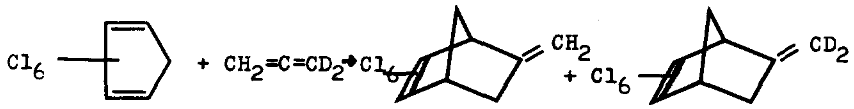
Tetrahedron Letters No.26, pp. 2263-2266, 1970. Pergamon Press. Printed in Great Britain.

SECONDARY DEUTERIUM ISOTOPE EFFECTS IN THE 1,3-DIPOLAR CYCLOADDITION OF TETRACYANOETHYLENE OXIDE TO STYRENE

William F. Bayne[1]
Department of Chemistry, Bryn Mawr College, Bryn Mawr, Penna. 19010
Eugene I. Snyder
Dept. of Chemistry, East Tennessee State University, Johnson City, Tenn. 37601

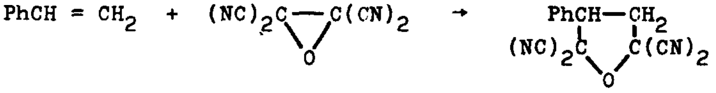
(Received in USA 7 March 1970; received in UK for publication 7 May 1970)

The reaction of tetracyanoethylene oxide (TCNEO) with olefins is but one example in the large class of 1,3-dipolar cycloadditions. The 1,3-dipole can be viewed as a 4 π-electron, 3-atom system isoelectronic with the allyl anion, and the thermal [4 + 2] cycloadditions are orbital symmetry allowed, concerted reactions. Linn has ascertained[2] such cycloadditions with TCNEO are stereospecific. Recently there has been renewed interest in using deuterium isotope effects as probes into the simultaneity of bond formation in cycloadditions. Viewed as a [4 + 2] cycloaddition the title reaction has many analogies to the Diels-Alder reaction where deuterium isotope effects have been studied by several groups.[3-6] The isotope effect reported by Dolbier,[6] using intramolecular competition in the system



seems most relevant, where $k_H/k_D = 0.95$ (per D atom).

The title reaction was studied using mixtures of light styrene and each of the monodeuterated styrenes competing for 0.1 mole equivalent of TCNEO in solutions of 1,2-dibromoethane at 125°. Designating light and heavy styrene and product by S_H, S_D, P_H, P_D, resp., and initial concentrations

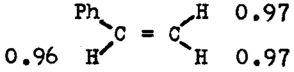


S P

by S_H^o, S_D^o, then

$$\frac{k_H}{k_D} = \frac{\ln(1 - P_H/S_H^o)}{\ln(1 - P_D/S_D^o)} \sim \left(\frac{P_H}{P_D}\right)\left(\frac{S_D^o}{S_H^o}\right)$$

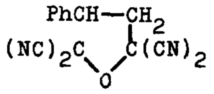
with the approximation valid for $P/S \ll 1$, guaranteed by experimental conditions.[7] The indicated ratios were measured mass spectrometrically at low ionizing voltage (12 and 14 eV for styrene and adduct, resp.). The isotope effect, k_H/k_D, at 125° at each of the vinylic positions is indicated below.



Because the experimental error in k_H/k_D is ±.01, the results show that all three positions exhibit the same inverse isotope effect. Our observations exclude a 2-step reaction where the second step is fast relative to the

$$S + TCNEO \xrightarrow{slow} I \xrightarrow{fast} P$$

first step. For in this case the first step, regardless of the precise nature of the intermediate (zwitterion, diradical) undoubtedly would be bonding at the β-position of styrene to give



and an inverse isotope at the α-position would not result.[8,9] The identity of isotope effects at the α- and β-positions indicates equality, or nearly so, of these C-H force constants in the activated complex and suggests that both C-C bonds have formed to comparable extents, i.e., a quite synchronous concerted process. The magnitude of the inverse isotope effects suggests the transition state is more reactant-like than product-like, a conclusion also made for the [4 + 2] Diels-Alder reaction.

