39. Stereochemical Criteria Providing Unambiguous Experimental Evidence for the Intermediacy of Ion/Molecule Complexes in the Generation of Enolates from Gaseous Alkoxides

Short Communication

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Dedicated to Prof. *Josef Seibl* on the occasion of his 65th birthday

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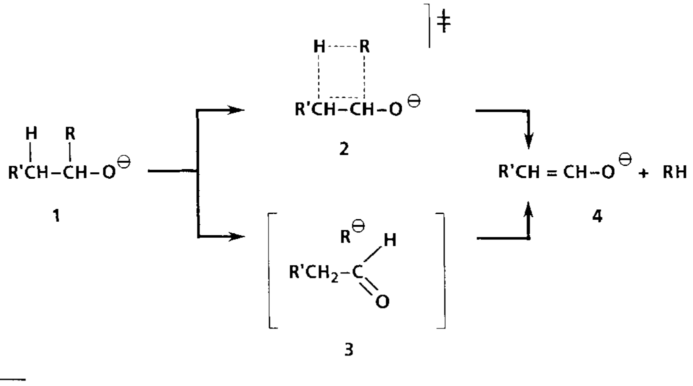
The epimeric alkoxides **6a** and **6b**, generated in the gas phase by deprotonation of the stereospecifically deuterated isoborneols **5a** and **5b**, undergo loss of H_2 and HD in a 1:1 ratio. This result, ruling out a concerted one-step process, establishes the intermediacy of an ion/molecular complex ('solvated' hydride ion) in the course of formation of enolates from the alkoxide anions in the gas phase.

Alkoxide anions, generated in the gas phase by deprotonation of alcohols, upon collisional or photochemical activation, undergo loss of RH (R = alkyl, H) to yield enolate ions [1] [2][1]. The study of labeled precursors leaves no doubt that the reaction conforms to a formal 1,2 elimination [1]; *ab-initio* studies [1b, c] and the energy dependency [2] of the primary and secondary isotope effects associated with the formation of isotopomers of RH *suggest* that the reaction is not a concerted 1,2 elimination (*Scheme 1; path* ⓐ) but rather follows a stepwise mechanism (path ⓑ). This multi-step reaction involves the initial formation of an intermediate ion/molecule complex **3** followed by an

Scheme 1



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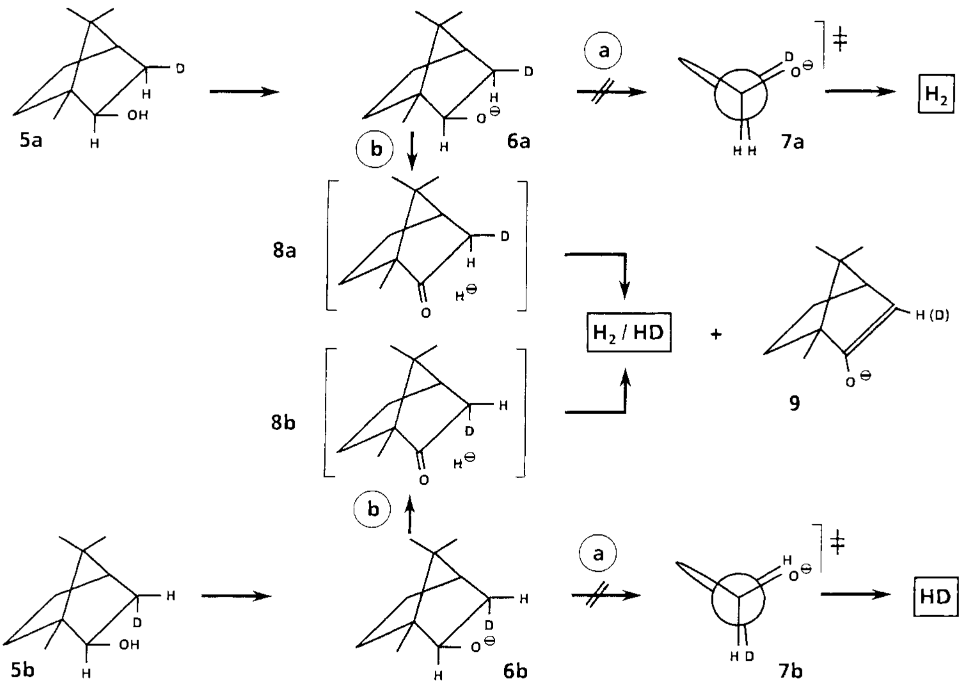
[1] There is considerable precedent for ion/molecule complexes as intermediates in unimolecular reactions of gaseous cations. For reviews, see [3].

H transfer within the complex [3]. While the first step **1**→**3** shows an unusually large secondary isotope effect for R = CD_3 [2] and a medium primary isotope effect for R = D [2b, c], the subsequent cleavage of the C(β)–H(D) bond **3**→**4** is associated with an much smaller primary isotope effect [2b, c] [3].

