

dihydrophthalic anhydride, be immune to similar side reactions contradicts all experience.

It is simpler to believe the origin of the anomaly to be no more profound than its magnitude and to attribute it to the incursion of a marginal side reaction. The predominant reaction path avoids all such inter-

mediates. It is to be regarded as a retrodiene decarboxylation.

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## The Mechanism of a Diels–Alder Reaction. II. The Structure of the Transition State<sup>1</sup>

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*Carbon and oxygen kinetic isotope effects ( $k_{12}/k_{13} = 1.030$  and  $k_{16}/k_{18} = 1.014$ ) have been determined for decarboxylation of the maleic anhydride adduct of  $\alpha$ -pyrone. Subjected to both approximate and exact theoretical analysis, they require a one-center transition state: the C–C bond connecting the labile lactone to the remainder of the molecule is effectively broken in the transition state whereas the C–O connecting bond remains virtually intact. Exact analysis provides a more quantitative description and relates structural to experimental uncertainties. The reliability of these conclusions is shown to depend critically on the use of heavy atom kinetic isotope effects measured at multiple, adjacent sites. Some more general aspects of the one-center and two-stage descriptions of Diels–Alder addition are discussed.*

### Introduction

In Part I,<sup>3</sup> decarboxylation of the maleic anhydride adduct of  $\alpha$ -pyrone was experimentally classified as a Diels–Alder retrogression and the accepted structures of reactants and products were confirmed. In this part, kinetic isotope effects are evaluated and used to explore the structure of the transition state.

### Experimental

$\alpha$ -Pyrone maleic anhydride adduct and dimethyl phthalate were prepared and purified as described.<sup>3</sup>

*Apparatus and Procedure.* The decarboxylations were carried out in a long-necked, round-bottom flask connected to a high-vacuum stopcock by the sample drop tube.<sup>3</sup> With 1.2108 g. of adduct in the

drop tube-supported vial and 55.74 ml. of dimethyl phthalate in the flask, the latter was degassed to  $10^{-5}$  mm. by 12 repetitions of the sequence: freeze (carbon dioxide–trichloroethylene), evacuate, and melt. The flask and contents were permitted to reach temperature equilibrium with a constant-temperature ( $130.21 \pm 0.05^\circ$ ) bath (1 hr.), the vial was dropped into the solvent, and the flask was agitated while the sample dissolved ( $<1.5$  min.). After 55 min. (10% decomposition) the flask was removed from the bath, rapidly cooled, and returned to the vacuum line. The carbon dioxide was purified by sublimation through a  $70 \times 1$  cm. column kept at  $100^\circ$  and packed with 14–20 mesh silica gel into a cooled (nitrogen) trap. Samples from complete reaction were identically obtained and purified except that reaction time exceeded 10 half-lives at  $160^\circ$  (170 min.). Silica gel was regenerated by heating for at least 5 hr. at  $200^\circ$  *in vacuo*. Variations of traditional bulb-to-bulb distillation technique failed to remove traces of dimethyl phthalate (b.p.  $153^\circ$  at 12 mm.!) easily detected by mass spectrometry at  $m/e$  59 ( $\text{COOCH}_3^+$ ). A similar problem has been reported.<sup>4</sup>

*Isotopic Analysis.* A Consolidated Engineering Corporation 21–401 mass spectrometer was employed in both its analytical and isotope ratio modes. In the latter, one of its dual collectors records ions of  $m/e$  while the second records the sum of those at  $m/e - 1$  and  $m/e - 2$ . Ratio measurements on any one sample were reproducible to  $\pm 0.02$ – $0.05\%$  for carbon,  $\pm 0.03$ – $0.08\%$  for oxygen, and were always preceded, and often immediately followed, by (a) a background scan, (b) a scan of  $m/e$  4–100 for impurities which were never observed, and (c) isotope ratio determination of commercially obtained carbon dioxide.<sup>5</sup> Optimum resolution was ensured by maximizing the isotope ratio with respect to accelerating voltage and provided results identical with those obtained by the more tedious variation with respect to magnetic field. Each observed ratio of Table I is the average of four observations on each of two samples obtained from the same reaction vessel.

(1) The study was supported by the Air Force Office of Scientific Research under Contract No. 49(038)-942 and Grant No. 142-63. Preliminary experimental results and approximate analysis were the subject of a previous communication: M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **85**, 2673 (1963). The results of exact calculations were presented at the "International Symposium on Organic Reaction Mechanisms" held in Cork, Ireland, July 25, 1964.

(2) Union Carbide Corporation Research Fellow, 1962–1963. Taken, in part, from the dissertation to be submitted by G. L. T. to Cornell University in partial completion of the requirements for the Ph.D. Degree, Feb. 1965.

(3) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **87**, 1925 (1965).

(4) A. A. Bothner-By and J. Bigeleisen, *J. Chem. Phys.*, **19**, 755 (1951).

(5) Coleman grade, 99.99% minimum.

**Table I.** Experimental Carbon and Oxygen Kinetic Isotope Effects in 0.10 M Dimethyl Phthalate at 130.2°

<i>f</i>	$10^6 \times C^{13}/C^{12}$		$k_{12}/k_{13}$	$10^6 \times C^{12}O^{18}O^{18}/C^{12}O_2^{16}$		$k_{16}/k_{18}$
	Obsd.	Corr.		Obsd.	Corr.	
1.00 <sup>a</sup>	12159	11425		4211	4117	
1.00	12940	11425		4444	4113	
1.00	12182	11396		4213	4109	
1.00	12160	11379		4205	4105	
	mean 11406 ± 23			mean 4111 ± 5		
0.05	12532	11074	1.0305	4372	4059	1.0133
0.10	11806	11116	1.0271	<i>b</i>		
0.11	11782	11092	1.0302	<i>b</i>		
0.10	12615	11084	1.0301	4386	4057	1.0141
0.11	12600	11069	1.0320	4374	4047	1.0169
0.11	11881	11091	1.0304	4167	4062	1.0127
0.10	11858	11076	1.0308	4162	4061	1.0130
0.10	11845	11074	1.0311	4147	4059	1.0135
	mean 1.0303 <sup>c</sup> ± 0.0025			mean 1.0139 <sup>c</sup> ± 0.0019		

<sup>a</sup> Carbon dioxide samples at *f* = 1 were obtained at 160°. <sup>b</sup> No attempt was made to obtain oxygen ratios in these earliest experiments. <sup>c</sup> Equation 1 was used to calculate isotope effects and 2, with *f* = 0 and  $(k_1/k_h) = \bar{R}_1/\bar{R}_f$ , to evaluate the standard deviations listed.