Finally, it must be noted explicitly that our observed isotope effects do <u>not</u> exclude the 2-step sequence defended by Firestone[10] and which can be written

$$S + TCNEO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P$$

Let $S = PhCH = CH_2$, $S_\alpha = PhCD{=}CH_2$, $k_1^\alpha = k_1$ appropriate for S_α, etc. The measured isotope effect,

$$\left(\frac{P_H}{P_D}\right)\left(\frac{S_D^o}{S_H^o}\right)$$

for the above sequence is equivalent to the expression (for $PhCD{=}CH_2$),

$$\left(\frac{k_H}{k_D}\right)_\alpha = \frac{k_2k_1/(k_{-1} + k_2)}{k_2^\alpha k_1^\alpha/(k_{-1}^\alpha + k_2^\alpha)}$$

and a similar expression obtains for $PhCH{=}CHD$. For the α-deuteriostyrene, $k_1 = k_1^\alpha$, $k_{-1} = k_{-1}^\alpha$, but $k_2 < k_2^\alpha$. Assuming $k_{-1} \gg k_2$ - which Firestone has argued is responsible for the large negative activation entropy - one obtains

$$\left(\frac{k_H}{k_D}\right)_\alpha = \frac{k_2}{k_2^\alpha} < 1,$$

and an inverse isotope effect is expected at the α-position. For the β-deuteriostyrene $k_1 < k_1^\beta$, $k_{-1} > k_{-1}^\beta$, $k_2 = k_2^\beta$, and one obtains

$$\left(\frac{k_H}{k_D}\right)_\beta = \frac{k_1k_{-1}^\beta}{k_{-1}k_1^\beta} < 1.$$

Thus an inverse isotope effect is also expected at the β-position. However, it seems unlikely that this scheme would lead to identical, or nearly so, isotope effects at both positions.

Acknowledgement is made to the donors of the Petroleum Research Fund for partial support of this research. This work also was supported by National Science Foundation Grant GP-7939.

REFERENCES

1. NIH Predoctoral Fellow, 1967-9. Work done at the University of Connecticut; taken in part from the Ph.D. thesis of W. F. B., Univ. Conn., 1970.
2. W. J. Linn and R. E. Benson, J. Am. Chem. Soc., 87, 3657(1965).
3. D. E. van Sickle and J. O. Rodin, ibid., 86, 3091(1964).
4. S. Seltzer, ibid., 87, 1534(1965).
5. P. Brown and R. C. Cookson, Tetrahedron, 21, 1993(1965).
6. W. R. Dolbier, Jr., and S. H. Dai, J. Am. Chem. Soc., 90, 5028(1968).
7. The absolute error in k_H/k_D resulting from this approximation is estimated as 0.005, whereas the experimental error is 0.01.
8. cf. 2-Step free radical additions to olefins, e.g., M. Felć, A. P. Stefani, and M. Szwarc, J. Am. Chem. Soc., 84, 4451(1964); W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, ibid., 88, 1199(1966).
9. Presently there seems to be no adequate reference point for intermolecular secondary deuterium isotope effects in non-concerted cycloadditions where the second step occurs within a short time interval (several bond rotations) after initial bond formation. von Gustorf and coworkers (Tetrahedron Lett., 3113(1969)) have measured isotope effects in the thermal cycloaddition of dimethyl azodicarboxylate to vinyl ether and interpreted the isotope effect at the α-position ($k_H/k_D = 1.12$) in terms of a non-concerted [2 + 2] cycloaddition. However, the participation of one lone pair on nitrogen makes the azodicarboxylate similar in some ways to ketenes, whose cycloadditions to olefins are described as facile symmetry-allowed concerted thermal processes (R. B. Woodward and R. Hoffmann, Ang. Chem., Int. Ed., 8, 781(1969)). It is interesting that a similar isotope effect has been found for the α-position of styrene in its reaction with diphenylketene (J. E. Baldwin and J. A. Kapecki, J. Am. Chem. Soc., 91, 3106(1969)). Work in progress should give an unambiguous reference standard for intermolecular isotope effects in non-concerted cycloadditions.
10. R. A. Firestone, J. Org. Chem., 33, 2285(1968).