1-bromo-3-chloropropane, 1,2-dichlorobutane, 1,3-dichlorobutane, 1,2-dibromobutane, and 1,3-dibromobutane. 1,1-Dichloropropane, 1,2-chloropropane, 1,1-dichlorobutane, and 1,3-dibromo-3-methylbutane were obtained from the Chemical Samples Co. (Columbus, Ohio). 1,3-Diiodopropane was obtained from Fisher Scientific Co. 1-Chloro-3-iodopropane was prepared by the method of Henry.[8] 1-Bromo-3-chloro-2-methylpropane was prepared by the method of Asinger.[9] 1-Chloro-3-iodo-2-methylpropane and 3-chloro-1-iodobutane were also prepared by literature methods.[10,11] 3-Bromo-1-iodobutane was prepared as described in ref 8, starting with 1,3-dibromobutane. This preparation also yielded some 1,3-diiodobutane. 4-Chloro- and 4-iodo-2-methyl-2-butanal were prepared according to the procedure of Späth and Spitzy.[12] 4-Bromo-2-methyl-2-butanol (bp 57–60° (5 mm)) was prepared in 45% yield using methyl β-bromopropionate in the above procedure.[12]

Preparation of Ions and Their Nmr Studies. Solutions of ions in antimony pentafluoride–sulfur dioxide or fluorosulfuric acid–anti-

mony pentafluoride–sulfur dioxide solution were prepared as described previously.[2,3] Where low-temperature spectra were required, SO_2ClF was used instead of SO_2 as solvent.

Relative quantities of ions produced were determined by integration of the pmr spectra. The percentages quoted are averages of at least two experiments which generally showed good arrangement. Care was exercised to keep concentration of ions low to avoid complications of selective precipitation. Even so, solid material was sometimes observed to form at low temperature. This material was probably excess SbF_5–SO_2 complex crystallizing out. Solutions containing five-membered ring halonium ions were quenched in $NaOCH_3$–CH_3OH and the products were analyzed by vpc in order to confirm identification made on the basis of nmr spectra.

Ions not described in detail (pmr spectra) in this paper were already reported and characterized in our previous studies.

Nmr spectra were obtained on a Varian A-56-60A nmr spectrometer equipped with a variable-temperature probe. Chemical shifts are referred to external TMS.

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Secondary Deuterium Isotope Effects. The Transition State in the Reverse Diels–Alder Reaction of 9,10-Dihydro-9,10-ethanoanthracene.

A Potentially General Method for Experimentally Determining Transition-State Symmetry and Distinguishing Concerted from Stepwise Mechanisms[1]

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Abstract: Secondary α-deuterium isotope effects were studied in the reverse Diels–Alder reaction of 9,10-dihydro-9,10-ethanoanthracene, and its -*11,11-d₂* and -*11,11,12,12-d₄* derivatives, in an effort to determine the symmetry of the Diels–Alder transition state. The isotope effects of the d_2/d_0 adducts (k_2/k_0) and the d_4/d_0 adducts (k_4/k_0) in diphenyl ether solvent at 219.84 ± 0.015° were measured simultaneously with a ratio mass spectrometer. The isotope effects for each run were tested for their mechanistic significance. The possibility of having two different transition states for the dideuterated adduct, depending on whether protium or deuterium were next to the bond being broken, was taken into consideration. For the concerted, symmetrical transition state, $(k_2/k_0)^2 - (k_4/k_0) \equiv x = 0$; for a stepwise transition state, $x = (1 - k_2/k_0)^2 \equiv y$. The average isotope effect at 219.84 ± 0.015° for $k_2/k_0 = 0.924 ± 0.005$, and the average isotope effect for $k_4/k_0 = 0.852 ± 0.007$. The difference between the mechanistic extremes was 0.6%. The most positive mean value of the mechanistic index, x/y, was determined to be 0.043, indicating a transition state displaced only 4.3% from the concerted extreme. Therefore, it is concluded that the mechanism is concerted, with a symmetrical or nearly symmetrical transition state. This conclusion is *independent* of the absolute values of the observed isotope effects; it depends only on a comparison of k_4/k_0 and $(k_2/k_0)^2$. The only assumptions involved in this conclusion are: (1) that a "rule of the geometric mean" type assumption is valid in comparison of reactant and transition state; (2) that $f_A \neq f_B$ (where f_A is the isotope effect at bond C_9–C_{12} and f_B is the isotope effect at bond C_{10}–C_{11}) unless the mechanism is concerted; (3) that the mean value of x/y has significance within the experimental scatter of the data. These are the only assumptions required, and each of them is believed to be valid, (1) and (2) to a high degree of precision, and (3) to precision indicated by the statistical analysis.

The symmetry of the Diels–Alder transition state is still uncertain.[2] Theoretical[3a] and experimental[3b] evidence seems to indicate that in most reactions a con-

certed transition state is preferred. It is also uncertain just how much higher in energy the free-radical transi-

(1) (a) Previous paper: E. D. Kaplan and E. R. Thornton, *J. Amer. Chem. Soc.*, 89, 6644 (1967); (b) supported in part by the Petroleum

tion state lies in a given reaction. The fact that a free-radical transition state is accessible in certain reactions has been shown experimentally. In thermal reactions, the free-radical transition state leads to 1,2-addition instead of the Diels–Alder products;[4] in photochemical reactions, the Diels–Alder as well as the 1,2 addition products are formed.[5]

The transition-state structure has been studied by observing the rate effect of added substituents.[6]

The relative rates of reaction of isoprene with ethylene, acrolein, and maleic anhydride indicated a transition state where one bond is much more fully formed than the other with overlap at both 1 and 4 positions. The result was not surprising for an asymmetric addend (acrolein).

A relatively good correlation was noted between the para localization energy of anthracene and five derivatives (four symmetric, one asymmetric) and their rate of addition as Diels–Alder dienes. The correlation would be expected if both para carbons were removed from the delocalized electron system of the aromatic hydrocarbons in the transition state; i.e., the transition state would be concerted and probably symmetrical. The correlation with localization energy at just one position (a model for the stepwise mechanism) was much poorer.

The conclusion, of course, is approximate since neither the para localization energy nor the localization energy plots gives a perfect straight line. Dibenz-[a,c]anthracene fits neither plot, which might be indicative of a perturbed potential energy surface in the monobenzo and dibenzo derivatives of anthracene. It is difficult to estimate how much perturbation might also account for noncorrelation in the localization energy vs. rate profile.

The study of kinetic isotope effects circumvents the problem of an altered potential energy surface.[7] The cumulative nature of isotope effects provides a useful mechanistic tool.[8] However, kinetic isotope effects

have the disadvantage of producing small rate effects, especially in the case of secondary deuterium isotope effects.

Isotope effects in the Diels–Alder reaction have been studied to determine the nature of the bond-forming processes.[9] It has, however, been difficult to interpret the value of the absolute magnitude of the isotope effect.

The retrodiene decomposition of the adduct of 2-methylfuran and maleic anhydride **1**[10] with deuterium in either the 5 or 6 position gives an isotope effect of

1
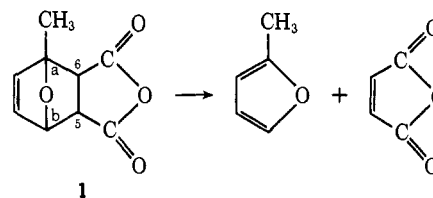
1.08 ± 0.01; deuterium in both the 5 and 6 positions gives an isotope effect of 1.16 ± 0.01. The ratio of the *5-d* adduct to the *6-d* adduct remained constant (1.00 ± 0.04) during the reaction, yet the effect of deuterium substitution in the methyl group was only 1% per D. These elegant experiments indicate that the mechanism is concerted, as opposed to stepwise with bonds a and b broken the first half or nearly half the time, since the isotope effect at methyl should be considerably larger than observed if bond a were being broken in a slow step as much as half the time. However, if two transition states (stepwise, or concerted but unsymmetrical) were of nearly equal energy (not unlikely for **1**, since both should be reactant-like and the two differ only in the position of methyl substitution at bonds already stabilized for cleavage by the oxygen atom and the double bond of the furan moiety), and if the isotope effects for deuterium substitution at positions 5 and/or 6 were slightly stronger for that transition state which was attained more slowly (not unlikely, since the transition state attained more slowly might be expected to be more product-like), then the observed ratio of 1.00 could be observed. Though the effect of deuterium substitution in the methyl group "indicates" a nonstepwise mechanism, this argument does not distinguish concerted mechanisms having various degrees of inequality of bond breaking of bonds a and b in the transition states from a mechanism with equal amounts of bond breaking. Further, the methyl argument depends upon the absolute magnitude of the isotope effect ("small"), and therefore is dependent on the goodness of the model—a stepwise mechanism might be consistent with the observed isotope effect, given the reactant-like nature of the transition state and the possibility that, as bond a breaks, the interaction of the developing radical with the oxygen atom and double bond may drastically reduce the hyperconjugative interaction with the methyl group.