**Corrections to Observed Ratios.**<sup>6</sup> Observed ion current ratios are only imprecisely identical with sample isotope ratios for reasons that have been discussed.<sup>7</sup> Tank carbon dioxide provided a constant reference on the assumption that its isotopic ratios were those determined on an absolute basis<sup>8</sup> ( $S_{13} = C^{13}/C^{12} = 0.011205$ ,  $S_{18} = O^{18}O^{16}/O_2^{16} = 0.004094$ , and  $S_{17} = O^{17}O^{16}/O_2^{16} = 0.000750$ ). (Small uncertainties ( $<3 \times 10^{-3}$ ) in these values represent a constant, not random, error and cancel in such experiments.) Both instrumental mass discrimination and the contributions of  $C^{13}O_2^{16}$  and  $C^{12}O^{16}O^{17}$  to  $R_{18}^{obsd}$  were evaluated according to E.1 and E.2 where the *R* ratios refer to experimental samples, *T* to those of tank carbon dioxide, and *S* to those above.

$$R_{13}^{corr} = R_{13}^{obsd} \frac{(S_{13} + S_{17})}{T_{13}^{obsd}} - S_{17} \quad (E.1)$$

$$R_{18}^{corr} = \frac{R_{18}^{obsd} S_{18} \left[ \frac{1 + R_{13}^{corr} + S_{17}}{1 + S_{13} + S_{17}} \right]}{T_{18}^{obsd}} \quad (E.2)$$

The further consequences of O<sup>17</sup> fractionation on E.1 and E.2 were evaluated on the assumption that  $k_{16}/k_{17} = 1 + 0.5[(k_{16}/k_{18}) - 1]$ . Applied to the *R* ratios of partial decarboxylation, it diminished  $k_{12}/k_{13}$  by  $4.5 \times 10^{-4}$ . Corrections for instrumental background were estimated by obvious methods and for O<sup>18</sup> exchange with the silica gel surface by subjecting a sample to two successive purifications and analyses. Both were negligibly small. Possible corrections for incomplete mass resolution were undetectably small.

## Results

Approximately 1% of the maleic anhydride adduct of α-pyrone contains C<sup>13</sup> in the strained lactone and 0.4% contains O<sup>18</sup> in either of the two nonequivalent positions of this same functional group. To the extent that such molecules react more slowly than those containing only lighter isotopes, the evolved carbon dioxide is initially poorer in heavier isotopes. The ratio of rate constants of light to heavy molecules for

(6) The need for such corrections depends both on the instrument employed and the precision obtainable.

(7) (a) W. Dansgaard, *Medd. Groenland*, 165, No. 2 (1961); (b) A. O. Nier, *Re v. Sci. Instr.*, 21, 1019 (1950).

(8) A. O. Nier, *Phys. Rev.*, 77, 789 (1950).

each such isotopic pair is evaluated by eq. 1 where *f* is the fractional extent of reaction and *R<sub>f</sub>* and *R<sub>1</sub>* are the ratios of heavy to light carbon dioxide accumulated up to *f* and up to *f* = 1, respectively.<sup>9</sup> First-order

$$\frac{k_1}{k_h} = \frac{\ln \left[ 1 - f \left( \frac{R_1 + 1}{R_f + 1} \right) \right]}{\ln \left[ 1 - f \left( \frac{R_f}{R_1} \right) \left( \frac{R_1 + 1}{R_f + 1} \right) \right]} \quad (1)$$

kinetics and a quantitative yield of carbon dioxide are sufficient conditions for eq. 1 to be rigorous and both have been satisfied.<sup>3</sup> Results are presented in Table I.<sup>10</sup>

The traditional technique of analyzing only initially formed product was employed despite three potential sources of error: (a) inadequate time for temperature equilibration, (b) a subsequent change of mechanism, and (c) trace contamination.<sup>11</sup> By their exclusion, however, one gains both greater precision and a welcome simplification of numerical analysis. Expansion of eq. 1 produces 2 whose limiting value at

$$\frac{k_1}{k_h} = \frac{R_1}{R_f} \left[ 1 + \frac{1}{2} \left( \frac{R_1 - R_f}{R_1} \right) \left( \frac{R_1 + 1}{R_f + 1} \right) f + \dots \right] \quad (2)$$

*f* = 0<sup>12</sup> is quite adequate for all subsidiary use. Even at *f* = 0.11, the next term (linear in *f*) amounts to less than the standard deviation. A similar expansion (Appendix) equates the observed oxygen isotope effect to the arithmetic mean of those due to substitution at each of the lactone's oxygens. The conse-

(9) Experimental and theoretical aspects of kinetic isotope effects have been reviewed: (a) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, 1, 15 (1958); (b) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

(10) Despite the extensive literature devoted to carbon isotope effects,<sup>9a</sup> the only previous reports of kinetic oxygen isotope fractionation are those for (a) molten ammonium nitrate decomposition: L. Friedman and J. Bigeleisen, *J. Chem. Phys.*, 18, 1325 (1950); (b) malonic acid decarboxylation: P. E. Yankwich, R. L. Belford, and G. Fraenkel, *J. Am. Chem. Soc.*, 75, 832 (1953); P. E. Yankwich and H. S. Weber, *ibid.*, 78, 564 (1956); (c) solid lead oxalate decomposition: P. E. Yankwich and J. L. Copeland, *ibid.*, 79, 2081 (1957); and (d) aqueous hydrogen peroxide decomposition: A. E. Cahill and H. Taube, *ibid.*, 74, 2312 (1952). Only in a and d were the data seriously analyzed and mechanistically considered.

(11) Cf. V. F. Raaij, T. K. Dunham, D. D. Thompson, and C. J. Collins, *ibid.*, 85, 3497 (1963).

(12) J. Bigeleisen, *Science*, 110, 14 (1949).

quences of any reasonable degree of isotopic inhomogeneity are negligible.

