Secondary Deuterium Isotope Effect in the Cycloaddition of Dimethylketen to Styrene

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Summary The secondary deuterium isotope effect for the cyclo-addition of dimethylketen to [α-^{2}H]-styrene has been found to give $k_H/k_D = 0{\cdot}8$ and the mechanistic implications of this value are discussed.

Secondary deuterium isotope effects at carbon undergoing a change in hybridisation are well established as being normal *i.e.* $k_H/k_D > 1$ for the direction $sp^3 \rightarrow sp^2$ and inverse, $k_H/k_D < 1$ for a change in the opposite direction.[1] Concerted cycloadditions should therefore exhibit inverse isotope effects at both bonding loci.[2] In support of this, values reported for the Diels-Alder reaction include [^{2}H]-maleic anhydride and furan or 2-methylfuran[3] $k_H/k_D =$ 0·94 and 0·90 respectively; tetracyanoethylene and [^{2}H]-anthracene, 0·90.[4] These values are similar to those for radical additions to olefins, *e.g.* styrene polymerisation[5] (0·90) and methyl radical addition to styrene (0·90).[6] On the other hand a two-step cycloaddition involving a diradical intermediate would be expected to show the inverse isotope effect at the bonded centre but very little effect at the radical site. The two mechanisms should thereby be distinguished.

The cycloaddition of dimethylketen to olefins such as styrene is most likely a concerted reaction based on evidence from stereospecificity and stereoselectivity.[7] Expected values of k_H/k_D for [α-^{2}H]- and [β-^{2}H]-styrenes would both be <1 for a concerted reaction, and ~ 0 and <1 respectively for a two-step reaction since the benzylic carbon would surely be a radical site. The α-effect is thus the one which serves to distinguish the two mechanisms.

We have now measured the α-isotope effect by the competitive reaction technique previously described.[7b] A mixture of styrene and [α-^{2}H$_1$]-styrene (approx 1 : 1) was allowed to react with 0·05 molar equivalents of freshly distilled dimethylketen at 100° for 15 min and the product, 2,2-dimethyl-3-phenylcyclobutanone, isolated by g.l.c. The isotope ratio of both the styrene and the product was determined by mass spectroscopy at the minimum ionising voltsge (18 eV), a constant source pressure and multiple scanning (12—20 scans) over the molecular ion region. Contributions to the molecular ion intensities from $M + 1$ [^{2}H$_0$] and $M - 1$ [^{2}H$_1$] signals were estimated from the respective pure compounds and allowance made. A check on the analytical method was made by comparison with weighed mixtures. There is undoubtedly a considerable increase in the deuterium content of the product as compared with the styrene (Table) which corresponds to a secondary isotope effect $k_H/k_D = 0{\cdot}8$.

Table

	Styrene [^{2}H$_0$]/[^{2}H$_1$]	Product [^{2}H$_0$]/[^{2}H$_1$]	k_H/k_D
Run 1	1·303	1·026	0·787
Run 2	1·305	1·057	0·809
		Average	0·80 ± 0·05

Our results indicate considerable bond-formation between α-C and the keten in the transition state and support the other evidence for concertedness in this reaction. On the other hand the magnitude of the effect is considerably greater than those for Diels-Alder reactions and greater also than those found for other (2 + 2)-cycloadditions such as cyclohexene + diphenylketen (determined by the orientational preference), 0·885.[8] It contrasts with the value 1·12 for the cycloaddition of diethyl azodicarboxylate to ethyl vinyl ether [α-^{2}H] for which a two-step reaction is postulated.[9] We conclude that in our reaction hybridisation change at α-C is further advanced than is usual in Diels-Alder reactions. It may be pointed out that the maximum isotope effect calculated for the simultaneous conversion of two sp^2 hybrid carbons to sp^3, taking account of the transformation of bending frequencies from 770 to 1340 cm^{-1} is 0·45[10] or for one such centre in the carbonium ion series, about 0·7. One further measurement requires comment, the α-deuterium effect for the cycloaddition of diphenylketen to styrene for which $k_H/k_D = 1{\cdot}12$.[11] This value is highly unusual and, as the authors point out, inexplicable in terms of the effects of heavy atom substitution discussed above. A possible explanation might be sought in a mechanism involving reversible diradical intermediate formation with rate-determining collapse of the diradical. This should show a normal isotope effect[12] but seems improbable on chemical grounds. It evidently points to a difference in the reactions of diphenyl- and dimethyl-ketens and the need for further studies of secondary isotope effects on cycloadditions.

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