Primary isotope effects have been measured in the reverse Diels–Alder reaction of the adduct of α-pyrone

Taagepera, Ph.D. Dissertation in chemistry, University of Pennsylvania, 1970.

(2) For recent reviews of the Diels–Alder reaction mechanism, see: (a) A. Wasserman, "Diels–Alder Reaction," Elsevier, New York, N. Y., 1965, Chapters 4 and 5; (b) J. Sauer, Angew. Chem., Int. Ed. Engl., 6, 16 (1967); (c) H. Kwart and K. King, Chem. Rev., 68, 415 (1968).

(3) (a) M. G. Evans, Trans. Faraday Soc., 35, 824 (1939); R. Hoffmann and R. B. Woodward, J. Amer. Chem. Soc., 87, 2046 (1965); L. Salem, ibid., 90, 543 (1968); C. Trindle, ibid., 92, 3251, 3255 (1970); (b) R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959); J. A. Berson and A. Remanick, J. Amer. Chem. Soc., 83, 4947 (1961); S. W. Benson and J. A. Berson, ibid., 84, 152 (1962); S. W. Benson and J. A. Berson, ibid., 86, 259 (1964); R. A. Grieger and C. A. Eckert, ibid., 92, 2918 (1970); J. B. Lambert and J. D. Roberts, Tetrahedron Lett., 1457 (1965); C. Ganter, U. Scheideggar, and J. D. Roberts, J. Amer. Chem. Soc., 87, 2771 (1965).

(4) P. D. Bartlett, Science, 159, 833 (1968); R. Wheland and P. D. Bartlett, J. Amer. Chem. Soc., 92, 3824 (1970); see, however, S. W. Benson, J. Chem. Phys., 46, 4920 (1967), for a Diels–Alder product from a stepwise mechanism.

(5) J. P. Simons, Trans. Faraday Soc., 56, 391 (1960); N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, Chapter 8; W. L. Dilling and J. C. Little, J. Amer. Chem. Soc., 89, 2741 (1967); W. L. Dilling, ibid., 89, 2742 (1967); R. K. Murray and H. Hart, Tetrahedron Lett., 4995 (1968); H. Kato and R. Noyori, Tetrahedron, 25, 1661 (1969).

(6) M. J. S. Dewar and R. S. Pyron, J. Amer. Chem. Soc., 92, 3098 (1970).

(7) For reviews of kinetic isotope effects, see: (a) J. Biegeleisen and M. Wolfsberg, Advan. Chem. Phys., 1, 40 (1958); (b) E. A. Halevi, Progr. Phys. Org. Chem., 1, 109 (1963); (c) E. R. Thornton, Annu. Rev. Phys. Chem., 17, 349 (1966); (d) E. K. Thornton and E. R. Thornton in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand Reinhold, New York, N. Y., 1970, Chapter 4.

(8) V. J. Shiner, Jr., B. L. Murr, and C. Heinemann, J. Amer. Chem.

Soc., 85, 2413 (1963); E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press, New York, N. Y., 1964, p 209; V. J. Shiner, Jr., and J. G. Jewett, J. Amer. Chem. Soc., 87, 1382, 1383 (1965).

(9) (a) D. E. Van Sickle, Tetrahedron Lett., 687 (1961); (b) D. E. Van Sickle and J. O. Rodin, J. Amer. Chem. Soc, 86, 3091 (1964); (c) P. Brown and H. C. Cookson, Tetrahedron, 21, 1993 (1965).

(10) S. Seltzer, J. Amer. Chem. Soc., 87, 1534 (1965); 85, 1360 (1963); Tetrahedron Lett., 457 (1962).

and maleic anhydride,[11] eq 1. The bridge oxygen isotope effect was $k_{16}/k_{18} = 1.014 \pm 0.002$, and the bridge carbon isotope effect was $k_{12}/k_{13} = 1.013 \pm 0.002$.

$$+ CO_2 \qquad (1)$$
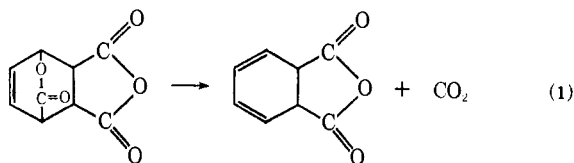
From extensive calculations for various model transition states, the results indicate that there is substantial C–C cleavage and much less C–O cleavage. This conclusion is dependent on the absolute values of the isotope effects by way of the reasonableness of the spectrum of transition-state force constant models for which calculations were made.

We have tried to circumvent the ambiguities of having two different isoenergetic transition states and of interpreting absolute values of isotope effects by taking into consideration the possibility of actually having two different transition states and by working with relative isotope effects.[7d]

The rate constants for the retro-Diels–Alder reaction of 9,10-dihydro-9,10-ethanoanthracene (2) (k_0) and its bridge deuterated analogs, CH_2CD_2 (k_2) and CD_2CD_2 (k_4), were determined. In a symmetrical concerted

2
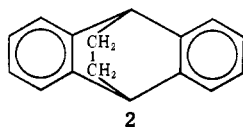
mechanism, bonds A and B in eq 2 (L = H or D) will

$$\overset{A}{---}CL_2\overset{B}{---}CL_2\overset{}{---} \qquad (2)$$
$$f_A \qquad\qquad f_B$$

be equally broken in the transition state and the isotope effect $f_A = f_B$. In a stepwise mechanism only one bond will be partly broken and $f_A \neq f_B$. The dideuterated adduct could decompose by two different pathways (unless the transition state were *perfectly symmetrical*), depending on whether deuterium were adjacent to bond A or bond B. The rate constant for one pathway would be $f_A k_0/2$, and $f_B k_0/2$ for the other, since for k_0 (with no deuterium) the rate is the same no matter which bond is labeled A, i.e., the rate for each "separate" pathway for the undeuterated adduct is $k_0/2$. Therefore, k_2 would be the sum of the two pathways, eq 3. Equation 3 is valid whether the mechanism is

$$k_2 = k_0(f_A + f_B)/2 \qquad (3)$$

concerted or stepwise, including the case of a perfectly symmetrical transition state wherein $f_A = f_B = f$, so that $k_2 = k_0 f$. The rate constant k_4 is subject to both f_A and f_B, and these should be almost precisely multiplicative, i.e., conform to the rule of the geometric mean (RGM);[12,13] k_4 is given by

$$k_4 = f_A f_B k_0 \qquad (4)$$

Solving eq 3 and eq 4 simultaneously leads to eq 5.

$$f_A, f_B = \frac{k_2}{k_0} \pm \left[\left(\frac{k_2}{k_0}\right)^2 - \frac{k_4}{k_0}\right]^{1/2} \qquad (5)$$

In the case of a symmetrical, concerted mechanism f_A and f_B would be exactly equal (to k_2/k_0). Therefore, $(k_2/k_0)^2$ would have to equal k_4/k_0. In the stepwise mechanism, where there is no isotope effect f_B when bond A is being broken ($f_B = 1$)

$$k_4/k_0 = 2k_2/k_0 - 1 \qquad (6)$$

Any intermediate value would indicate an asymmetrical, concerted mechanism, and the values of f_A and f_B could be calculated from eq 5.

Experimental Section

All melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Microanalyses were performed by Micro-Analysis, Inc., Wilmington, Del. Nmr spectra were run on Varian spectrometer A-60 in CCl_4 and C_6D_6 solution with an internal standard of tetramethylsilane. Vapor-phase chromatography was done on a Perkin-Elmer Flame Ionization Gas Chromatograph Model 226, using a Golay column of poly-(propylene glycol) UCON-Oil LB-550-X, on Chromosorb W. Ultraviolet spectra were taken on Perkin-Elmer Model 202 and Cary 16 spectrophotometers.

All isotope ratio measurements were made on a Nuclide Model 6-60-RMS-2 isotope ratio mass spectrometer (Nuclide Associates, State College, Pa.). The standard glass inlet system was modified to a stainless steel inlet system equipped with Varian valves. Pressure in the inlet system was adjusted by a set of stainless steel bellows (Robertshaw Controls Co.). The source was provided with a temperature regulator. The double collector system was equipped with external micrometers which permitted a bilaterally adjustable ion beam entry gap.

9,10-Dihydro-9,10-ethanoanthracene. The procedure of Thomas[14] was modified. Anthracene (Baker Chemical Co., mp 216–218°, 100 g, 0.561 mol) in 100 ml of toluene was placed into a reaction vessel. The reaction vessel was secured in a high-pressure bomb (Aminco No. 40-14450) and purged with 13 atm of ethylene (Matheson Co., 99% purity) for 5 min. Ethylene (50 atm) was introduced into the bomb and the shaking mechanism started. The bomb was heated to 244° in 3 hr and kept at this temperature for 8 hr. The pressure in the bomb reached a maximum of 126 atm at 228° after 2 hr 15 min and dropped to 116 atm after 8 hr of heating. The bomb was cooled and the excess ethylene bled. The crystallized crude product was recovered from the reddish brown solution. The adduct was recrystallized from toluene and twice from 95% ethanol in 78% yield. A part of the crude product was recrystallized to constant mp 143.4–144.0° (lit.[14] 143.5–144.0°).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.10; H, 6.90.

