Elimination of Dihydrogen from Collision-activated Alkoxide Negative Ions in the Gas Phase. An *Ab initio* and Isotope Effect Study

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Ab initio calculations indicate the loss of H_2 from the ethoxide negative ion to be a stepwise process in which the key intermediate is the 'long-lived' species $[H^- \cdots HCH_2CHO]$; deuterium isotope effects which are observed for the collision-induced eliminations of H_2 and HD from deuteriated ethoxide ions support the operation of a stepwise reaction.

Ion cyclotron resonance (i.c.r.) spectra of reaction systems involving alkoxide negative ions (*e.g.* EtO^-, PrO^-, or Pr^iO^-) are often dominated by the presence of stable (alkoxide $-H_2)^-$ species[1] which are likely to correspond to enolate ions. We infer from our i.c.r. and theoretical studies[2] of the formation of 'solvated' enolate ions and tetrahedral adducts that the most plausible mechanism for the elimination of H_2 from (say) the ethoxide negative ion is: $CH_3CH_2O^- \rightarrow H^- \cdots HCH_2CHO \rightarrow H_2 \cdots \bar{C}H_2CHO \rightarrow CH_2{=}CHO^- \cdots H_2 \rightarrow CH_2{=}CHO^- + H_2$. We now present the results of a joint *ab initio* and deuterium isotope effect study which essentially confirm this sequence.

The results of an extensive *ab initio* study for the elimination of H_2 from EtO^- (refined to the 6-311^{++}G level, Gaussian 82[3]) are summarised in Figure 1. The calculations indicate a stepwise reaction through reactive intermediate (**2**). Brauman,[4] on the basis of deuterium isotope effects, has suggested the laser-induced elimination of methane from the t-butoxide negative ion to be stepwise. We believe the two reactions are of the same type and completed 4-31G calculations on the t-butoxide system confirm this.

There has been recent debate whether isotope effects may be used to differentiate between a concerted reaction and a stepwise reaction in which two transition states (of comparable energies) are separated by a reactive intermediate occupying a substantial potential well.[5] The reaction shown in Figure 1 provides an interesting probe of this problem.

Collisional activation (He, 1×10^{-5} Torr in the second field-free region of a reverse-sector[6] Hitachi–Perkin-Elmer RMU 7D mass spectrometer) of $CD_3CH_2O^-$ and $CH_3CD_2O^-$ [produced by dissociative secondary electron capture (at 70 eV, accelerating voltage 3.6 kV) of the appropriate alkyl nitrite[7]] shows *specific* 1,2 elimination of HD from each ion. The product ion abundances for the corresponding losses of H_2 and HD from CH_3CHDO^- and $CH_2DCH_2O^-$ are H_2/HD† = 2.9 and 1.6 respectively‡ (similar values are obtained from appropriately labelled PrO^- and Pr^iO^- ions).

The observed isotope effects suggest that steps $EtO^- \rightarrow$ (**2**) and (**2**) $\rightarrow$ (**4**) are both kinetically significant.§ *The stability of*

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† Values corrected for statistical factors where appropriate.

‡ The abundance ratios H_2/HD were obtained by comparison of peak areas. They reflect averaged (and probably low) isotope effects since the reactant ions are collisionally activated with energy spreads above the threshold(s) required for the reaction(s).

§ The elimination of H_2 [*viz.* (**3**) → (**4**) → products] should be isotopically insensitive because of the excess energy of reaction at this stage.