### Structural Analysis of Kinetic Isotope Effects

It is a simple matter to relate the magnitudes of kinetic isotope effects to such properties of light and heavy reactants and transition states as moments of inertia ( $I_A$ ,  $I_B$ , and  $I_C$ ) and vibrational frequencies ( $\nu_i$ ) (cf. eq. 3).<sup>9</sup> It is more difficult to relate these

$$\frac{k_1}{k_h} = \frac{\left( (I_A I_B I_C)^{1/2} \int_{i=1,53} \frac{e^{-u_i/2}}{1-e^{-u_i}} \right)_{1^*}}{\left( (I_A I_B I_C)^{1/2} \int_{i=1,53} \frac{e^{-u_i/2}}{1-e^{-u_i}} \right)_{h^*}} \quad (3)$$

$$\frac{k_1}{k_h} = \frac{\left( (I_A I_B I_C)^{1/2} \int_{i=1,54} \frac{e^{-u_i/2}}{1-e^{-u_i}} \right)_1}{\left( (I_A I_B I_C)^{1/2} \int_{i=1,54} \frac{e^{-u_i/2}}{1-e^{-u_i}} \right)_h}$$

parameters in turn to those which must remain primary to any mechanistic description, those which are characteristic of covalent bonds. Although moments of inertia are readily derived from structure, the consequences of their variation are both minor and often misleading.<sup>13</sup> The estimation of selected vibrational frequencies is a more common pitfall, related perhaps to a belief that constancy of characteristic "bond frequencies" implies the localization of molecular vibrations at individual bonds. Unfortunately, except in the smallest and/or most symmetric molecules, both the number and the complexity of normal modes preclude the use of such frequencies as rational parameters.<sup>14</sup> Force constants, of some kind, become the appropriate local structural parameters to employ. Bond lengths, energies, or orders might have been preferred but all are related to force constants in a way that is obvious in a qualitative sense and has long been subject to quantitative correlation.<sup>15</sup> Experimental isotope effects were analyzed within this context by both approximate and exact methods.

**Approximate Analysis.** Bigeleisen and Wolfsberg had demonstrated some time ago that heavy-atom, kinetic isotope effects could be directly, if only crudely, related to force constant changes by the  $\bar{\gamma}$ -technique.<sup>9a,13</sup> Circumventing the formidable problem of vibrational analysis, eq. 4 was derived from eq. 3 with only the further condition that isotopic shifts of vibrational

(13) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225 (1964).

(14) The variations in normal modes and in their associated frequencies with the simplest structural changes introduces a higher order of complexity. Illustrations are provided by the exact vibrational analysis of selected alkanes (ref. 20) and of the  $\alpha$ -pyrone adduct (Supplementary Data).

(15) (a) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960; (b) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946); *ibid.*, **15**, 305 (1947); (c) T. L. Cottrell and L. E. Sutton, *Quart. Rev. (London)*, **2**, 260 (1948); (d) H. S. Johnson, *J. Am. Chem. Soc.*, **86**, 1643 (1964).

frequencies be much smaller than the frequencies themselves. It is here still further restricted to isotopic substitution at a single position.<sup>16</sup>

$$\frac{k_1}{k_h} = \frac{\nu_{L1}^*}{\nu_{Lh}^*} \left[ 1 + \frac{A\bar{\gamma}}{T^2} \left( \frac{1}{m_1} - \frac{1}{m_h} \right)^j \sum^{x,y,z} (a_{jj} - a_{jj}^*) \right] \quad (4)$$

$$A = \frac{N}{24} \left( \frac{h}{2\pi k} \right)^2 = 1.4636 \text{ (sec. deg.)}^2$$

$$\bar{\gamma} = \frac{12}{u} \left[ \frac{1}{2} - \frac{1}{u} + \frac{1}{e^u - 1} \right] \quad (4a)$$

$$\bar{u} = \frac{hc\bar{\nu}}{kT}$$

Each of three  $a_{jj}$  values is a diagonal cartesian force constant at the isotopically substituted atom: the component, along any one of the three cartesian axes, of the restoring force produced at this atom when it, alone, is displaced one unit along that axis. If these are summed over all three axes and the transition state value is subtracted from that of the reactant, the difference obtained concisely describes the total decrease in restraints about the atom (in dynes/cm.) and provides the major source of most kinetic isotope effects. The consequences of this diminished restraint depend on the difference in reciprocal isotopic masses (in a.m.u.), on the absolute temperature, and on the factor  $\bar{\gamma}$ . Related by eq. 4a to a hypothetical frequency,  $\bar{\nu}$ ,  $\bar{\gamma}$  is best regarded as no more than an incompletely adjustable parameter.<sup>13</sup>

The utility of the technique derives largely from the numerical insensitivity of  $\bar{\gamma}$  to any reasonable choice of  $\bar{\nu}^{9a}$  and hence also to both the mass and the location of the heavier isotope. It does, regrettably, require an independent estimate of the  $\nu_{L}^*$  ratio. This, the mass dependence of classical motion along the reaction coordinate, is estimated by identifying it with the mass dependence of a real vibrational frequency limited to an internal coordinate appropriate to the mechanism envisioned.<sup>17</sup>

Application of eq. 4 is illustrated by first the consequences of the simplest of two-center transition states. The  $\text{CO}_2$  and  $\text{C}_3\text{H}_6\text{O}_3$  rigid fragments separate along an axis joining their centers of mass with roughly equal weakening of the C-1-C-4 and C-2-O-3 bonds. (A, Figure 1. See Figure 2 for the numbering of significant atoms and Figure 2 of Part I<sup>3</sup> for that of others.) Such an internal coordinate leads directly to eq. 5<sup>18</sup> and the numerical results in column  $\bar{\gamma}1$  of Table II.

$$\frac{\nu_{L1}^*}{\nu_{Lh}^*} = \left[ \frac{\frac{1}{m_1^S} + \frac{1}{m^L}}{\frac{1}{m_h^S} + \frac{1}{m^L}} \right]^{1/2} \quad \begin{array}{l} m_1^S = 44 \\ m_h^S = 45 \text{ or } 46 \\ m^L = 150 \end{array} \quad (5)$$

(16) Extension to small hydrogen isotope effects was illustrated by M. Wolfsberg, *J. Chem. Phys.*, **33**, 2 (1960), and once previously applied to a problem of reaction mechanism by R. E. Davis, E. Bromels, and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962), albeit as the unmodified first quantum correction ( $\gamma = 1$ ).

(17) M. Wolfsberg, *J. Chem. Phys.*, **33**, 21 (1960).

(18) A referee has pointed out that eq. 5 and 7 require the assumption that the reaction coordinate separates out as a normal mode.

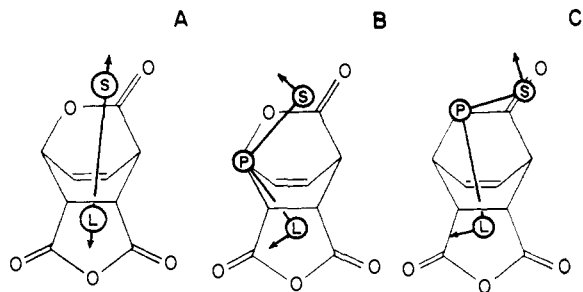


Figure 1. Simple models for three reaction coordinates: A,  $\bar{\gamma}1$ ; B,  $\bar{\gamma}2$ ; and C,  $\bar{\gamma}3$ .