The uv spectrum, in 95% ethanol run on a Cary 16 manual spectrophotometer, showed maxima at: 253.0 nm$_{\text{infl}}$ (log ϵ 2.80), 259.0 nm$_{\text{infl}}$ (log ϵ 2.94), 265.0 nm (log ϵ 3.16), 271.8 nm (log ϵ 3.25) (lit.[15] 253.0 nm$_{\text{infl}}$ (log ϵ 2.70)), 259.0 nm$_{\text{infl}}$ (log ϵ 2.87), 265.5 nm (log ϵ 3.12), 272.5 nm (log ϵ 3.23). The nmr spectrum in CCl_4 gave a triplet of the bridge protons centered at 1.67 ppm ($J_{\text{app}} = 1.7$ Hz), a quintet of the bridgehead protons centered at 4.23 ppm ($J_{\text{app}} = 1.5$ Hz), and a multiplet of phenyl protons centered at 7.09, with a ratio of protons 1.97:1.00:4.05, respectively (lit.[16] in $CDCl_3$ triplet at 1.77 ppm; quintet at 4.29 ppm).

9,10-Dihydro-9,10-ethanoanthracene-*11,11-d₂* and 9,10-Dihydro-9,10-ethanoanthracene-*11,11,12,12-d₄*. The best conditions for microscale preparation were determined by the use of undeuterated ethylene. Anthracene (1.56 g, 8.7 mmol) was weighed into the 4.5-ml platinum liner of a 5-ml pressure bomb (Tem-Pres Research Inc.), and 1 ml of toluene was injected into the liner with a syringe. The liner was placed inside the pressure vessel, attached to a vacuum

(11) M. J. Goldstein and G. L. Thayer, *J. Amer. Chem. Soc.*, **87**, 1933 (1965).

(12) J. Bigeleisen, *J. Chem. Phys.*, **23**, 2264 (1955); J. Bigeleisen, *ibid.*, **28**, 694 (1958); J. Bigeleisen and T. Ishida, *ibid.*, **48**, 1311 (1968).

(13) The assumption is RGM-like and reduces to the RGM only when the transition state is symmetrical. If the transition state were concerted but unsymmetrical, the multiplicativity assumption should be

as valid as if it were symmetrical (maybe *more* so, because symmetry tends to give greater coupling). If the transition state were at the stepwise extreme with f_A or $f_B = 1.000$, no assumption at all is required.

(14) C. L. Thomas, U. S. Patent 2,406,645 (1946).

(15) H. Birnbaum and R. C. Cookson, *J. Chem. Soc.*, 1224 (1961).

(16) S. J. Cristol, *J. Org. Chem.*, **31**, 581 (1966).

line, and degassed twice. Ethylene (0.28 ml, 11 mmol) was measured into the vacuum line from a take-off tube and stored in a U-tube under liquid nitrogen. The pressure vessel was checked for leaks with soap solution before the introduction of ethylene. The ethylene was introduced and kept under liquid nitrogen. To complete the transfer of ethylene, the reaction vessel was closed and warmed up to allow the ethylene to dissolve in toluene. The reaction vessel was again cooled with liquid nitrogen and the remaining ethylene transferred. The reaction vessel was closed off (allowed to come to room temperature and again checked for leaks), placed into a preheated 240° furnace, heated from 8 to 12 hr, cooled, and placed back on the vacuum line to recover the excess ethylene. The product was obtained by taking the reaction mixture up in excess toluene. No color formation was observed as was the case in the large scale reaction when the pressure bomb was not completely free of air. The crude product was further recrystallized to a constant melting point in 95% ethanol.

(a) 9,10-Dihydro-9,10-ethanoanthracene-*11,11,12,12-d₄* was prepared from ethylene-*1,1,2,2-d₄* (Merck Sharp and Dohme of Canada, 99% min isotope purity), repeating the described procedure four times, crude yield 70%. Most of the crude product was recrystallized to constant mp 143.5-144.0°. The uv spectrum in 95% ethanol showed maxima at 253.0 nm (log ϵ 4.07); this includes anthracene impurity (<0.5%) which was not present in the pure sample used for uv kinetics, 259.0 nm$_{infl}$ (log ϵ 2.95), 265.0 nm (log ϵ 3.14), 271.8 nm (log ϵ 3.23). The nmr spectrum in CCl₄ showed no bridge protons (detectable to a 5% level), a singlet of bridgehead protons centered at 4.23 ppm, and a multiplet of phenyl protons centered at 7.08 ppm in the ratio of 1.00:3.92, respectively.

(b) 9,10-Dihydro-9,10-ethanoanthracene-*11,11-d₂* was prepared from ethylene-*1,1-d₂* (Merck Sharp and Dohme of Canada, 98% min isotopic purity), repeating the described procedure five times, yield 92%. Most of the crude product was recrystallized to 143.5-144.0°. The uv spectrum in 95% ethanol showed maxima at 253 nm$_{infl}$ (log ϵ 2.83), 259 nm$_{infl}$ (log ϵ 2.94), 265.0 nm (log ϵ 3.15), 271.8 nm (log ϵ 3.24). The nmr in CCl₄ showed a doublet of the bridge protons (with further fine splitting by the opposite bridgehead proton) centered at 1.68 ppm, a triplet of the bridgehead protons (with further fine splitting by the opposite bridge protons) centered at 4.23 ppm, and the phenyl protons in a multiplet centered at 7.10 ppm in a ratio of 1.00:1.01:4.03, respectively. [The high value for the phenyl protons comes from a benzene contamination. C₆D₆ (containing C₆HD₅ impurity) was used as a solvent for a previous nmr spectrum, evaporated and replaced with CCl₄.]

Uv Kinetics. A Perkin-Elmer 202 and a Cary 16 spectrophotometer were calibrated at 357 and 356.5 nm, respectively, by plotting log (I/I_0) vs. anthracene (zone-refined, from J. Hinton, Valparaiso, Fla.) concentrations of standard solutions. The correspondence was linear.

The rate of the 9,10-dihydro-9,10-ethanoanthracene decomposition was determined by measuring the anthracene produced. 9,10-Dihydro-9,10-ethanoanthracene (0.00206 g, 0.010 mmol) in 5 ml of diphenyl ether (J. T. Baker Chemical Co., Baker grade, <1 ppm impurities as checked on the Perkin-Elmer gas chromatograph) was placed into a constricted tube. The reaction tubes were placed on a manifold and degassed three times to 0.001 mm and sealed on the manifold. The sealed tubes were heated at 278 ± 2° in an acenaphthene vapor bath, at 241 ± 2° in a β-methylnaphthalene vapor bath, and at 228.95 ± 0.015° in a "Hitec" constant temperature bath calibrated with a National Bureau of Standards certified platinum resistance thermometer. The sealed tubes were removed from the bath, placed in ice water to quench the reaction, and opened, and the contents placed into 100-ml volumetric flasks and filled with absolute alcohol. The anthracene concentration was determined. The reaction followed good first-order kinetics.

The above procedure was also followed to determine the rate of the 9,10-dihydro-9,10-ethanoanthracene-*11,11,12,12-d₄* decomposition.

Mass Spectrometer Kinetics. A standard solution was prepared by dissolving 9,10-dihydro-9,10-ethanoanthracene (4.0 g, 0.019 mol), 9,10-dihydro-9,10-ethanoanthracene-*11,11-d₂* (1.7 g, 0.008 mol), and 9,10-dihydro-9,10-ethanoanthracene-*11,11,12,12-d₄* (0.3 g, 0.0015 mol) in 15 ml of diphenyl ether. One-twentieth of this standard solution was weighed out for the 100% reaction and added to 15 ml of diphenyl ether. The samples were placed into constricted tubes and degassed three times on a manifold equipped with a mercury diffusion pump to ca. 4 × 10⁻⁴ mm, and the tubes were sealed. The 3% reaction was carried out in the 219.84 ± 0.015° constant temperature bath and the 100% reaction in the 278° acenaphthene

vapor bath to 16 half-lives. The sealed tubes were placed into the mass spectrometer inlet tubes, which were provided with a straight-bore stopcock. After the inlet system was evacuated to 0.015 mm, the capillary seal of the sealed tube was broken by turning the stopcock and the ethylene was directly transferred into the mass spectrometer. The ethylene was frozen out in the collector with liquid nitrogen, and the inlet system was degassed.

