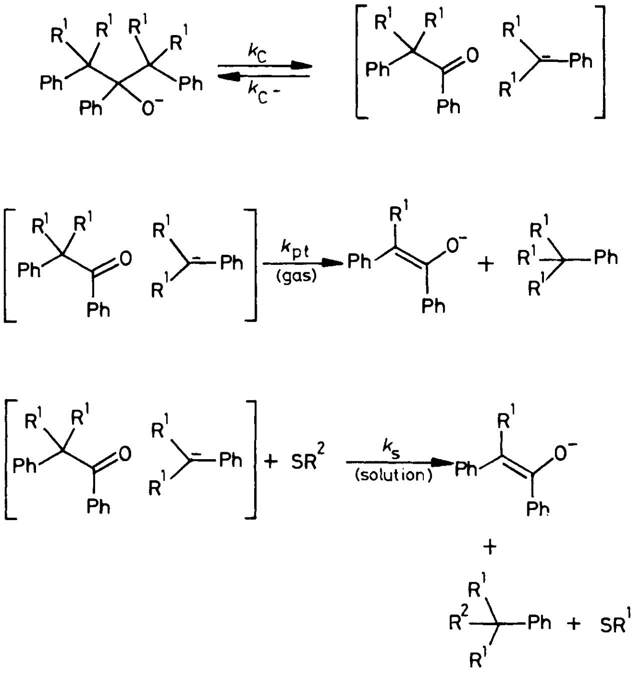
The experiments with (**1a**) and (**1b**) provide a control for analytical methods, and confirm that the benzyl anion is not protonated by the deoxybenzoin, but by solvent. A similar conclusion follows from the formation of [d_1]-toluene only from reaction of the symmetrically deuteriated (**1c**).

Within our mechanistic framework, the ratio of [d_1]- and [d_0]-enolates from (**1c**) measures the primary hydrogen kinetic isotope affect (k.i.e.) on the deprotonation of the deoxybenzoin, complicated by a (probably small) secondary α-D k.i.e. on the proton transfer. The ratio, 2.87, is consistent with the unsymmetrical transition structure expected for exothermic transfer (21.4 kcal mol^{-1})[4] of proton to dimsyl anion. With the unsymmetrically deuteriated (**1d**), the simplest situation arises if $k_s[\text{SR}] \gg k_{C^-}$; then the ratio of [$d_1$]- to [$d_0$]-enolates should correspond to a secondary α-D k.i.e. on that step, as should the ratio of [d_0]- and [d_2]-toluenes. The observed ratios, 1.53 and 1.39, respectively, overlap within uncertainties associated with incomplete deuteriation of substrate and, at 1.23 or 1.18 per D, are in the range expected for $sp^3 \rightarrow sp^2$ rehybridisation[5] at a benzylic carbon. Comparison may be made with experimental measurements for proton transfer between fluorenide anions where the α-D kinetic and equilibrium i.e.s are 1.11 and 1.19, respectively.[6] Our measurements thus support classification of elimination of toluene from the alkoxide as a formal *E*1 process.

Deprotonation of (**1a**) by Bu^nO^- in the source of a mass spectrometer[7] yielded negative ions at *m/z* 287 ($M - 1$) and 195 corresponding to the alkoxide itself and the anticipated deoxybenzoin enolate. From available thermochemical data[8] heats of deprotonation from oxygen, benzylic, or aromatic carbon in (**1**) are approximately -4, $+4$, and $+25$ kcal mol^{-1}, respectively, excluding possible proton abstraction from aromatic methine. With (**1b**), the ions are observed at 291, corresponding to the [d_4]-alkoxide, and at 196 for the [d_1]-enolate, showing that the benzylic hydrogens are not lost or exchanged in formation of the $M-1$ anion.

Measurements were of relative abundances of daughter ions from alkoxide parents using *B/E* linked scans. Those quoted and discussed below were of unimolecular metastable processes in which the energy of parent ions was minimal.[9] Preliminary investigations of collision induced dissociation of the same parents showed no difference in the kinetic isotope effects observed. For this reaction, on the instrument used (Concept 1S mass spectrometer, Kratos Analytical Ltd.) parent ion resolution was sufficient to allow observation of daughters from a single isotopomeric parent. The data are also collected in Table 1.

The alkoxide of (**1c**) yielded fragments at both *m/z* 195 and 196. As with the solution experiments, the ratio of these [d_1]- and [d_0]-enolates measures the primary hydrogen k.i.e. on the proton transfer step. The value obtained, 2.30, is for transfer of proton from deoxybenzoin to benzyl anion rather than

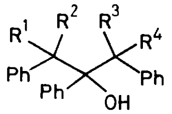


Scheme 1. Elimination of toluene from 1,2,3-triphenylpropoxide (R^1, R^2 = H or D).

Table 1. Deuterium incorporation in alkoxides and products from fragmentation in DMSO solution and in the gas phase.