Most significantly the classical contribution to the oxygen isotope effect alone exceeds the experimental value (1.014). Its mechanistic consequences become still more apparent by cancelling  $\bar{\gamma}$  between two equations like 4 to obtain 6

$$\frac{1/2 (\Delta a^* (3) + \Delta a^* (5))}{\Delta a^* (4)} = \frac{\left(\frac{1}{12} - \frac{1}{13}\right) \left(\frac{k_{16}/k_{18}}{\nu_{L16}^*/\nu_{L18}^*} - 1\right)}{\left(\frac{1}{16} - \frac{1}{18}\right) \left(\frac{k_{12}/k_{13}}{\nu_{L12}^*/\nu_{L13}^*} - 1\right)} \quad (6)$$

where  $\Delta a^* (i) = \sum_{j=x,y,z} (a_{ij} - a_{ij}^*)$  at atom  $i$ .

The quantity on the left now represents the average decrease in diagonal cartesian force constants at O-3 and O-5 divided by that at C-4. Evaluated by substituting the values from Tables I and II for the

Table II.  $\nu_{L1}^*/\nu_{Lh}^*$  for Model Transition States

Location of heavier isotope	$\bar{\gamma}1$	$\bar{\gamma}2$	$\bar{\gamma}3$
C-4	1.009	1.008	1.017
O-3	1.017	1.002	1.000
O-5	1.017	1.030	1.047

appropriate variables on the right, the ratio amounts to only  $-0.13 \pm 0.09$ , negative, if not in fact zero. It is unlikely that this might result from  $\Delta a^* (3) \cong \Delta a^* (4) \cong -\Delta a^* (5)$ , *i.e.*, diminished restraint at O-3 compensated by an increase at O-5. With O-5 and C-4 covalently linked, one is hard pressed to imagine how a negative  $\Delta a^* (5)$  and a positive  $\Delta a^*(4)$  of comparable absolute magnitude might coexist. A simpler interpretation is that  $\Delta a^* (3) \ll \Delta a^* (4)$ , but this, in turn, contradicts the initial assumption of equivalent weakening of both bonds. Hence, the model is to be rejected.

An alternative ( $\bar{\gamma}2$ ) is next elaborated from the assumption that only the C-1-C-4 bond is weakened. An appropriate model then contains only three point masses:  $m^P$ , the pivot atom C-2,  $m^S$ , the smaller, again that of  $CO_2$ , and  $m^L$ , that of the remaining atoms located at their new center (B, Figure 1). The simplest internal coordinate, a valence angle bend, would however require that C-2 move roughly in the direction of C-1 and so result in increased, rather than dimin-

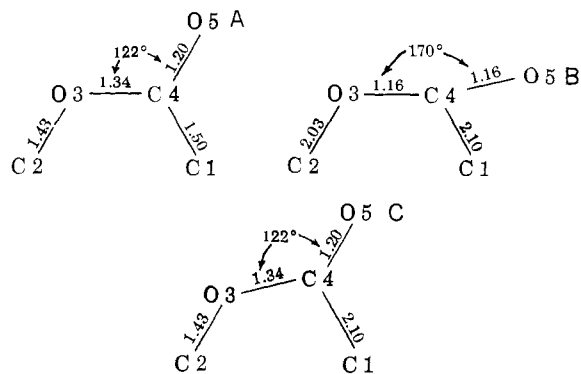


Figure 2. Lactone geometry in the transition state.

ished, angle strain in the transition state. Both this difficulty and a less tractable computation are avoided by requiring that P be stationary with respect to an external coordinate system. The mass dependence of such an "unfolding" motion is given by eq. 7 where

$$\frac{\nu_{L1}^*}{\nu_{Lh}^*} = \left[ \frac{1}{m_1^S (d_1^{PS})^2} + \frac{1}{m^L (d^{PL})^2} \right]^{1/2} \quad (7)$$

$d^{PS}$  and  $d^{PL}$  are distances, from P, to S, and to L, respectively. This "coordinate," unlike that of  $\bar{\gamma}1$ , is sensitive to geometry and should attach far greater importance to the mass of O-5 than to that of O-3 were this distinction not lost by including both in one point mass. Fortunately, the center of mass of S, and therefore  $d^{PS}$ , is now isotopically dependent and so reflects the distinguishability of the two oxygens in just the proper sense, if not magnitude, to compensate for this neglect. The resulting "coordinate" can hardly be considered an internal one nor could the mass dependence of "interatomic" distance ever be tolerated for a truly triatomic molecule. Both devices serve only to compel the model to move in a manner whose mass dependence mimics that presumed for the real molecule.

The calculated classical contributions to the isotope effects are listed in column  $\bar{\gamma}2$  of Table II. Again, that for carbon is much less than the experimental isotope effect so that  $\Delta a^* (4)$  is appreciable, a conclusion consistent with this mechanism. It is no less consistent to believe that  $\Delta a^* (3) = \Delta a^* (5) = 0$ . Should this be so, the predicted oxygen isotope effect is simply the average of the two  $\nu_{L}^*$  ratios, or 1.016. Agreement with the experimental value, 1.014, is sufficient for so crude a model. To show this result not to be simply a fortuitous one, P was relocated at O-3 (C, Figure 1) and the values in column  $\bar{\gamma}3$  of Table II were then obtained. This time the average oxygen isotope effect, calculated in the same way, is 1.023, quite significantly greater than that observed.

The  $\bar{\gamma}$ -technique thus suffices both to demonstrate the considerably greater cleavage of the C-1-C-4 than the C-2-C-3 bond and to exclude two, otherwise reasonable, models for the transition state:  $\bar{\gamma}1$  and  $\bar{\gamma}3$ . It cannot, however, estimate how accurately the three-atom model,  $\bar{\gamma}2$ , reflects the structure of the more complex real transition state, nor can it easily

consider the rather extensive number of quantitatively distinguishable two-center transition states.

### Exact Calculations

These limitations can only be avoided by use of high-speed digital computers. Large molecules become accessible to exact vibrational analysis and eq. 3 can then be used without approximation.<sup>19</sup> Such exact kinetic isotope effect calculations have indeed been employed for some time,<sup>15,21</sup> but most often toward rather different ends and never for so large a molecule.<sup>22,23</sup>

As before, a reaction mechanism is described by a quantitatively defined, though now more realistically detailed, model of a transition state. Exact calculations guarantee only that such transition states will require an unambiguous set of kinetic isotope effects. The initial choice of possible models derives wholly from preconceived ideas of chemical bonding and molecular structure as applied to a problem of reaction mechanism. Further limitation of the vast number of such models to be considered is rationally provided by examining the sensitivity of computed results to the choice of input parameters (section A, below). The final decision relies upon agreement between observed and predicted kinetic isotope effects unambiguously, if arbitrarily, defined by 95% confidence limits (section B).