Mass Spectrometer Conditions. The ratio measurements were taken at 15-eV ionization potential, 0.2-mA trap current, 4.4-A filament current, 1.7-mA emission current, 3000-eV accelerating voltage, and at 220° source temperature. The air background was checked before injection and during a run by freezing out the sample with liquid nitrogen. The air background was negligible. The decade dividers were switched and no differences in the ratio readings were detected.

Kinetic Data. Uv. The rate constants of the retro-Diels–Alder reaction of 9,10-dihydro-9,10-ethanoanthracene are the following: at 278°, $k = 7.11 \times 10^{-5}$ sec⁻¹; at 241°, $k = 3.20 \times 10^{-6}$ sec⁻¹, and at 228.95°, $k = 1.18 \times 10^{-6}$ sec⁻¹. From these rate constants the kinetic parameters of the reaction were calculated: $\Delta H^{\pm} = 49.1$ kcal/mol and $\Delta S^{\pm} = 12$ eu. An isotope effect, $k_0/k_4 = 1.205$, was determined for the undeuterated vs. the tetradeuterated adduct. Higher precision than that obtainable on the uv was needed to differentiate between the models proposed for the stepwise ($k_0/k_2 = 1.093$) and the concerted ($k_0/k_2 = 1.098$) mechanism.

Kinetic Data. Ratio Mass Spectrometer. The isotope effects were calculated by obtaining the ratios of the tetradeuterated, dideuterated, and undeuterated ethylene at ca. 3% reaction, and correcting these ratios for the initial starting ratios of adducts, which are equivalent to the ratios of ethylenes at 100% reaction. At small conversions

$$k_D/k_H = (d^H/d^D)(p^D/p^H) \tag{7}$$

where d^H/d^D is the 100% molar ratio of the isotopically substituted ethylenes and p^D/p^H is the molar product ratio.[17] Corrections for a known per cent reaction on the isotope effect can be made by applying the Biegeleisen–Wolfsberg equation[7a] (i in Table I). In addition to peaks at m/e 28 for ethylene, m/e 30 for dideuterioethylene, and m/e 32 for tetradeuterioethylene, peaks were observed at m/e 29 [the (M + 1) peak of ethylene and (M − 1) peak of dideuterioethylene] and at m/e 31 [the (M + 1) peak of dideuterioethylene]. It was not possible to correct for these satisfactorily; therefore, two ratios of ratios were taken for k_2/k_0 (30/29 × 29/28) and four ratios for k_4/k_0 (32/31 × 31/30 × 30/29 × 29/28). The mass spectrometer was regulated so as to obtain maximum sensitivity for ratio measurements while minimizing fragmentation contributions: (M − 4) of m/e 32, and (M − 2) of m/e 30 to m/e 28 and (M − 2) of m/e 32 to m/e 30. Corrections for the fragmentation contributions were made (g in Table I); decade divider readings of the ratio mass spectrometer and the calculated isotope effects are presented in Table I. A possible fragmentation contribution from the trideuterioethylene and monodeuterioethylene (both ∼2% in the reaction mixture) is negligible; i.e. < 0.01%.

Discussion

The reaction parameters of the dissociation of 2 are similar to those observed previously for retro-Diels–Alder reactions.[9c,18,19] The transition state is of high activation energy, there is considerable bond rupture, but the $\Delta S^{\pm}$ of 12 eu is only ca. one-third of the total ΔS° for the reaction; i.e., the transition state is structurally reactant-like.

The k_0/k_4 isotope effect, determined by both uv and the average of the mass spectrometric runs, of 1.08 at 50° can be compared to previously determined α-deuterium isotope effects for the Diels–Alder reaction as shown in Table II.

The isotope effect for the Diels–Alder reaction is much smaller than that observed in solvolysis reactions

(17) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, 1960, Chapter 2.
(18) Reference 2a, p 63.
(19) Reference 2c, p 436.

