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SECONDARY DEUTERIUM ISOTOPE EFFECT ON THE MALEIC ANHYDRIDE-CYCLOPENTADIENE REACTION

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IT was demonstrated by Streitwieser et al.[1] that cyclopentyl tosylate-1-d is solvolyzed at 1/1.15 the rate of the protium analogue at 60°. The rate depression was ascribed to the change in bending frequency of the hydrogen (or deuterium) in proceeding from sp^3 hybridization in the reactant to nearly sp^2 in the transition state. Recently, Seltzer[2] has reported an inverse isotope effect where the hybridization change is from sp^2 in the reactant toward a partial sp^3 in the transition state. Maleic acid-2,3-d_2 was found to be converted to fumaric acid-2,3-d_2 at 1.17 times the rate of the protium analogue when catalyzed by thiocyanate ion at 60°.

We would like to report a small, inverse isotope effect in a common Diels-Alder reaction. Maleic anhydride-d_2 was synthesized by a procedure essentially identical to that of Seltzer's[2,3]. Mass spectral evidence indicated that the composition was 89.6% d_2, 7.7% d_1, and 2.7% d_0 corres-

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[1] A. Streitwieser, Jr., R.H. Jagow, R.C. Fahey and S. Suzuki, J.Amer. Chem.Soc. 80, 2326 (1858).

[2] S. Seltzer, J.Amer.Chem.Soc. 83, 1861 (1961); Chem. & Ind. 1313 (1959).

[3] A preprint of Dr. Seltzer's article was graciously sent prior to publication.

ponding to an atom fraction deuterium of 0.934. Combustion analysis[4] of an aliquot from a mixture of 4.995 g of the deuterated maleic anhydride and 4.928 g of normal isotopic species showed the atom fraction deuterium to be 0.4659 and 0.4668 in duplicate runs. This corresponds to an atom fraction deuterium of 0.9356 in the synthesized material.

The mixed maleic anhydrides were made up to 50.00 ml with methylene chloride, four 1/10 aliquots were brought to 0°, and reacted with cyclopentadiene sufficient to form adduct with 40% to 70% of the maleic anhydride. The cyclopentadiene was purified by passage through a Beckman GC-2 gas phase chromatography apparatus, calibrated by the recorder chart peak area, and passed directly into the reaction mixture. Reaction was assumed to be quantitative.[5]

The adduct (*cis*-3, 6-*endo*-methylene-1,2,3,6-tetrahydrophthalic anhydride) was isolated by removal of the residual maleic anhydride with fractional sublimation at 50°, and recrystallization of the product from toluene followed by sublimation at 100°. The melting points of the samples submitted for combustion analysis ranged from 158 to 162°. This product has been shown to have the endo configuration and to be formed by kinetic control.[6,7]

Calculation of the k_D/k_H ratio was done by substituting appropriate quantities in the equation[8]

$$k_D/k_H = \frac{\log a_D/a_D^{\circ}}{\log a_H/a_H^{\circ}} \qquad (1)$$

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[4] Deuterium analyses were by Josef Nemeth, Urbana, Ill.

[5] O. Diels and K. Alder, *Liebigs Ann*. **460**, 98 (1928).

[6] D. Craig, *J.Amer.Chem.Soc*. **73**, 4889 (1951).

[7] J.A. Berson, R.D. Reynolds and W.M. Jones, *J.Amer.Chem.Soc*. **78**, 6049 (1956).

[8] L. Melander, *Isotope Effects on Reaction Rates* p. 49. The Ronald Press Co., New York (1960).

Since the amount of maleic anhydride-d_1 is small and the k_D/k_H ratio is close to unity, the ratio of adduct-d_1 to adduct-d_2 was assumed to be the same as the maleic anhydride-d_1-maleic anhydride-d_2 ratio in the starting mixture. The table below summarizes the results:

Wt. cyclopentadiene (g)	Moles cyclopentadiene / Moles maleic anhydride	Atom fraction deuterium in adduct[4]	k_D/k_H
0.259	0.391	0.1189	1.05
0.336	0.507	0.1196	1.07
0.387	0.584	0.1188	1.05
0.451	0.681	0.1185	1.06
		Average:	1.06

It is clear that a small, but real, inverse isotope effect is present in the reaction. Using a simplified equation derived by Streitwieser,[1]

$$k_D/k_H = e^{-0.187/T\sum_i(\nu_{Hi} - \nu^{\ddagger}_{Hi})} \qquad (2)$$

and taking only the change in the out-of-plane bending motion as significant (769 cm^{-1} to 1340 cm^{-1}), one finds the maximum isotope effect to be 2.2 for the simultaneous conversion of two sp^2 carbon atoms to sp^3; the expected maximum for a single carbon atom hybridization change is 1.5. From the temperature dependence of the isotope effect, Seltzer[2] has estimated that his rate enhancement of 15% corresponds to a transition state approximately one-half way between sp^2 and sp^3 (for one carbon atom). Whether the rate-determining step of the Diels-Alder reaction involves one[9] carbon atom of the dienophile or both,[10] the hybridization change at the transition state for the maleic anhydride-cyclopentadiene case is seen to be small.

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[9] R.B. Woodward and T.J. Katz, Tetrahedron 5, 70 (1959); Tetrahedron Letters No. 5, 19 (1959).

[10] M.J.S. Dewar, Tetrahedron Letters No. 4, 16 (1959).

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