We hold the point that a *definitive* exclusion of path ⓐ can only be accomplished by a stereochemical study. On energetic grounds step **1**→**2** requires a strict *syn*-alignment of the relevant C–R/C–H bonds involved in the formation of the transition structure **2**. Thus, if a rigid alkoxide anion, stereospecifically 'labeled' at the C(β)-position, is chosen, an unambiguous *distinction* between the two mechanistic pathways ⓐ *vs.* ⓑ can be conceived. For our study, the stereospecifically labeled isoborneols (= *exo*-1,7,7-trimethylbicylo[2,2,1]heptan-2-ol) **5a** and **5b** have been investigated²). If the loss of molecular hydrogen from the corresponding alkoxides **6a** and **6b** proceeds *via* path ⓐ, the former should give rise to specific loss of H_2, while from the latter HD should be generated *(Scheme 2)*. If, however, the reaction follows a multi-step sequence, the ion/molecule complex formed from **6a** and **6b** should not be subjected to the constrain for a concerted *syn*-elimination; rather, the initially formed 'solvated' H^- may attack both the *exo*- and *endo*-C–H (C–D) bonds in the ion/molecule complexes **8a** and **8b**, thus, eventually generating both H_2 and HD from either precursor **5a** and **5b**.

The experimental result is unambiguous: both **6a** and **6b** (generated by 70-eV EI ionization of a mixture of the corresponding isoborneols **5a** and **5b**, respectively ($p \approx 10^{-4}$

Scheme 2



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[2] For a detailed elegant study of the electron-impact-induced H_2O loss from borneols, see [4].

Torr) and N_2O ($p \approx 10^{-5}$ Torr) in the chemical ionization source of a ZAB-HF-3F mass spectrometer (*VG Instruments;* emission current 50 µA; temp. of the ion source housing *ca.* 200°), and mass-selected by means of B(1) E[3]) undergo, in the field-free region between E and B(2) at a background-pressure of $p < 10^{-8}$ Torr, losses of both HD and H_2 in a ratio 1:1. If He is introduced as a collision gas, only minor changes in the ratio of the competitive, reductive eliminations of H_2 *vs.* HD are observed; starting from **5a** HD and H_2 are generated in a ratio 1.1:1, while from **5b** the formation of H_2 is favored over that of HD in exactly the same ratio.

These findings *i*) clearly rule out that the dehydrogenation of the alkoxide anions **6a** and **6b** follows a concerted pathway; *ii*) they indicate that the intramolecular S_N attack of the *exo*-C–H(C–D) bond by the nucleophile H^- is slightly favored over the corresponding *endo*-bond; and *iii*) the data show that in the dehydrogenation of the isoborneol alkoxides **6a** and **6b** no discernible kinetic isotope effects are involved in the decomposition of the ion/molecule complexes **8a** and **8b**.

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REFERENCES

[1] a) R. Houriet, D. Stahl, F. J. Winkler, *Environ. Health Persp.* **1980,** *36,* 63; b) R. N. Hayes, J. C. Sheldon, J. H. Bowie, D. E. Lewis, *J. Chem. Soc., Chem. Commun.* **1984,** 1431; c) R. N. Hayes, J. C. Sheldon, J. H. Bowie, D. E. Lewis, *Aust. J. Chem.* **1985,** *38,* 1197.

[2] a) W. Tumas, R. F. Foster, M. J. Pellerite, J. I. Brauman, *J. Am. Chem. Soc.* **1983,** *105,* 7464; b) W. Tumas, R. F. Foster, M. J. Pellerite, J. I. Brauman, *ibid.* **1987,** *109,* 961; c) W. Tumas, R. F. Foster, J. I. Brauman, *ibid.* **1988,** *110,* 2714.

[3] a) T. H. Morton, *Tetrahedron* **1982,** *38,* 3195; b) D. J. McAdoo, *Mass Spectrom. Rev.* **1988,** *7,* 363; c) N. Heinrich, F. Louage, C. Lifshitz, H. Schwarz, *J. Am. Chem. Soc.* **1988,** *110,* 8183; d) N. Heinrich, H. Schwarz, in 'Ion and Cluster Ion Spectroscopy and Structure', Ed. J. P. Maier, Elsevier, Amsterdam, 1989, p. 329.

[4] R. Robbiani, J. Seibl, *Org. Mass Spectrom.* **1973,** *7,* 1153.

[5] T. Weiske, Ph. D. Thesis, Technische Universität Berlin, D83, 1985; b) J. K. Terlouw, T. Weiske, H. Schwarz, J. L. Holmes, *Org. Mass Spectrom.* **1986,** *21,* 665; c) K. Eckart, H. Schwarz, *Helv. Chim. Acta* **1987,** *70,* 489.

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[3]) For a description of the apparatus and for further details, see [5].