A. Of the three sets of input parameters: masses, geometry, and force constants, only the last two are adjustable and, of these, geometry tends to have the lesser influence.<sup>24</sup> Computed isotope effects are insensitive to the choice of reactant geometry but trivially sensitive to its changes in the transition state. Only three extreme possibilities were therefore considered for the latter (Figure 2). A is identical with that of the reactant, B is appropriate as an extreme of two-center cleavage, and C is appropriate as the one-center extreme.<sup>25</sup> As will become obvious (Tables V, VII, VIII, and IX), differences between these extremes have no more effect on computed results than the smallest of force constant perturbations.

(19) The FORTRAN program employed uses the Wilson *FG* matrix technique. Written by J. H. Schachtschneider<sup>20</sup> and subsequently modified by M. Wolfsberg,<sup>13</sup> it was further altered, if only trivially, both to make it compatible with the Cornell C. D. C. 1604 and to expedite the unusually lengthy computations required for this study.

(20) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta.*, **19**, 85, 117 (1963).

(21) (a) H. S. Johnston, *Advan. Chem. Phys.*, **3**, 131 (1960); T. Sharp and H. S. Johnston, *J. Chem. Phys.*, **37**, 1541 (1962); (b) H. S. Johnston, W. A. Bonner, and D. J. Wilson, *ibid.*, **26**, 1002 (1957); H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.*, **83**, 1 (1961); W. E. Falconer, B. S. Rabinovitch, and R. J. Cvetanovic, *J. Chem. Phys.*, **39**, 40 (1963); J. H. Current and B. S. Rabinovitch, *ibid.*, **38**, 1967 (1963).

(22) The only prior attempt at mechanistic exploitation is that of A. V. Willi, *Helv. Chim. Acta*, **47**, 647, 655, 837 (1964).

(23) In practice, the magnitude of the still-significant computational effort was reduced by "cutting off" the four hydrogens not bonded to C-1 or C-4 (see ref. 21a and 15 for justification of this technique). Those torsional coordinates not redundant with angle bends were also ignored. Forty frequencies were thereby obtained for every sixteen atom problem in 52 internal coordinates. The latter compromise required minor auxiliary corrections (Supplementary Data) which also compel obedience to the product rule.

(24) This seems to be quite general: M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964).

(25) Interatomic distances for stretched bonds were calculated from the Pauling bond order-bond length relationship,<sup>14b</sup>  $r_n = r_{n-1} - 0.6 \log n$  with  $n = 0.1$ , but without prejudice to other values of this parameter or to other such relationships that might have been employed.

Force constants derive importance only by their changes in going to the transition state. Those chosen for the reactant (Table III) are realistic but by no means unambiguous and, indeed, reproduce the five obviously characteristic infrared maxima (at 2882, 1869, 1776, 1727, and 1616  $\text{cm}^{-1}$ ) rather badly (errors of 1.4, 3.8, 1.1, 4.3, and 3.1%). That this is of no concern is demonstrated in Table IV. Diminishing the C-2-O-3 stretching force constant from 5.4 to 4.8  $\text{mdynes}/\text{\AA}$ . in *both* reactant and transition states changes the computed isotope effects by an experimentally undetectable amount.<sup>26</sup>

Table III. Valence Force Constants

	Mdynes/ $\text{\AA}$ .	Ref.
Stretching force constants		
C—H	4.7	a
C—C	4.3	a
C=O	10.5	b
C—O	5.4	c
Bending force constants		
H—C—H	0.54	a
H—C—C	0.64	a
Three heavy atoms	1.0	a,c
C=O out-of-plane wag	0.30	d

<sup>a</sup> Reference 20, calculation V. <sup>b</sup> S. Bratoz and S. Besnainou, *Compt. Rend.*, **248**, 564 (1959). <sup>c</sup> E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 175. <sup>d</sup> J. Overend and J. C. Evans, *Trans. Faraday Soc.*, **55**, 1817 (1959).

Table IV. Consequences of an Erroneous Force Constant Assignment<sup>a</sup>

Location of heavy isotope	$Q_h/Q_t^b$	$Q_h^*/Q_t^*$	$k_1/k_h$
C-4	1.266 631	1.225 637	1.033 447
	1.266 626	1.225 634	1.033 446
O-3	1.278 286	1.271 697	1.005 181
	1.275 208	1.268 602	1.005 208
O-5	1.249 610	1.211 912	1.031 106
	1.249 608	1.211 911	1.031 105

<sup>a</sup> Upper lines result from  $F_{C_2-O_3}$  (stretch) = 5.4, lower lines from 4.8  $\text{mdynes}/\text{\AA}$ . The transition state force field is that of Table IX, column 1. <sup>b</sup> Ratios of isotopic partition functions.

This is, of course, consistent with eq. 4 and with the results of other exact calculations.<sup>13</sup> With much the same justification, only the 12 force constants which incorporate positions of isotopic substitution (of a total of 52) were varied. A significant limitation on their freedom is provided by the requirement that a transition state possess one, and only one, new unrestrained mode. Insufficient and excessive attenuation of the reactant force constants (conveniently achieved by factors  $X_i = F_{ii}^*/F_{ii}$ ) generates either no or two such reaction coordinates and are thereby excluded. No other restrictions were placed on  $\nu^*_L$ , the "frequency" of this mode, permitting it to be either zero or imaginary. The former implies a transition state too short to detect curvature at the top of a

(26) The values of Table III depend in part on the force fields and approximations of the references cited. Yet we know of no C—O stretching constant reported to be less than 5.0  $\text{mdynes}/\text{\AA}$ .

Table V. Two-Center Transition States<sup>a</sup>

		$X_{C-2-O-3} = 1$				
$X_{C-1-C-4}$		0.5	0.4	0.3	0.1	
$\nu^*_{Ll}/\nu^*_{Lh}$	O-3 <sup>b</sup>		1.0124 1.0148	1.0105	1.0052	
		1.0166				
	O-5		1.0150 1.0123	1.0164	1.0209	
		1.0109				
	C-4	1.0088 1.0094	1.0088 1.0091	1.0087	1.0074	
$k_l/k_h$	O-3		1.0159 1.0214	1.0139	1.0083	Acceptable range
		1.0233				
	O-5		1.0174 1.0139	1.0194	1.0250	
		1.0120				
	C-4	1.0258 1.0290	1.0289 1.0313	1.0320	1.0373	
$\bar{O}^c$			1.0167 1.0177	1.0166	1.0166	1.0125— 1.0153
		1.0176				
	C-4	1.0258 1.0290	1.0289 1.0313	1.0320	1.0373	1.0287— 1.0319

<sup>a</sup> Geometry: A, for upper values; B, for lower rules. <sup>b</sup> Location of heavy isotope. <sup>c</sup> Computed average oxygen isotope effects.

barrier; the magnitude of the imaginary  $\nu^*_{Ll}$  measures this curvature. Further limitations proved desirable only for two-center transition states and were there provided by requiring that both bending and stretching force constants which incorporate any weakened bond be attenuated equally.