Table I. Isotope Effects from Mass Spectrometer Decade Divider Ratios

Run #	% Reaction (x)	29/28 x%	29/28 100%	29/30 x%	29/30 100%	31/30 x%	31/30 100%	31/32 x%	31/32 100%	30/28 x%	30/28 100%	32/28 x%	32/28 100%	29/28	29/30	31/30	31/32	30/28 (k₂/k₀)	32/28 (k₄/k₀)
1ᵃ	3.0ᶜ	0.878701ᶠ0.902111		0.290388 0.273138		0.156421 0.161807		0.345061 0.328939		0.302470 0.330115		0.137016 0.162106		0.974050	1.063155	0.966713	1.049012	0.9163	0.8452
		0.878086 0.901340		0.290329 0.273088		0.156465 0.161788		0.346679 0.329576		0.304633ᵍ0.333133		0.140356 0.166626		0.974201	1.063133	0.967099	1.051894	0.9145ᵍ	0.8423
				0.290503 0.273240		0.156900 0.161644		0.345339 0.329630							1.063179	0.970652	1.047656	0.9132ⁱ	0.8403
		Av 0.878394 0.901726		0.290407 0.273155		0.156595 0.161746		0.345693 0.329382						0.974201	1.063156	0.968155	1.049521		
														±0.000107ʰ±0.000023	±0.002171	±0.002233			
1ᵇ		0.893631 0.921038		0.315550 0.299341		0.156364 0.161337		0.353247 0.337247		0.283955 0.308489		0.125263 0.147334		0.970243	1.054149	0.967317	1.047443	0.9205	0.8502
		0.899534 0.926875		0.315945 0.299681		0.156277 0.161497		0.354877 0.338785		0.285598 0.310776		0.128085 0.151107		0.970502	1.054271	0.967677	1.047499	0.9190	0.8477
									0.353933 0.337899							1.054210	0.967497	1.047452	0.9178	0.8456
		Av 0.896582 0.923957		0.315748 0.299511		0.156171 0.161417		0.354019 0.337977						0.970372	1.054210	0.967497	1.047465		
														±0.000183	±0.000086	±0.000255	±0.000030		
2ᵃ	3.17ᵈ	0.932650 0.964250		0.328304 0.313462		0.158640 0.164824		0.355934 0.340251		0.283769 0.307419		0.126405 0.148925		0.967228	1.047349	0.962481	1.046092	0.9231	0.8488
		0.931510 0.963750		0.328407 0.313482		0.158607 0.164774		0.356057 0.340097		0.285393 0.309655		0.129265 0.152756		0.966547	1.047610	0.962573	1.046928	0.9217	0.8462
				0.328681 0.313793		0.158584 0.164709		0.356209 0.340028							1.047445	0.962813	1.047587	0.9205	0.8441
		Av 0.932080 0.964000		0.328464 0.313579		0.158610 0.164769		0.356067 0.340125						0.966888	1.047468	0.962622	1.046869		
														±0.000481	±0.000132	±0.000171	±0.000749		
2ᵇ		0.934990 0.965830		0.330968 0.314265		0.157275 0.163478		0.365437 0.347722		0.282822 0.307698		0.122593 0.145610		0.968069	1.053149	0.962056	1.050946	0.9192	0.8420
		0.937945 0.968420		0.331104 0.314354		0.157271 0.163455		0.365615 0.347572		0.284457 0.309974		0.125318 0.149310		0.968067	1.053284	0.962167	1.051912	0.9177	0.8393
									0.357430 0.341009							1.053217	0.962111	1.048154	0.9164	0.8371
		Av 0.936243 0.967215		0.331036 0.314310		0.157273 0.163467		0.362827 0.345434						0.968068	1.053217	0.962111	1.050337		
														±0.000001	±0.000095	±0.000078	±0.001952		
3	3.13ᵉ	0.887445 0.925949		0.309218 0.297988		0.157936 0.163577		0.349358 0.335858		0.289642 0.313640		0.130895 0.152947		0.958417	1.037686	0.965515	1.040196	0.9235	0.8558
		0.889726 0.929001		0.306875 0.295683		0.157704 0.163837		0.349029 0.335465		0.291416 0.316130		0.133943 0.156078		0.957723	1.037851	0.962566	1.040433	0.9218	0.8533
		0.896482 0.934930		0.306994 0.295847				0.349274 0.335788						0.958876	1.037678		1.040162	0.9207	0.8512
		0.891218 0.929960		0.307696 0.296506		0.157820 0.163707		0.349220 0.335704						0.958339	1.037738	0.964041	1.040263		
														±0.000581	±0.000098	±0.002085	±0.000148		
4ᵃ	3.05	0.955088 0.982813		0.322919 0.309480		0.155341 0.160752		0.348301 0.334876		0.297224 0.319795		0.132671 0.153488		0.971790	1.043424	0.966339	1.040089	0.9294	0.8644
		0.961250 0.991188		0.322659 0.309268		0.155396 0.160720		0.348050 0.334904		0.299693 0.322988		0.137127 0.159208		0.969796	1.043299	0.966874	1.039253	0.9279	0.8613
		0.961170 0.991670		0.322650 0.309125				0.347872 0.334910						0.969244	1.043753		1.038703	0.9268	0.8594
		0.959562 0.990712												0.968558					
		Av 0.959268 0.989096		0.322743 0.309291		0.155369 0.160736		0.348074 0.334897						0.969847	1.043492	0.966607	1.039348		
														±0.001390	±0.000234	±0.000378	±0.000698		
4ᵇ		0.973125 1.002534		0.332351 0.317530		0.156945 0.162279		0.350669 0.337291		0.293497 0.316479		0.131313 0.152158		0.970665	1.046676	0.967131	1.039663	0.9274	0.8630
		0.974818 1.004636		0.332021 0.317196		0.156924 0.162206		0.350602 0.337412		0.295802 0.319509		0.135670 0.157772		0.970320	1.046738	0.967436	1.039092	0.9258	0.8599
		0.975500 1.004663		0.331700 0.316942		0.156900 0.162148		0.350942 0.337462						0.970972	1.046564	0.967635	1.039945	0.9247	0.8580
		Av 0.974481 1.003944		0.332024 0.317223		0.156923 0.162211		0.350738 0.337388						0.970652	1.046659	0.967339	1.039567		
														±0.000326	±0.000088	±0.000265	±0.000435		
5ᵃ	3.21	0.963382 0.992525		0.330471 0.312865		0.157459 0.162876		0.351352 0.335666		0.293382 0.319736		0.131695 0.155138		0.970638	1.056273	0.966742	1.046731	0.9188	0.8489
		0.972547 1.002237		0.330014 0.312464		0.157467 0.162860		0.351283 0.335683		0.296177 0.322979		0.135935 0.160760		0.970672	1.056166	0.966886	1.046472	0.9170	0.8456
		0.972190 1.002010		0.330009 0.312419		0.157475 0.162833		0.351159 0.335576						0.970240	1.056303	0.967095	1.046437	0.9157	0.8434
		0.971631												0.970376					
		Av 0.699938 1.000988		0.330165 0.312583		0.157467 0.162856		0.351265 0.335642						0.970482	1.056247	0.966908	1.046547		
														±0.000208	±0.000072	±0.000178	±0.000161		
5ᵇ		0.975563 1.004300		0.329998 0.315537		0.157854 0.163183		0.360020 0.344380		0.295328 0.317960		0.131713 0.153307		0.971386	1.045830	0.967343	1.045415	0.9288	0.8591
		0.973950 1.002988		0.329824 0.315434		0.157567 0.163018		0.350756 0.335385		0.297813 0.321145		0.135969 0.158817		0.971049	1.045620	0.967175	1.045831	0.9273	0.8561
		0.973440 1.002070						0.157906 0.163224		0.350743 0.335308				0.971429		0.967419	1.046032	0.9262	0.8541
		Av 0.974318 1.003119		0.329911 0.315486		0.157809 0.163142		0.353840 0.338358						0.971288	1.045725	0.967312	1.045759		
														±0.000208	±0.000148	±0.000125	±0.000315		
6ᵃ	3.30	0.975400 1.002283		0.328661 0.315210		0.158027 0.163019		0.351578 0.336280		0.296427 0.317779		0.133174 0.154041		0.973178	1.042673	0.969378	1.045492	0.9328	0.8645
		0.975038 1.002375		0.328572 0.315074		0.157983 0.163014		0.351770 0.336356		0.299932 0.320934		0.137505 0.159585		0.972728	1.042841	0.969138	1.045826	0.9314	0.8616
		0.971612 0.999337		0.328523 0.315027		0.158035 0.163058		0.351808 0.336337						0.972257	1.042842	0.969195	1.045988	0.9303	0.8596
		Av 0.974017 1.001332		0.328585 0.315104		0.158015 0.163030		0.351719 0.336324						0.972721	1.042785	0.969237	1.045772		
														±0.000461	±0.000097	±0.000125	±0.000259		
6ᵇ		0.969404 0.997222		0.328870 0.315795		0.157625 0.162533		0.350390 0.335340		0.294882 0.315948		0.132603 0.153093		0.972105	1.041403	0.969803	1.044880	0.9333	0.8662
		0.970167 0.997840		0.328850 0.315680		0.157602 0.162556		0.350308 0.335352		0.297319 0.319021		0.136893 0.158570		0.972267	1.041719	0.969524	1.044598	0.9320	0.8633
				0.328898 0.315704				0.350810 0.335670							1.041792		1.045104	0.9309	0.8613
		Av 0.969786 0.997531		0.328873 0.315726		0.157614 0.162545		0.350503 0.335454						0.972186	1.041638	0.969664	1.044861		
														±0.000256	±0.000207	±0.000197	±0.000253		
7	3.30	1.063590 1.101570		0.360546 0.344312		0.155518 0.161164		0.354112 0.339384		0.294991 0.319771		0.129354 0.151661		0.965522	1.047149	0.964967	1.043396	0.9225	0.8529
		1.062300 1.099430		0.360137 0.343993		0.155034 0.160689		0.354355 0.339510		0.297528 0.323103		0.133502 0.157108		0.966283	1.046931	0.964808	1.043725	0.9209	0.8498
									0.353850 0.339030									1.043713	0.9196	0.8475
		1.062975 1.100500		0.360342 0.344153		0.155276 0.160927		0.354106 0.339308						0.965902	1.047040	0.964887	1.043611		
														±0.000537	±0.000184	±0.000113	±0.000187		

ᵃ Mass spectrometer readings on day 1. ᵇ Mass spectrometer readings on day 2. ᶜ Temperature of constant temperature bath varied from 203° to 217°, reaction time is estimated. ᵈ Temperature at 207.5 ± 0.015°. ᵉ Temperature at 219.84 ± 0.015° for this and all the rest of the runs. ᶠ The ratio 29/28 was read to ±0.002%, 29/30 to ±0.002%, 31/30 to ±0.004%, and 31/32 to ±0.004%. One reading consisted of 4–5 sets of traces; the instrument was refocussed and the zero checked for the next reading. ᵍ Corrected for fragmentation contribution according to

$$k_0/k_2 = \frac{\dfrac{28}{30}\left[\dfrac{1 - f(30/28) - (k - fh)(32/28)}{1 - h(32/30)}\right]_{2\%}}{\dfrac{28}{30}\left[\dfrac{1 - f(30/28) - (k - fh)(32/28)}{1 - h(32/30)}\right]_{100\%}} \quad ; \quad k_0/k_4 = \frac{[(28/32) - f(30/32) - k - fh]_{2\%}}{[(28/32) - f(30/32) - k - fh]_{100\%}}$$

where $f = [(M - 2) \text{ of } 30]/30$; $h = [(M - 2) \text{ of } 32]/32$, and $k = [(M - 4) \text{ of } 32]/32$. For runs 1, 2, and 3: $k = 0.096$, $h = 0.037$, $f = 0.037$. For run 4, $k = 0.094$, $h = 0.055$, $f = 0.069$. For runs 5, 6, and 7: $k = 0.090$, $h = 0.052$, $f = 0.067$. Possible error from correction factor estimation: ±0.00006 for 32/28 and ±0.00003 for 30/28. ʰ Standard deviation. ⁱ Corrected for % reaction.

$(k_H/k_D = 1.15$ at 25°).[20] It is possible that in the structurally adduct-like transition state, the H–C leaving group bending force constants do not decrease as much as they do in solvolysis reactions even though considerable bond breaking has taken place.[10]

There are three qualifications to the theoretical argument presented in the introductory statement for treating cumulative isotope effects and taking into consideration the possibility of having a nonsymmetrical transition state: (1) the system might not conform

perfectly to the rule of the geometric mean; (2) there might be a β-D isotope effect on bond A as bond B is being broken and vice versa; and (3) the mechanism might be stepwise with the second step rate determining.

The contributions to the partition function ratio of the reactants vs. the transition state, which ratio determines the isotope effect, come from the translational and rotational motions, from the zero-point energy differences, and from the vibrational excitation factors. The translational motions should cancel precisely since the reaction is unimolecular. The rotational motions should nearly cancel since the transition state is re-

(20) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

Table II. α-Deuterium Isotope Effects in the Diels–Alder Reaction

Reaction	Temp, °C	$k_H/k_D{}^{a,b}$ per atom	Ref
Addition			
Anthracene-9,10-d_2 + maleic anhydride	25	0.94	9c
Anthracene-9,10-d_2 + tetracyanoethylene	25	0.94	9c
Butadiene-1,1,4,4-d_4 + maleic anhydride	25	0.93	9b
		0.92	c
Anthracene + maleic anhydride-d_2		0.95	9b
Butadiene + maleic anhydride-d_2	25	0.99	9b
Cyclopentadiene + maleic anhydride-d_2 (endo adduct)	25	0.97	9b
Dissociation			
2-Methylfuran-5-d + maleic anhydride	50	1.08	10
Anthracene-9,10-d_2 + tetracyanoethylene	50	1.09	9c
2-Methylfuran + maleic anhydride-d_2	50	1.08	10
Anthracene + ethylene-1,1,2,2-d_4	50	1.08	This work

[a] Temperature was corrected according to

$$\frac{(k_H/k_D)_{T_1}}{(k_H/k_D)_{T_2}} = \frac{e^{(h\nu_H - h\nu_D)/2RT_1}}{e^{(h\nu_H - h\nu_D)/2RT_2}}$$

[b] Isotope effect (IE) per D atom = (IE)$^{1/x}$, where x is the number of deuterium atoms. [c] S. J. Weininger, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pa., 1964.

actant-like, and there is very little change in the moment of inertia when two or four deuterium atoms are substituted for protium. Since the forms of the normal vibrations will change somewhat on isotopic substitution, the zero-point energy effects and vibrational excitation factors will not be quite multiplicative. The effect on the vibrational excitation factors will be small for the high frequencies involved.

