# The Use of Deuterium Isotope Effects in Establishing Mass Spectral Fragmentation Mechanisms

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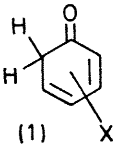
*Summary*. Isotope effects on competing metastable transitions are employed to show that elimination of ethylene from the molecular ion of *p*-bromophenetole proceeds *via* a 4-membered transition state.

THE use of primary kinetic deuterium isotope effects to determine reaction mechanisms involving organic neutrals is well established.[1] The occurrence of such an isotope effect indicates that a bond to hydrogen is stretched in the transition state of the rate-determining step, and mechanistic inferences can often be made. Deuterium isotope effects have also been observed for reactions from organic ions in the mass spectrometer,[2] but in most cases the reactions investigated were those in which C–H cleavage in the rate-determining step would be expected (*e.g.* loss of H or $H_2$). We report the investigation of deuterium isotope effects on competing reactions from positive organic ions in the first drift region of a double-focussing mass spectrometer, with a view to providing mechanistic information. Metastable reactions are employed because these low-energy reactions yield higher isotope effects than decompositions in the ion source.[2c]



(1)

A primary deuterium isotope effect may of course occur upon a reaction not involving elimination of a hydrogen-containing neutral, and in the mass spectrometer it is not possible to investigate such an isotope effect by the direct comparison of metastable ion abundances for loss of H- and D-containing fragments (*e.g.* loss of H and D from $CH_3CD_3$).[2b] This problem may be obviated by choosing a compound with a reference metastable.

The elimination of CO from the molecular ion of phenol and substituted phenols has long been regarded as occurring from a cyclohexadienone structure (1). Since formation of (1) from the ionised phenol structure involves a hydrogen transfer reaction, a primary deuterium isotope effect upon the rate of loss of CO may occur. The molecular ion of *p*-bromophenol competitively eliminates Br and CO in metastable transitions, so the isotope effect on CO loss from this molecular ion may be investigated for suitably deuteriated compounds. The metastable abundance ratios $m^*[M^+-Br]/m^*[M^+-CO]$ are shown in the Table for the *p*-bromophenols (2)—(4).

TABLE

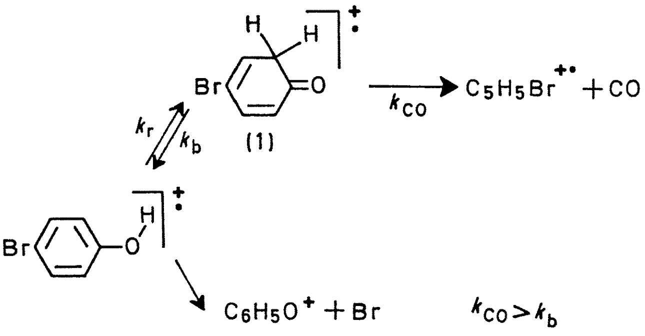
*Competing metastable abundance ratios for reactions from the molecular ion of* p-*bromophenol, the* $M^+-C_2H_4$ *ion of* p-*bromophenetole, and their deuteriated derivatives*

| No. | Compound | Decomposing ion ($A^+$) | $m^*[A^+-Br]/$ $m^*[A^+-CO]$ |
|---|---|---|---|
| (2) | *p*-Br $C_6H_4$ OH | $M^+$ | 20 ± 1 |
| (3) | *p*-Br $C_6H_4$ OD | $M^+$ | 62 ± 4 |
| (4) | 4 Bromo-2,6-dideuteriophenol | $M^+$ | 22 ± 2 |
| (5) | *p*-Br $C_6H_4$ $OC_2H_5$ | $M^+-C_2H_4$ | 19 ± 1 |
| (6) | *p*-Br-$C_6H_4$ $OC_2D_5$ | $M^+-C_2D_4$ | 50 ± 3 |

The comparison of the metastable abundance ratio for *O*-deuterio-*p*-bromophenol (3) with those for its derivatives

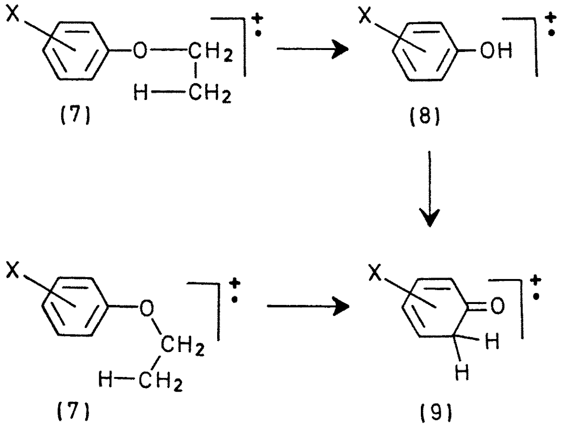
(2) and (4) shows that there is a deuterium isotope effect on the rate of CO loss from M$^+$, assuming no deuterium isotope effect on Br loss. The rate of transfer of H is greater than the rate of transfer of D in these low-energy metastable ions, due to the lower activation energy for the H transfer. This is believed to be the first illustration of a deuterium isotope effect on a mass spectral reaction not involving elimination of a hydrogen-containing fragment.

Transfer of hydrogen occurs in the rate-determining step [probably to form (1)] followed by loss of CO as shown in the Scheme. The hydrogen rearrangement competes with bromine loss. The fact that (2) and (4) yield identical metastable ratios (within experimental error) shows that the rate of CO loss from (1) is fast compared with the transfer of a methylene hydrogen back on to the oxygen atom.



SCHEME

This isotope effect may be used to yield positive mechanistic information on the elimination of ethylene from the molecular ion of phenetoles. Previous evidence has been forthcoming[3] to suggest that this reaction yields an ion which has the same decomposing structure as the corresponding ionised phenol. The only point of conjecture is whether the elimination of ethylene from (7) occurs *via* a 4-membered transition state to yield (8), or *via* a 6-membered transition state to yield (9).



Isotope effect evidence (see Table) shows that (7) → (8) is occurring. First, the similarity in metastable abundance ratios for compounds (2), (4), and (5) and for compounds (3) and (6) confirm that the decomposing metastable ions have the same structure and energy, whether formed directly from *p*-bromophenol or indirectly from *p*-bromophenetole. Second, the isotope effect in the case of compounds (5) and (6) demonstrates that the sequence (7) → (8) → (9) is occurring, since the direct reaction (7) → (9) would not present an opportunity for an isotope effect on the further loss of CO.

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[1] See, for example, (a) L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, 1960; (b) V. Gold *Adv. Phys. Org. Chem.*, 1969, **7**, 259.

[2] See, for example, (a) B. J.-S. Wang and E. R. Thornton, *J. Amer. Chem. Soc.*, 1968, **90**, 1216; (b) U. Löhle and Ch.Ottinger, *J. Chem. Phys.*, 1969, **51**, 3097; (c) I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1971, **93**, 99.

[3] P. D. Woodgate and C. Djerassi, *Org. Mass Spectrometry*, 1970, **3**, 1093, and refs. cited therein.