B. Two-center transition states are appropriately defined by the assumption that a smaller increase in potential energy results from the *concurrent* extension of both the C-1-C-4 and C-2-O-3 bonds than by equal, but *successive*, extensions of each.<sup>27</sup> Its mathematical equivalent is the introduction of a cross term to the quadratic potential function (eq. 8) with negative  $F_{ab}^*$  and with  $S_a$  and  $S_b$  identified as increments of C-1-C-4 and C-2-O-3 bond length. The term vanishes for consecutive extension ( $S_a$  or  $S_b = 0$ ) but diminishes  $V^*$  if extension is concurrent. Equation 8a

$$V^* - V_0^* = F_{ab}S_aS_b + \frac{1}{2}\sum F_{ii}^*S_i^2 \quad (8)$$

$$F_{ab}^* \leq -(F_{aa}^*F_{bb}^*)^{1/2} \quad (8a)$$

conveniently generates a transition state irrespective of the attenuation of the C-1-C-4 and C-2-O-3 force constants.<sup>28,29</sup>

Table V illustrates the results of weakening only the C-1-C-4 bond. The computed  $k_{16}/k_{18}$ , very largely a classical isotope effect, is much too large despite the absence of any C-2-O-3 force constant attenuation. The physical origin of  $F_{ab}^*$ , moreover, remains obscure so long as such attenuation is absent. There are, however, a number of ways to diminish  $k_{16}/k_{18}$  and thereby permit some marginal weakening of the C-2-O-3 bond.

Rather than investigate them all, a limiting force field was carefully constructed to make  $k_{16}/k_{18}$  as insensitive as possible to such weakening and so to set

(27) Concurrent contraction must likewise be favored over consecutive. The properties of a transition state are independent of the direction from which it is approached.

(28) An analogous definition,  $F_{ab} \geq (F_{aa}F_{bb})^{1/2}$ , has long been employed for concerted displacement reactions: D. R. Herschbach, H. S. Johnston, K. S. Pitzer, and R. E. Powell, *J. Chem. Phys.*, **25**, 736 (1956); F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(29) In practice, eq. 8a did not quite achieve this end since, with bonds contained in the same ring, their extensions are not quite independent. Multiplication of  $F_{ab}$  by only 1.1 corrected this deficiency without other detectable consequence.

a minimal value for  $X_{C-2-O-3}$  (Table VI). It is important to note that the convenient single reaction progress variable,  $\alpha$ , cannot also be applied to the C-1-C-4 bond if agreement with the experimental  $k_{12}/k_{13}$  is to be retained. Whatever else occurs, this bond must be very largely (but not completely) broken. To further minimize the consequences of C-2-O-3 bond weakening, the corresponding reactant stretching constant was assigned the low value, 4.8 mdynes/Å., so that a fixed fractional decrease produced a smaller absolute decrease and therefore a smaller isotope effect.

Table VI. Limiting Force Fields for Two-Center Transition States

Bond	—Stretching force constants, mdynes/Å.—		
	Reactant	Product	Transition state
C-1-C-4	4.3	0	0.43
C-4-O-5	10.5	15.5	<i>a</i>
C-4-O-3	5.4	15.5	<i>a</i>
C-2-O-3	4.8	0	<i>a</i>

<sup>a</sup>  $F_{ii}^* = F_{ii}^{\text{reactant}} + \alpha(F_{ii}^{\text{product}} - F_{ii}^{\text{reactant}})$ .

The results (Table VII) reveal a most unusual example of overcompensation; as the C-2-O-3 bond is progressively *weakened*, the predicted  $k_{16}/k_{18}$  *diminishes*, if not nearly so rapidly as  $k_{12}/k_{13}$ . Both computed isotope effects are acceptable with  $\alpha = 0.2$  for the extended geometry B, perhaps with slightly lesser  $\alpha$  for geometry A. However brutally achieved, a two-center transition state is quite possible though with the restriction that there be no more than 20% weakening of the C-2-O-3 bond and, if that, no less than 90% weakening of the C-1-C-4 bond.

One-center transition states are defined by the conditions that  $X_{C-2-O-3}$  (stretches and bends) = 1 and that  $X_{C-1-C-4}$  (stretch) be either negative or zero. Table VIII shows that the first possibility (imaginary  $\nu_L$ ) cannot be fitted to the experimental data despite independent variation of three parameters.

By contrast, the second possibility ( $\nu_L = 0$ ) is realized with only minimal variation of parameters (Table IX). It was here essential to set the C-1-C-4

**Table VII. Limiting Two-Center Transition States<sup>a</sup>**

$\alpha$		0.1	0.2	0.3	0.4	
$X_{C-1-C-4}$		0.1	0.1	0.1	0.1	
$X_{C-2-O-3}$		0.9	0.8	0.7	0.6	
$X_{C-4-O-3}$		1.18	1.37	1.55	1.73	
$X_{C-4-O-5}$		1.05	1.10	1.14	1.19	
	O-3	1.0064 1.0079	1.0068 1.0083	1.0074 1.0089	1.0080	
$\nu^*_{Li}/\nu^*_{Lh}$	O-5	1.0194 1.0179	1.0193 1.0177	1.0192 1.0175	1.0189	
	C-4	1.0079 1.0073	1.0080 1.0075	1.0081 1.0076	1.0082	
	O-3	1.0091 1.0129	1.0091 1.0124	1.0096 1.0123	1.0103	Acceptable range
	O-5	1.0217 1.0192	1.0200 1.0172	1.0182 1.0152	1.0164	
$k_l/k_h$	$\bar{O}$	1.0154 1.0160	1.0145 1.0148	1.0139 1.0137	1.0134	1.0125– 1.0153
	C-4	1.0330 1.0334	1.0286 1.0297	1.0244 1.0262	1.0204	1.0287– 1.0319

<sup>a</sup> Geometry: A, for upper values; B, for lower values.