Although the previous paragraph does not include the reaction coordinate motion explicitly, it is complete, for the ratio $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ only represents the high-temperature *limit* of the kinetic isotope effect. A more detailed discussion of the RGM is given in the Appendix.

The small isotope effect observed, however, indicates that the RGM-like assumption should be followed closely. Even if the mechanism is stepwise, the isotope effect is no more than 10% per D, which shows that the force constants to isotopic atoms are not changed much in going from reactant to transition state.

Since the RGM theory relates to the ratio of transition state to reactant partition functions, and since the transition state resembles the reactant, the deviations from the RGM will be in the same direction for both reactant and transition state and should thus very nearly cancel.

β-D isotope effects have been studied in the solvolysis of 11-methyl-11-chloro-9,10-dihydro-9,10-ethanoanthracene and its *12,12-d_2* and *9,10-d_2* analogs.[21] An isotope effect of 1.07 per D was determined for the *12,12-d_2* analog where the developing empty orbital was par-

allel to the composite orbital of the two protons on the adjacent bridge position. An isotope effect of 0.993 per D, not appreciably different from unity, was determined for the *9,10-d_2* analog, where the developing empty orbital was perpendicular to the C–H(D) bond. The major cause of the isotope effect seems to be hyperconjugation, which is prohibited in the *9,10-d_2* case.

In the free-radical decomposition of azobis-α-phenylethane-β,β,β-d_3 and its undeuterated analog, the β-D isotope effect was much smaller than in the carbonium ion transition state, $k_H/k_D = 1.018$ per D atom.[22]

In the stepwise dissociation of **2**, the developing empty orbital would be in the nodal plane of the composite molecular orbital of the protons on the adjacent bridge position and would probably go through a free-radical intermediate. Since inductive effects are also expected to be small, less than a 0.1% contribution per D would be estimated for the β-D isotope effect.

In the case of the concerted mechanism the α and β deuterium isotope effects would be indistinguishable. The criterion for mechanism in our case is, however, independent of whether the isotope effects are α or β.

Another mechanistic possibility which should be considered is a stepwise mechanism where the second step is rate determining, in which case $f_A \neq f_B$ unless the transition state is virtually product-like. The absolute magnitude of the isotope effect (5% per D if $f_A = f_B$), however, is too small for a possible product-like transition state.

The k_2/k_0 and k_4/k_0 values of Table I can be tested against the mechanistic predictions of eq 5. In analyzing the data, both systematic and accidental errors have to be examined.[23,24]

Systematic errors could be introduced by the instrument, the sampling, or the operator. The mass spectrometer was tested against a standard CO_2 sample; the decade dividers were switched from side 1 to side 2 with no change in the observed ratios. Two different kinetic techniques, a complete reaction followed by uv and a small conversion read and corrected from the ratio mass spectrometer, RMS, gave close k_4/k_0 values: uv, 0.83 ± 0.05; RMS, 0.852 ± 0.007. No trend was noticed in the sampling; *i.e.*, the data have a random distribution in time.

Accidental errors are treated by the *Gaussian law of errors* which assumes a normal distribution of data. The concerted and stepwise extremes were calculated for each k_2/k_0 and k_4/k_0 set. The experimental value of the mechanistic index, $x = (k_2/k_0)^2 - k_4/k_0$, was normalized by dividing through by the x value obtained (eq 5) for the stepwise extreme, $x = (1 - k_2/k_0)^2 \equiv y$, as shown in Table III. The standard deviation, σ, and the standard deviation of the mean, σ_m, were determined and normal distribution curves constructed as shown in Figure 1. Assuming a major error contribution from the mass spectrometer rather than from the sample, the 2-day readings were averaged where applicable and shown in Figure 2. Making the further assumption that the temperature correction is not entirely multiplicative and does enter significantly into the values for the mechanistic extremes MS run 1

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(24) E. B. Wilson, Jr., "An Introduction to Scientific Research," McGraw-Hill, New York, N. Y., 1952, Chapter 9.
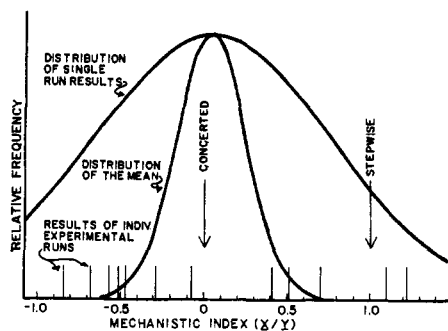
Figure 1. Normal distribution corresponding to the 12 experimental data points (n), with mean value $m = 0.043$ and $\sigma = 0.72$. The distribution of the mean ($\sigma_m = \sigma/\sqrt{n} = 0.21$) is the expected distribution of 12-run means, if such 12-run sets were repeated.
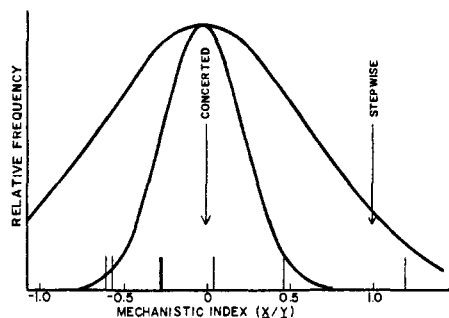

Figure 2. Normal distribution corresponding to the 2-day averaging of the experimental points with $m = -0.026$, $\sigma = 0.64$, and $\sigma_m = 0.24$.

is eliminated. MS run 6 is also eliminated since the absolute values of the isotope effects are abnormally high ($k_2/k_0 > 4$ av dev). This yields the distribution as presented in Figure 3.

Table III. Values for the Normalized Mechanistic Index as Calculated from Equation 5 for the Isotope Effects Listed in Table I

Run no.	Mechanistic index $x = (k_2/k_0)^2 - k_4/k_0$	Stepwise mechanism $x = (1 - k_2/k_0)^2 \equiv y$	Normalized index x/y
1a	-0.0063	0.0075	-0.84
b	-0.0032	0.0068	-0.47
2a	0.0032	0.0063	0.51
b	0.0028	0.0069	0.41
3	-0.0036	0.0063	-0.57
4a	-0.0004	0.0054	-0.07
b	-0.0029	0.0057	-0.51
5a	-0.0048	0.0071	-0.68
b	0.0038	0.0054	0.70
6a	0.0060	0.0048	1.22
b	0.0053	0.0048	1.10
7	-0.0019	0.0065	-0.29

No matter which analysis is used, the mean varies from the concerted mechanism by only -14% to $+4\%$ (or -0.0008 to $+0.0003$ on the absolute x scale). The averaging as well as the exclusion of the questionable values served to narrow the standard deviation. The averaging increased the standard deviation of the mean slightly while the exclusion of the questionable values decreased the standard deviation of the mean.
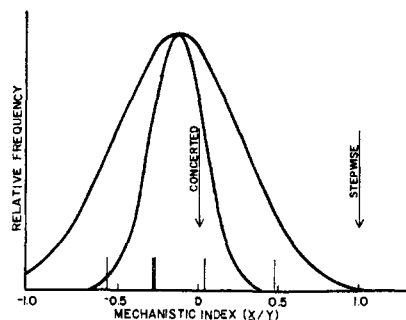
Figure 3. Normal distribution corresponding to the exclusion of the extreme values, with $m = -0.14$, $\sigma = 0.39$, and $\sigma_m = 0.17$.

The point of setting forth three analyses of the data is to show that the errors are probably random, in that the conclusion is the same even if drastic steps—ignoring some of the data—are taken. If these analyses demonstrate that the errors are random, as we believe, then the scatter of data between the concerted extreme and the stepwise extreme is fully balanced by scatter on the left side of the concerted extreme, as expected for a Gaussian distribution, to give a mean x which is very close to the concerted extreme.

