β-Secondary Deuterium Isotope Effect on the Fragmentation of an Oxetan Molecular-ion

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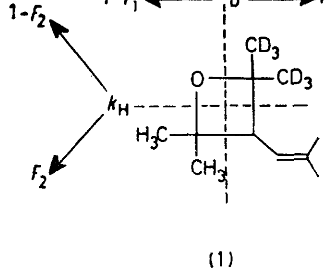
Summary Mass spectral decomposition of 4,4-dimethyl-3-(2-methylprop-1-enyl)-2,2-bis(trideuteriomethyl)oxetan gives preferentially ([$^2H_0$]-2,5-dimethylhexa-2,4-diene)$^{+\cdot}$; a secondary deuterium isotope effect on the direction of oxetan cleavage (1·08 per deuterium atom at 10 eV) may be calculated.

WE have observed a β-secondary deuterium isotope effect for a fragmentation in the mass spectrometer. The data suggest a mechanism for the system under investigation and also point to the potential prejudicial influence of remote deuterium substitution on bond cleavages at low ionizing energy, which could be an important complicating factor in labelling studies.



(1)

The oxetan (**1**), prepared by irradiation of 2,5-dimethyl hexa-2,4-diene (**2**) and [$^2H_6$]acetone (>99·5% $^2H_6$) following the procedure for unlabelled acetone,[1]† gave almost exclusively products of two-bond cleavage upon decomposition at 10—70 eV. Secondary fragmentation for (**1**) was identified with reference to the mass spectra of acetone, [$^2H_6$]acetone, and (**2**). A metastable ion corresponding to *m/e* (110 → 95) [also found in the spectrum of (**2**)] was observed for (**1**) and identified as [$^2H_0$]-(**2**)$^{+\cdot}$ — CH$_3$. Deuterium scrambling in the molecular ion of (**1**) was not important since fragment ions of intermediate deuterium

TABLE 1. Mass spectral data for (**1**).[a,b]

m/e		10 eV	15 eV	20 eV	50 eV	70 eV
58 (43)	..	—	27	44	69	79
116 (101, 98)	..	95	103	100	114	115
64 (46)	..	—	13	20	36	38
110 (95)	..	150	146	155	171	175

[a] Relative abundances from two or more spectra; base peak = 100; average deviation ±1% of base peak. [b] Numbers in parentheses identify secondary fragments, the intensities for which the primary abundances were corrected. This correction amounted to 40—50% of the primary ion abundance at *m/e* 110 and 116, even at low voltages, and would be problematic in terms of interpreting the isotope effect if the secondary fragments arise from (M — CH$_3$ or CD$_3$)$^+$. However, the latter unobserved ions should also give rise to ions at *m/e* 43 and 46, yet these abundances are negligible at low voltages.

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† The n.m.r. spectrum of (**1**) was consistent with deuterium incorporation only at the 2-methyl position (>97%).

content were not detected. Fragmentation patterns for (**1**) as a function of ionizing energy, corrected for secondary fragmentation and accounting for 96 and 69% of the ion current at 10 and 70 eV, respectively, are shown in Table 1.

The total isotope effect (6 deuterium atoms) on the direction of cleavage of (**1**) is given by equation (1) and calculated using ion abundances from Table 1. Ion product ratios are related to the total isotope effect as shown in equations (2) and (3) with reference to the fragmentation scheme accompanying structure (**1**), where F_1 and F_2 refer to the fractions of ion current associated with [$^2H_6$]-(**2**) and [$^2H_0$]-(**2**) ions for cleavages k_D and k_H, respectively. Calculated isotope effects (total and per deuterium atom) and charge fractionation factors as a function of ionizing energy are shown in Table 2.

$$\left(\frac{k_H}{k_D}\right)_{tot} = \frac{[^2H_0]\text{-}(\mathbf{2})^{+\cdot} + ([^2H_6]\text{acetone})^{+\cdot}}{[^2H_6]\text{-}(\mathbf{2})^{+\cdot} + ([^2H_0]\text{acetone})^{+\cdot}} \qquad (1)$$

$$\frac{[^2H_0]\text{-}(\mathbf{2})^{+\cdot}}{[^2H_6]\text{-}(\mathbf{2})^{+\cdot}} = \left(\frac{k_H}{k_D}\right)_{tot}\left(\frac{F_2}{F_1}\right) \qquad (2)$$