**Table VIII. One-Center Transition States<sup>a</sup>**

		$X_{C-2-O-3} = 1$ $X_{C-1-C-4} < 0$				
$X_{C-1-C-4}$ (stretch)		-0.1	-0.2	-0.1	-0.1	
$X_{C-1-C-4}$ (bends)		0.8	0.8	0.1	0.1	
$X_{C-4-O-5}$ (stretch)		1	1	1	1	
	O-3	1.0043 1.0034	1.0044 1.0033	1.0033 1.0024	1.0033 1.0024	
$\nu^*_{Li}/\nu^*_{Lh}$	O-5	1.0158 1.0161	1.0125 1.0135	1.0152 1.0157	1.0152 1.0157	
	C-4	1.0071 1.0069	1.0085 1.0083	1.0069 1.0067	1.0069 1.0067	
	O-3	1.0049 1.0042	1.0048 1.0040	1.0058 1.0051	1.0058 1.0051	Acceptable range
	O-5	1.0166 1.0169	1.0126 1.0137	1.0188 1.0193	1.0154 1.0159	
$k_l/k_h$	$\bar{O}$	1.0107 1.0105	1.0087 1.0088	1.0123 1.0121	1.0106 1.0105	1.0125– 1.0153
	C-4	1.0181 1.0343	1.0311 1.0372	1.0401 1.0429	1.0371 1.0399	1.0287– 1.0319

<sup>a</sup> Geometry: A, for upper values; C, for lower values.

**Table IX. One-Center Transition States<sup>a</sup>**

$X_{C-4-O-5}$ (stretch)	1.0	1.1	1.2	1.3	Acceptable range
O-3	1.0052 1.0079	1.0052	1.0052 1.0079	1.0079	
O-3	1.0311 1.0273	1.0277	1.0244 1.0206	1.0175	
$\bar{O}$	1.0180 1.0273	1.0163	1.0147 1.0142	1.0127	1.0125– 1.0153
C-4	1.0334 1.0363	1.0305	1.0276 1.0304	1.0277	1.0287– 1.0319

<sup>a</sup> Geometry: A, for upper values; C, for lower values.

bending constants to zero in order to generate a reaction coordinate. Gentle tightening of the carbonyl stretching constant (by 2.1 mdynes/Å.) then

suffices to reproduce the experimental values with the extended geometry C. It is gratifying to note that the carbonyl stretching constant of the formyl radical is reported to be greater than that of formaldehyde.<sup>30</sup>

### Discussion

Exact calculations add both rigor and precision to the conclusions earlier derived by the  $\bar{\gamma}$  approximation but leave their qualitative sense unchanged. The experimental kinetic isotope effects are most simply accommodated by a transition state in which the carbon-carbon bond is broken, the carbonyl bond is tightened, and the C-2-O-3 bond is kept wholly intact. Some weakening of this last bond cannot be excluded but quantitative evaluation has shown its permissible

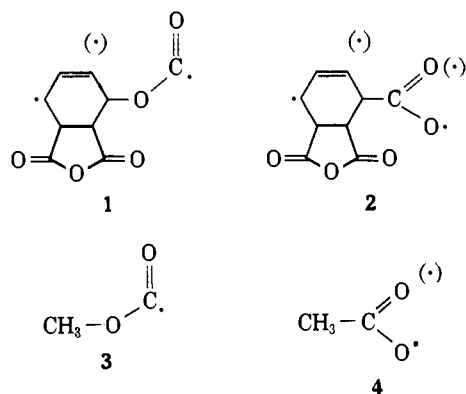
(30) G. E. Ewing, W. E. Thompson, and G. C. Pimentel, *J. Chem. Phys.*, **32**, 927 (1960).

extent to be small, even with the most biased of assumptions.<sup>31</sup>

Such detailed structural information has not hitherto been available for so complex a transition state. In its absence, several reasonable generalizations have been proposed, each attempting to deduce some structural feature of a transition state by comparing its energy with those of its precursors and/or products of known structure. It now becomes instructive to apply such rules to  $\alpha$ -pyrone adduct decarboxylation and so to judge their predictive power.

The first of these concerns the degree to which the structure of the transition state might resemble that of the reactant either more or less than it does that of the product. As elaborated by Hammond,<sup>32</sup> it would anticipate a "reactant-like" transition state structure for what is here presumed to be a highly exothermic reaction. How appropriately this describes the structure elucidated is very much a matter of opinion. On the other hand, the data do not really preclude an initial, though necessarily rate-controlling, endothermic formation of the biradical **1** (Chart I) as an unstable intermediate. One would then expect the transition state to resemble **1** much more than it does the reactant, and this prediction agrees more obviously with the experimental conclusion.

Chart I



The second rule concerns the relative weakening of the C-1-C-4- vs. the C-2-C-3 bond in the transition state. Relying, as does the first, on an assumed correlation of rates with equilibria,<sup>32b</sup> it would predict the preferred direction of cleavage to be that tending to generate the more stable biradical; a lesser bond dissociation energy is taken to imply a weaker bond in the transition state.<sup>33</sup> Since **1** and **2** contain the same ring system, their relative stability is more simply estimated from those of the carbomethoxyl and acetoxyl radicals (**3** and **4**). A choice is directly available since mercury-photosensitized decomposition of methyl acetate permits scavenging of the carbomethoxyl but not the acetoxyl radical.<sup>34</sup> Within context then, the

(31) This reservation is both real and important but has sufficiently little bearing on the essentially qualitative discussion to follow that it will not again be explicitly considered.

(32) (a) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); (b) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938), and preceding references cited.

(33) (a) R. Huisgen, *Angew. Chem.*, **75**, 742 (1963); (b) M. G. Ettlinger and E. S. Lewis, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1960, p. 95P.

(34) R. F. Pottle and F. P. Lossing, *Can. J. Chem.*, **39**, 1900 (1961). In solution, the carbo-*t*-butoxyl radical may be trapped (P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *J. Am. Chem. Soc.*, **84**, 3101 (1962)) but

carbomethoxyl would appear the more stable and hence **1** more so than **2**. The preferred direction could indeed have been anticipated.

The last question, the one of greatest concern, is that of any inherent preference for one-center vs. two-center cleavage and is best regarded by considering the microscopic reversal of decarboxylation. The unrealized Diels-Alder addition of carbon dioxide to *cis*-1,2-dihydrophthalic anhydride must proceed in two stages. The first of these includes both the breaking of one of the four formal C-O bonds of the "dienophile" and the formation of a new one, to be the C-2-O-3 bond of the product. It terminates approximately at the transition state whereupon the second stage, formation of the C-1-C-4 bond, results in collapse to product. This addition has presumably been discouraged by its necessary requirement that essentially all the stabilization energy of carbon dioxide be lost in the transition state.<sup>35</sup>

A two-stage mechanism is, to be sure, in keeping with the hypothesis that such processes are to be expected of all Diels-Alder reactions.<sup>36</sup> The semantic difficulties of this hypothesis, noted by others,<sup>37</sup> should now be reconsidered. "Two-stage" implies the ability to describe events lying along the approaches to a transition state but without commitment that intermediates be found there. Unfortunately, these regions are inaccessible to experimental evidence in the absence of such intermediates. As illustration, the addition of 1,1-dichloro-2,2-difluoroethylene to the isomeric 2,4-hexadienes is now known to proceed in two discrete steps through a biradical intermediate.<sup>38</sup> This is known because the reaction was observed to lack the full stereospecificity hitherto associated with all cycloaddition reactions.<sup>39</sup> It must of course proceed in two stages but then such a description becomes superfluous in this example and inapplicable to the more general case of stereospecific addition.