Taking Figure 2 as probably the most representative, certain probabilities can be assigned to the various mechanistic schemes. The probability that the mean of any other set of runs would be at or beyond the stepwise extreme is 0.001%. The probability that the mean would be more than halfway toward the stepwise mechanism (greater than ca. $2\sigma_m$ in Figure 2) is 2%. A mechanism halfway toward the stepwise extreme would be an asymmetrical, concerted mechanism where, with $k_2/k_0 = 0.920$, the isotope effect at bond A, f_A, would be 0.98, and $f_B = 0.86$. The probability that the mean would be at or beyond $1\sigma_m$ (at $1\sigma_m$, with $k_2/k_0 = 0.92$, $f_A = 0.96$, $f_B = 0.88$) is 16%. The probability that the center would be at the concerted mechanistic extreme within $\pm 1\sigma_m$ is 68%.

The most positive value of the mechanistic index, x/y, derived by treatment of our data, is 0.043, indicating a transition state displaced only 4.3% from the concerted extreme. Therefore, we conclude that the mechanism is concerted, with a symmetrical or nearly symmetrical transition state, in agreement with indications obtained by others for similar reactions.[6,10]

This conclusion is *independent* of the absolute values of the observed isotope effects; it depends only on a comparison of k_4/k_0 and $(k_2/k_0)^2$. The only assumptions involved in this conclusion are, as discussed above: (1) that a "rule of the geometric mean" type assumption is valid in comparison of reactant and transition state;[25] (2) that $f_A \neq f_B$ unless the

(25) This really requires obediance to the rule only for *experimental rate constants*, and does not even require that transition-state theory be exact, since small deviations are very likely to cancel in the computation of an isotope effect (being a ratio of two rates for reactions occurring on the same potential energy surface), and further cancellation should occur in the comparison of two isotope effects, as in the computation of x. Furthermore, it can be argued that the constant state of collision of species present in solution ensures that the major assumption of transition-state theory—thermal equilibrium of excited reactants with energies very close to that of the transition state—will be very closely true in *solution* [*cf.* ref 7d and J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 91–109].

mechanism is concerted; (3) that the mean value of x/y has significance within the experimental scatter of data. We believe we have shown that these are the only assumptions required, and that each of them is vaid, (1) and (2) to a high degree of precision, and (3) to precision indicated by our statistical analysis.

Conclusion

Although care must be taken and research is required to establish the degree of validity of the RGM-like assumption in experiments such as this, the method is potentially applicable to a wide variety of mechanistic problems, particularly in so-called "no-mechanism" land (thermal reorganizations, nonclassical structures, etc.). In view of this potential for solving hitherto intractable mechanistic problems, we believe further studies aimed at establishing the validity and generality of the method will be valuable. Furthermore, it is in principle possible to design experimental systems (involving multiple isotopic substitutions of both a symmetrical and an unsymmetrical nature in the same reaction) to test the validity of the method, and, indeed, the validity of transition-state theory itself.

Appendix

Because the accuracy of the rule of the geometric mean type assumption is essential for the application of the present method to this and other mechanistic problems, a discussion is here appended. For any particular reaction, a sound approach would be to show (if possible) by means of computation of normal modes and thence partition functions that all reasonable force fields agree closely with the assumption. This is a major computational problem[26] which we hope to undertake, but, even so, it does not speak for cases other than the models chosen. Therefore, it may be useful, and may add additional weight to our argument, to describe what we do know at present.

In terms of partition functions, eq 4 requires that eq 8 be valid, in which the functions f are partition

$$\frac{f_4^{\pm}s_4^{\pm}}{f_4 s_4}\frac{f_0 s_0}{f_0^{\pm}s_0^{\pm}} = \frac{f_{2A}^{\pm}f_{2B}^{\pm}}{f_2^2}\frac{f_0^2 s_0^2}{(f_0^{\pm})^2(s_0^{\pm})^2}$$

$$\frac{f_{2A}^{\pm}f_{2B}^{\pm}/f_2^2}{f_4^{\pm}f_0^{\pm}s_4^{\pm}s_0^{\pm}/f_4 f_0 s_4 s_0} = 1 \qquad (8)$$

functions for reactants, the functions $f^{\pm}$ are quasi-partition functions for transition states, with the subscripts 0, 2, and 4 denoting the numbers of deuterium atoms, and the numbers s are the corresponding symmetry numbers (those for species with two deuterium atoms being omitted because they are unity for all mechanisms). It will be noted that symmetry is already included in the rate constant expressions of eq 3 and 4; in particular, eq 3 is valid for both stepwise and concerted mechanisms, but for different reasons: for stepwise,

because there really are two transition states A and B with two deuterium atoms, but there is a corresponding symmetry effect with zero and four deuterium atoms, the reactant having a symmetry number of 2 and being thus made less probable (less populated) by a factor of 2, but the transition state having a symmery number of unity; for concerted, because there is now only one transition state with two deuterium atoms, but the transition states with zero and four deuterium atoms have symmetry numbers of 2. Since symmetry is already explicitly included in eq 3 and 4, it cannot be included a second time; that is, the expressions for f_A and f_B in terms of partition functions must, as in eq 8, remove symmetry factors. For mechanistic elucidation, it is required that the ratio in eq 8 differ from unity by considerably less than the mechanistic index variation between mechanistic extremes. In the present case, the criterion is that the ratio deviate from unity by much less than the 0.6% difference between concerted and stepwise extremes.

According to eq 8, within the harmonic approximation and neglecting quantum mechanical tunneling,[27] the ratio separates into independent factors involving (a) molecular masses only, (b) moments of inertia only, and (c) vibrations only. The vibrational factor separates further into independent factors for each normal vibration, and the contribution from each normal vibration separates into zero-point energy and excitation factors.[7,26] This separation occurs for transition state quasi-partition functions (within the transition-state theory approximation[25]) in exactly the same way as for reactants; the difference is merely that there is a "missing" normal vibration in the transition state, since that normal mode of motion which is the reaction coordinate does not contribute a factor in the vibrational partition function at all. The reaction coordinate motion is already subsumed in the universal frequency factor kT/h, which is isotope independent. The factor $\nu_{1L}^{\pm}/\nu_{2L}^{\pm}$ frequently seen in expressions for isotopic rate ratios, which is the ratio of the imaginary frequencies for motion along the reaction coordinate for two isotopic transition states, is a useful artifact of the application of the Teller–Redlich product rule expression for the mass and moment of inertia contribution to isotopic partition function ratios; it is useful because it can be shown that, at sufficiently high temperatures, everything else in the complete expression for kinetic isotope effects cancels (except symmetry numbers, if any), leaving $\nu_{1L}^{\pm}/\nu_{2L}^{\pm}$ as the high-temperature limit of the kinetic isotope effect.[7] However, if we evaluate the mass and moment of inertia contributions to eq 8 directly, the ratio of imaginary frequencies simply does not enter the discussion.[7d] We elaborate this point because the ratio of imaginary frequencies seems sometimes to be accorded the status of an "additional" isotope rate effect, above and beyond the partition function effects. In this particular case,

(26) The cut-off procedure [M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225 (1964)] cannot be used, since it does not give correct $\nu_{1L}^{\pm}/\nu_{2L}^{\pm}$ ratios.

(27) It is not possible to discuss the problem at all without these assumptions. While it is possible to argue that we cannot therefore draw any conclusions from our work, the requirement of absolute rigor would, if uniformly applied, remove most of science from the realm of knowledge; there is every indication that these assumptions are closely valid for the reaction in question, involving as it does small, secondary isotope effects, and there is additionally the cancellation effect implicit in eq 8, which requires not absolute adherence to the assumptions, but only that the discrepancy for doubly deuterated species in the numerator be halfway (in the geometric sense) between the discrepancies for the undeuterated and tetradeuterated species in the denominator.

the point is relevant, in that it can be argued that the ratio of the imaginary frequencies could give rise to a β kinetic isotope effect for the stepwise mechanism which could be comparable in magnitude to the observed isotope effects and could thus destroy the assumption embodied in eq 6 that the β effect would be close to unity for the stepwise mechanism. However, the available analogies suggest, as discussed in connection with ref 21 and 22 above, that the β effect should be small. If it is not small, that fact could affect the interpretation of mechanism as discussed in the body of this paper, but it in no way affects the discussion of eq 8; it only affects the discussion of eq 6.

It is possible to discuss the separate contributions to eq 8 in turn. For unimolecular reactions, the transition state always equals the reactant in mass, so the mass contribution to eq 8 is precisely unity. At this point, any estimate of deviations of eq 8 from unity requires models of reactant and transition state. For the present case, the small absolute magnitude of the isotope effect demonstrates that the transition state resembles the reactant closely. Because of the extensive ratio taking, and accompanying cancellation of effects, inherent in eq 8 (that is, transition states and reactants are separately expected to give factors close to unity in eq 8, but in addition the transition-state deviation from unity occurs in a direction reciprocal to the reactant deviation, thus giving further cancellation), a crude estimate of the moment of inertia effect is sufficient. Distances measured on Dreiding models for reactant, together with an estimate of a carbon–carbon bond order of 0.5 for the transition-state reacting bonds, lead to calculated moments of inertia which add a factor of ca. 1.0003 (i.e., 0.03%) to the ratio of eq 8. An upper limit, which might occur for a more product-like transition state, would seem to be 0.1%. An effect this size would have a small, but not quite negligible, influence on the mechanistic index.