Reaction	D-Label content	Initial alcohol/%	Solution reaction[a]		Gas reaction
			Enolates (d_1/d_0)	Toluenes (d_0/d_2)	enolates (d_1/d_0)
(**1a**)	d_0	100	100.0	100.0	100.0
(**1b**)	d_4	91.8			
	d_3	8.2			
	d_2			94.2	100.0
	d_1		95.7	5.0	
	d_0		4.3	0.8	
(**1c**)	d_2	94.5			
	d_1	4.3	72.26 (2.87)	98.6	69.7 (2.30)
	d_0	1.2	27.74	1.4	30.3
(**1d**)	d_2	91.1		38.1	
	d_1	4.1	57.2 (1.53)	0.9 (1.39)	40.6 (0.68)
	d_0	4.8	42.8	61.0	59.4

[a] For solution reactions, the k.i.e.s on enolate production are calculated assuming that d_0-alkoxide yields only d_0-product, and d_1-alkoxide yields equal amounts of d_1- and d_0-product. The extreme case ratios, *i.e.*, if the d_1-alkoxide yields exclusively d_0- or d_1-product are 2.55 and 3.24 for enolates from (**1c**), and 1.40 and 1.69 for enolates from (**1d**). For the toluenes from (**1d**), we again assume that d_0-alkoxide yields only d_0-product, and that d_1-alkoxide yields either d_1- or d_0-product.



(**1**) **a**; $R^1, R^2, R^3, R^4 = H$
b; $R^1, R^2, R^3, R^4 = D$
c; $R^1, R^3 = H; R^2, R^4 = D$
d; $R^1, R^2 = H; R^3, R^4 = D$

dimsyl and is consistent with the more exothermic (37 kcal mol^{-1}) process and fits the pattern of k.i.e.s of 6.0, 2.5, and 1.6 which have been reported for gas phase transfers of proton from acetone to CF_3^-, Ph^-, and CH_3^- with exothermicities of 7, 28, and 48 kcal mol^{-1}, respectively.[2,10] The behaviour of (**1d**) reveals a dramatic difference between gas and solution mechanisms. The observed effect, 0.68, is inverse, and cannot be reconciled simply with a secondary α-D k.i.e. on benzyl anion formation. If, however, proton transfer is rate limiting, and the primary k.i.e. operates against an equilibrium secondary α-D *i.e.* on $C \cdots C$ bond cleavage (*ca.* 1.2 per D based on the solution data), ratios close to the observed value are to be expected. An intrinsic barrier of $\sim$12 kcal mol^{-1} has been suggested[11] for proton transfer between delocalised carbanions. Application of an appropriate version of the Marcus relationship[12] yields a barrier of $\sim$7 kcal/mol^{-1} for proton transfer within the deoxybenzoin–benzyl anion complex which sets an upper limit to the barrier to carbon–carbon bond formation. The complex itself could be stabilised[13] by as much as 15 kcal mol^{-1}, so that its formation from alkoxide may be close to thermoneutral. Data on such negative ion–dipole complexes are rare,[2] most work having been carried out on the positively charged species.[13]

Finally, we note that similar measurements on the gas phase fragmentation of deuteriated t-butoxide to methane and acetone enolate indicate rate limiting $C \cdots C$ bond cleavage.[10] We believe that the change in rate limiting step is associated with a higher barrier to proton transfers occurring between delocalized carbanions[11] in the reaction of (**1**).

Received, 19th August 1988; Com. 8/03353F

References

1 D. J. Cram, 'Fundamentals of Carbanion Chemistry,' ch. 4, Academic Press, New York, 1965.
2 R. N. Hayes, J. C. Sheldon, J. H. Bowie, and D. E. Lewis, *Aust. J. Chem.*, 1985, **38**, 1197; W. Tumas, R. F. Foster, and J. I. Brauman, *J. Am. Chem. Soc.*, 1988, **11**, 2714, and references therein.
3 S. M. Partington and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 2*, 1988, 983.
4 E. M. Arnett and K. G. Venkatasubramanian, *J. Org. Chem.*, 1983, **48**, 1569.
5 A. Streitweiser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, 1958, **80**, 2326.
6 J. R. Murdoch, J. A. Bryson, D. F. McMillen, and J. I. Brauman, *J. Am. Chem. Soc.*, 1982, **104**, 600.
7 J. M. Moncur, R. S. Brown, S. Ibrahim, and J. M. Wilson, *Rapid Comm. Mass Spectr.*, 1988, **2**, 77.
8 J. E. Bartmess and R. T. McIver, Jr., 'Gas Phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, 1979, vol. 2.; S. W. Benson, 'Thermochemical Kinetics,' Wiley-Interscience, New York, 1976.
9 R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973.
10 W. Tumas, R. F. Foster, M. J. Pellerite, and J. Brauman, *J. Am. Chem. Soc.*, 1987, **109**, 961.
11 M. D. Brickhouse and R. R. Squires, *J. Am. Chem. Soc.*, 1988, **110**, 2706; W. E. Farneth and J. I. Brauman, *ibid.*, 1976, **98**, 7891.
12 S. Wolfe, D. J. Mitchell, and H. B. Schlegel, *J. Am. Chem. Soc.*, 1981, **103**, 7694.
13 R. D. Bowen and D. H. Williams, *J. Am. Chem. Soc.*, 1980, **102**, 2752; T. H. Morton, *Tetrahedron*, 1982, **38**, 3195; D. J. McAdoo, *Mass Spectrom. Rev.*, 1988, **7**, 363; S. Hammerum, *J. Chem. Soc., Chem. Commun.*, 1988, 858; S. Hammerum and H. E. Audier, *ibid.*, 1988, 860.