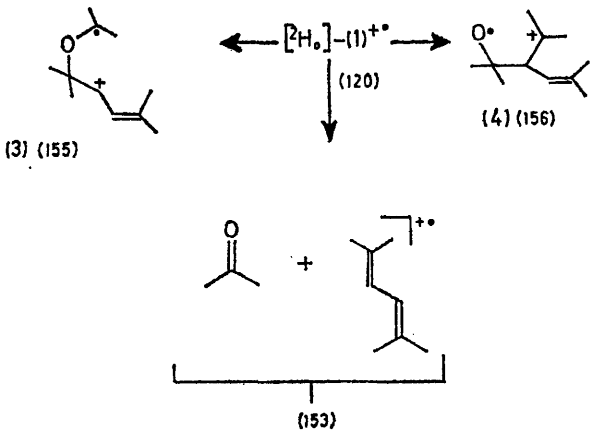
$$\frac{([^2H_0]\text{-acetone})^{+\cdot}}{([^2H_6]\text{-acetone})^{+\cdot}} = \left(\frac{k_D}{k_H}\right)_{tot}\left(\frac{1-F_1}{1-F_2}\right) \qquad (3)$$

The isotope effect represents a ratio of rates for cleavage averaged over the distribution of internal energies of ions undergoing decomposition. At low voltages the ratios of daughter ion abundances approximate to the first-order rate constant ratios for molecular-ion decomposition. The value of k_H/k_D (1·08), which is probably near maximum at 10 eV, may be superficially compared with k_H/k_D values (per deuterium atom) for limiting solvolyses, which are *ca.* 1·1 for β-D-labelled secondary and tertiary substrates.[2] Further comparison may be made with the β-secondary deuterium isotope effect observed for a retro-Diels–Alder reaction (1·00),[3] which offers a model for the isotope influence on a homolytic cleavage at carbon.

TABLE 2. Isotope effects and the development of charge in product ions in cracking of (**1**) under electron impact

	10 eV	15 eV	20 eV	50 eV	70 eV
$(k_H/k_D)_{tot}$ ..	1·58	1·22	1·22	1·13	1·10
$(k_H/k_D)_{tot}^{1/6}$ ..	1·08	1·03	1·03	1·02	1·02
F_1	1·00	0·79	0·70	0·62	0·59
F_2	1·00	0·92	0·89	0·83	0·82

That stabilization of charge in product ions is important for decomposition of (**1**)$^{+\cdot}$ is further supported by the preference for formation of ions of (**2**) over acetone (ionization potentials for acetone and MeCH=CHCH=CH_2 are 9·7 and 8·7 eV, respectively[4]) and for formation of ions bearing protium *vs.* deuterium reflecting the relative hyperconjugative capacities of the isotopes. The isotope effect could be 'kinetic' in origin by controlling the preference for cleavage to ring-opened ions (**3**) and (**4**) (with k_H/k_D <1 and >1, respectively). However, thermochemical calculations of the heats of formation of the ions based on the group additivity principle[5] (values in kcal/mol shown in parentheses in the Scheme) do not suggest a necessity for ring opening. We favour a single-step mechanism for decomposition of (**1**) in which the requirement for formation of product ion of lowest electron affinity[6] controls the direction of cleavage and residence of charge.‡



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The isotope effect and fractionation factors F_1 and F_2 are attenuated at high electron energies.[7] Their values cannot be assessed quantitatively owing to the contributions of ions of low internal energy and other factors at high voltages. The qualitative inference is, however, that the isotope effect on the direction of cleavage largely reflects relative activation energies with perhaps a residual relative frequency factor influence favouring k_H over k_D.§ The isotope influence on the dependence of fractionation of charge on ionizing energy should be noted as well.

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‡ Others have suggested (K. Pihlaja, K. Polviander, R. Keskinen, and J. Jalonen, *Acta Chem. Scand.*, 1971, **25**, 765; P. O. Virtanen, A. Karjalainen, and H. Ruotsalainen, *Suomen Kemi.* (*B*), 1970, **43**, 219) a two-step mechanism involving C–C cleavage for substituted oxetans based on regioselectivities in cracking. Our data for aryloxetans support this view (G. Jones, II, and L. P. McDonnell, *Org. Mass Spectrometry*, 1975, **10**, 1; and unpublished work). Ring opening and overall two-bond cleavage are calculated for these systems to be thermoneutral or slightly exothermic in contrast to the situation for (**1**).

§ A factor in β-secondary effects may be the relative entropy loss in freezing out of the more ponderous rotor (CD_3 *vs.*CH_3) with the onset of hyperconjugation; H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1968, **72**, 1866; R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, 1966, **88**, 2589.

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