An example of the vibrational influence is the case of water, for which accurate frequencies are known.[28] It is found that essentially the entire deviation from the rule of the geometric mean for the vibrations of the species H_2O, HDO, and D_2O is predicted by the isotopic sum rule,[29] which says that the sum of the *squares* of the frequencies of H_2O plus D_2O equals twice the sum of the squares of the frequencies of HDO. Furthermore, the frequencies break up into groups which separately obey the sum rule. The O–H stretch of HDO and the (symmetric and antisymmetric) O–H stretches of H_2O, the O–D stretch of HDO and the O–D stretches of D_2O, and the HOD bend of HDO and the HOH bend of H_2O together with the DOD bend of D_2O obey the sum rule separately as groups. The stretches, which occur in groups which are either essentially "all H" or "all D," also conform to the rule of the geometric mean (eq 8) very closely, for the symmetric–antisymmetric splittings of the stretches in H_2O and D_2O are not large (ca. 100 cm⁻¹), and thus both the squares of the frequencies and the frequencies themselves obey sum rules. The feature which gives a substantial deviation from the rule of the geometric mean is the bends, for there are no symmetric and antisymmetric bends in H_2O or D_2O; in these small molecules,

there cannot be separate H–O and D–O bends in HDO, and therefore the sum rule in this case includes the HOH bend of H_2O and the DOD bend of a different molecule, D_2O. These bends in the latter two molecules are over 400 cm⁻¹ different in frequency, so that the sums of the squares of the frequencies obey a sum rule, but the frequencies themselves do not obey the sum rule very well. Thus, the major source of deviation from the rule of the geometric mean is the unpaired bending frequency (the symmetric bend), the antisymmetric "bend" being in fact a molecular rotation.

With the source of the discrepancy in water understood, it is possible to examine the vibrational situation in the reaction at hand. First, there will be no problem of unpaired bends, because these large molecules will have both symmetric and antisymmetric bends in pairs for all the motions of the isotopic atoms. If it is assumed that the frequencies break up into groups which separately obey the sum rule—as is the case with water—then for each normal mode (or small group of normal modes with nearly equal frequencies) of the d_2 species, there will be a pair (or corresponding double-sized group) of frequencies in either the d_0 or the d_4 species (or, in the case of groups with nearly equal frequencies, in both the d_0 and the d_4 species) to which the sum rule applies with great precision. Therefore, considering the stretches and bends of the isotopic atoms, one sees that the situation is entirely analogous to the stretching frequencies of the water molecules—but in this case there will always be paired frequencies in either the d_0 or the d_4 species, for bends as well as stretches. The effect of the sum-rule type deviations can be readily estimated for hypothetical frequencies. The result is that the deviation of eq 8 from unity is larger at lower frequencies, and could be significant compared with 0.6% under certain conditions, particularly if there were large symmetric–antisymmetric splittings in the d_4 case at frequencies less than 1000 cm⁻¹, splittings which were not present in the d_2 case. Unfortunately, it is not possible to estimate these splittings reliably, for the small molecules, such as ethane and ethylene, which have been carefully studied with asymmetric deuterium substitution all have the unpaired frequency problem, as well as splittings which result from substantial changes in amounts of carbon atom motion coupled with hydrogen atom motion, required in order to keep the center of gravity of the molecule fixed upon vibration. The much more massive molecules we have studied were *chosen* so as to be, hopefully, nearly devoid of such splittings. Adherence to eq 8 therefore depends on the question of whether those splittings are sufficiently small. We *believe* they will be small, just as the moment of inertia effect is small for these heavy molecules, but we cannot be certain if they will be small enough. The only direct way of being certain would be a complete vibrational analysis of the reactants. We have examined the infrared spectra, but they are much too complex for simple assignment of the low-frequency vibrations (the stretches obey eq 8 very precisely, as might be expected).

In addition to the stretches and bends of the isotopic atoms, a number of other frequencies will be affected by isotopic substitution. The argument presented for the stretches and bends in the previous paragraph applies to these vibrations also, except that, since they are

(28) W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, 24, 1139 (1956).

(29) J. C. Decius and E. B. Wilson, Jr., *ibid.*, 19, 1409 (1951).

motions largely of atoms other than the isotopic ones, they are likely to contribute considerably less to the deviation of eq 8 from unity.

However, the reactant has a pair of frequencies, approximately the symmetric and antisymmetric stretching modes of the two C–C bonds which are broken in the course of the reaction, but the corresponding motions of the transition state include a real vibration involving these two bonds, and the reaction coordinate motion itself. The exact nature of these two transition-state motions depends on whether the mechanism is concerted or stepwise. In the concerted extreme, where $f_{2A}^{\pm} \equiv f_{2B}^{\pm} \equiv f_2^{\pm}$ in eq 8, the reaction coordinate is the symmetric stretch of these two C–C bonds and the anti reaction coordinate is the antisymmetric stretch. For mechanisms which are not concerted, there will be two separate transition states, A and B, differing only in the position of deuterium substitution, in the case of the d_2 species. The concerted extreme will have a single d_2 transition state whose anti reaction coordinate motion is intermediate in frequency between the anti reaction coordinate frequencies of the d_0 and d_4 transition states. As the mechanism loses concertedness and approaches the stepwise extreme, the two d_2 transition states (A and B) must be taken into account. But one of these two will have an anti reaction coordinate frequency close to that of the d_0 transition state (slightly lower), and the other will have an anti reaction coordinate frequency close to that of the d_4 transition

state (slightly higher). If the sum rule applies to this group of frequencies, then the anti reaction coordinate frequencies obey the relationship $\omega_0^2 + \omega_4^2 = \omega_A^2 + \omega_B^2$. If $\omega_A \neq \omega_B$, the deviation of eq 8 from unity will be less than for the concerted extreme, where they are equal. However, these antireaction coordinate frequencies will all be similar, for the motion is one which involves primarily carbon atoms and relatively little motion of H and D atoms. While it is true that the reaction coordinate motion—and therefore also the anti-reaction coordinate motion—will be changed in form somewhat by making the unsymmetrical substitution of two D atoms, this problem will also be greatest for the concerted extreme of mechanism (since nonconcerted mechanisms have less coupling of the two C–C stretches, lack of such coupling being the *definition* of nonconcertedness).

In sum, the problems which might arise in eq 8 are delineated by the above discussion. The anti-reaction coordinate motion may be expected to be the worst offender, particularly if the mechanism is concerted. In view of the fact that a concerted mechanism should offer the worst problems, and in view of the fact that we can identify these problems as being associated primarily with normal modes which are not greatly affected by isotopic substitution (being largely C–C stretching modes), it seems that our experimental data, which support a *concerted* mechanism, are a valid indication of mechanism and, as well, an indication that eq 8 is valid.

Free-Radical Halogenation of Adamantane. Selectivity and Relative Lifetime of 1- and 2-Adamantyl Radicals

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Abstract: Free-radical halogenation of adamantane was carried out under nitrogen and oxygen. In the absence of oxygen, the ratios of products, 1-haloadamantane:2-haloadamantane, under different conditions were dramatically dependent on the halogenating reagent employed. Under oxygen, there took place oxygenation as well as normal halogenation. The principal oxygenated product was 1-adamantanol and only traces of 2-oxygenated adamantanes, if any, were formed. These results were interpreted in terms of different lifetimes of 1- and 2-adamantyl radicals and a conclusion is drawn that 1-adamantyl is remarkably more long-lived than 2-adamantyl despite the very indiscriminate behavior of the former radical compared with the latter in the condition of competitive bromination–chlorination. The origin of the present reactivity–selectivity relationship is discussed.

$\mathbf{M}$uch effort has been devoted to the investigation of bridgehead radicals in recent years. A criterion for the stability of a bridgehead radical has been based on the observation that the rate of its formation is considerably fast. One point to be made is, however, that there has been no convincing experimental evidence for the parallelism between the facility of the formation of a radical and its stability.

Further complication arises from the polar contribution to the transition state of radical reactions. The transition state of many hydrogen abstraction reactions

may be depicted as

$$\overset{+}{R}\text{---}H\text{---}X^{\delta-}$$
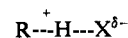
$$X = Br, Cl, \text{ and } CCl_3, \text{ etc.}$$

owing to the electrophilic nature of the usual hydrogen abstracting radicals (bromine, chlorine, and trichloromethyl, etc.). Even the decomposition of a *tert*-butyl perester, which is commonly used as one of the best ways to assess the stability of a radical,[1] still has some (not

(1) (a) W. A. Pryor, "Free Radicals," McGraw-Hill, New York,