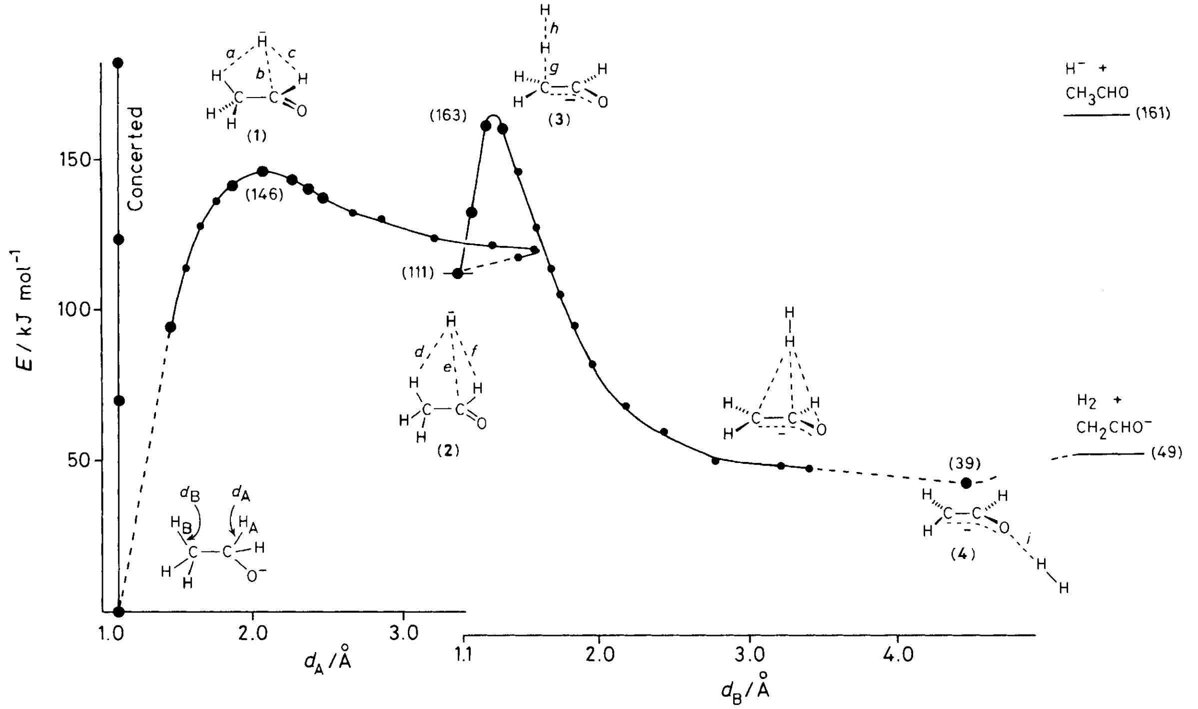

Figure 1. Results of *ab initio* calculations on the intermediates in the elimination of H_2 from EtO^-. Large points are fully optimized geometries. Small points are derived from force relaxation runs (potential surface scans). Distances (in Å): (**1**), a = 2.52, b = 2.10, c = 2.44; (**2**), d = 2.97, e = 3.44, f = 2.67; (**3**), g = 1.34, h = 1.73; and (**4**), i = 2.24.

intermediate (**2**) *must be the critical parameter in determining the isotope effect in the second step.* The classical approach to stepwise reactions[5] (particularly stepwise reactions in the condensed phase) could be used to rationalise the experimental observations. Another effect must, however, be taken into consideration. The formation of (**2**) from (**1**) and (**3**) from (**2**) both involve a number of complex rotational changes whose total effect is for H_A to travel a half spiral around the C–C axis. These rotational steps are slow; thus (**2**) is impeded from passing through (**1**) and (**3**) irrespective of what enthalpy barriers are involved. In the extreme case, a stable (**2**) could cause the steady-state approximation[8] to be contravened, with $EtO^- \rightarrow$ (**2**) and (**2**) $\rightarrow$ (**4**) then being separate reactions. Whether this rotational (entropy) effect is fully or only partially responsible for the kinetic significance of both steps is a matter of debate.

Isotope effect calculations[9,10] confirm that the experimental H_2/HD ratios are consistent with primary deuterium isotope effects operating for the separate reactions described above. In transition state (**1**) the C–H_A bond order is very small, and the geometry indicates a relatively large deuterium isotope effect (there is a large contribution to the isotope effect from angle bending modes; *cf.* ref. 11). In transition state (**3**) the $C \cdots H_B \cdots H_A^-$ system is linear, and the primary deuterium isotope effect for this process will be smaller than that operating for the first reaction.

Ab initio calculations establish that the loss of H_2 from the ethoxide negative ion is a stepwise 1,2 elimination with the key intermediate being the acetaldehyde solvated hydride ion (**2**). Care must be exercised in using isotope effects as a definitive mechanistic probe in this type of reaction without recourse to appropriate theoretical calculations.

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References

1 R. N. Hayes, J. H. Bowie, and G. Klass, *J. Chem. Soc., Perkin Trans. 2,* 1984, 1167.

2 G. Klass, J. C. Sheldon, and J. H. Bowie, *Aust. J. Chem.*, 1982, **35**, 2471.

3 J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Shlegel, E. M. Fluder, and J. A. Pople, Gaussian 82, Carnegie Mellon University.

4 W. Tumas, R. F. Foster, M. J. Pellerite, and J. I. Brauman, *J. Am. Chem. Soc.*, 1983, **105**, 7464.

5 J. G. Belasco, W. J. Albery, and J. R. Knowles, *J. Am. Chem. Soc.*, 1983, **105**, 2475.

6 T. Wachs, P. F. Bente, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, 1972, **9**, 333; J. H. Bowie, T. Blumenthal, M. H. Laffer, S. Janposri, and G. E. Gream, *Aust. J. Chem.*, 1984, **37**, 1447.

7 K. Jaeger and A. Henglein, *Z. Naturforsch., Teil A*, 1967, **22**, 700; R. T. McIver and J. S. Miller, *J. Am. Chem. Soc.*, 1974, **96**, 4323; D. P. Ridge and J. L. Beauchamp, *ibid.*, 1974, **96**, 3595.

8 See, for example: P. W. Atkins, 'Physical Chemistry,' 2nd edn., Oxford University Press, 1982, pp. 942—950; M. Scarlett, *Chem. Aust.*, 1983, **50**, 338.

9 L. B. Sims, G. W. Burton, and D. E. Lewis, QCPE No. 337, 1977; L. B. Sims and D. E. Lewis, in 'Isotopes in Organic Chemistry,' eds. E. Buncel and C. C. Lee, Elsevier, Amsterdam, 1984, Vol. VI, Ch. 4.

10 K. D. King and R. D. Goddard, *J. Am. Chem. Soc.*, 1975, **97**, 4504.

11 W. P. Huskey and R. L. Schowen, *J. Am. Chem. Soc.*, 1983, **105**, 5704.