By contrast, carbon dioxide addition may or may not proceed in two steps. It must, however, proceed in two stages. This is known because the relevant structure of the transition state is known and clearly distinguishes the rather different microscopic processes which precede it from those which follow. Although this conclusion *cannot* be extrapolated to other cycloaddition reactions, the elucidation of transition state structure *can*. Whether or not such reactions will be found to proceed in two stages is, in any event, at last accessible to experimental evidence.

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not the pivaloyloxyl (P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960)) if under somewhat different conditions.

(35) A less happy corollary is that this stabilization cannot contribute to the lowering of decarboxylation activation energy whose dissection frustrates any simple-minded analysis.

(36) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(37) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

(38) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964).

(39) S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **85**, 2341 (1963); ref. 3a; K. Alder and M. Schumacher, "Fortschritte der Chemie Organischer Naturstoffe," Vol. X, L. Zechmeister, Ed., Springer-Verlag, Vienna, 1953, p. 2.



berg with regard to exact force field calculations is most gratefully acknowledged.

## Appendix

*Averaging of Computed Isotope Effects.* The observed oxygen isotope effect,  $k_{16}/k_{18}$ , is the average of that resulting from substitution at O-3 (Figure 2), denoted as  $k_{16}/k_{18}^3$  and that from substitution at O-5,  $k_{16}/k_{18}^5$ . One must consider not only the proper formulation of this average but also its sensitivity to an unequal distribution of O<sup>18</sup> between the two non-equivalent oxygens.

We define  $r$ , the initial isotopic inhomogeneity, to be the initial concentration of O-3-labeled adduct divided by that of O-5-labeled material and then derive equation A.1 by conventional means. Expansion about  $f = 0$  produces eq. A.2 which is further simplified to eq. A.3 so long as the isotope effects are small.

$$(1+r) \left[ 1 - \frac{R_f}{R_i} f \left( \frac{1+R_1}{1+R_f} \right) \right] = r \left[ 1 - f \left( \frac{1+R_1}{1+R_f} \right) \right]^{k_{18}^3/k_{16}} + \left[ 1 - f \left( \frac{1+R_1}{1+R_f} \right) \right]^{k_{18}^5/k_{16}} \quad (\text{A.1})$$

$$\left( \frac{k_{18}}{k_{16}} \right)_{\text{obsd}} = \frac{R_f}{R_i} = \frac{r(k_{18}^3/k_{16}) + (k_{18}^5/k_{16})}{r+1} \quad (\text{A.2})$$

$$\left( \frac{k_{16}}{k_{18}} \right)_{\text{obsd}} = \frac{r(k_{16}/k_{18}^3) + (k_{16}/k_{18}^5)}{r+1} \quad (\text{A.3})$$

*Isotopic Inhomogeneity.* Although every reaction used to prepare the adduct proceeds in high yield, at least one of them, the acid-catalyzed, decarbonylative condensation of malic to coumalic acid, provides ample opportunity for an intramolecular isotope effect.

This must result in a value of  $r$  equal to it in magnitude and independent of yield.

The problem is least ambiguously evaluated by first assuming isotopic homogeneity and then inquiring how large a discrepancy in isotopic composition might be tolerated before the resulting error reaches the experimental uncertainty. The error is defined as

$$\epsilon \equiv (k_{16}/k_{18})_r - (k_{16}/k_{18})_{r=1}$$

Substitution in eq. A.3 produces eq. A.4 which shows  $\epsilon$  to depend both on  $r$  and on the difference between the

$$\epsilon = \frac{1}{2} \left( \frac{r-1}{r+1} \right) \left( \frac{k_{16}}{k_{18}^3} - \frac{k_{16}}{k_{18}^5} \right) \quad (\text{A.4})$$

two isotope effects to be averaged. Predicted differences between the two ratios have never exceeded 0.026. With  $\epsilon \leq 0.0019$  (the standard deviation),  $r$  (or its reciprocal) becomes dangerous only if greater than 1.34, a value to be compared with 4.5%, the maximum variation of natural O<sup>18</sup> thus far detected,<sup>7a</sup> and 19%, the (unrealistically high) room temperature maximum value of an O<sup>18</sup> isotope effect as evaluated by Bigeleisen some time ago.<sup>12</sup> Isotopic homogeneity is a comfortable assumption.

## Supplementary Data

These have been deposited with the American Documentation Institute, c/o Library of Congress, Washington 25, D. C., as Document No. 8266 and may be obtained by remitting \$1.75 for microfilms and \$2.50 for photographs. They include the assignments of atomic cartesian coordinates, valence coordinate, selected moments of inertia and frequencies, a complete list of essential data obtained for the 23 transition state force fields and two reactant force fields investigated, and details of auxiliary corrections.<sup>23</sup>

## Cyclononatetraenide. A Ten- $\pi$ -Electron Aromatic System

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*Cyclononatetraenide, isolated and characterized as the tetraethylammonium salt, shows aromatic character as established from <sup>1</sup>H and <sup>13</sup>C n.m.r. data and intense absorption in the ultraviolet. Reaction of C<sub>9</sub>H<sub>9</sub><sup>-</sup> with water leads to a mixture of products including indene, dihydroindene, and presumably the labile cyclononatetraene. Evidence for the existence of the tetraene was found in partial reconversion of the water-treated product to C<sub>9</sub>H<sub>9</sub><sup>-</sup> and hydrogenation to cyclononane. Cyclononatetraenide undergoes electron transfer with tetracyanoethylene and proton exchange with cyclopentadiene.*

Validation of the Hückel ( $4n + 2$ )  $\pi$ -electron rule<sup>1</sup> for aromaticity in carbomonocyclic systems has been well established where  $n = 1$ . In spite of several attempts to uncover systems where  $n = 2$ , the cyclooctatetraene dianion until recently constituted the single example<sup>2</sup> of a ten- $\pi$ -electron carbomonocyclic system. A second example has been found in the

(1) E. Hückel, *Z. Physik*, **70**, 204 (1931).

(2) (a) A. R. Ubbelohde, *Chem. Ind. (London)*, 153 (1956); (b) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (c) H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 231 (1961).