Kinetic Isotope Effect in the Thermolysis of Methylenecyclobutane

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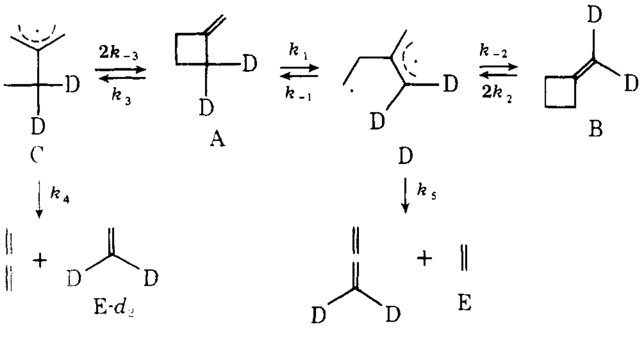
The intramolecular kinetic isotope effect for the thermolysis of equilibrated methylenecyclobutane-d_2 was investigated at 515 °C as a function of pressure. A high-pressure value of k_H/k_D (ethylene/ethylene-d_2) = 0.9 was obtained at 13 cm of N_2 pressure. This value decreased to 0.86 at 70 μm total pressure. No intermolecular kinetic isotope effect was measured for the formation of ethylene from labeled and unlabeled methylenecyclobutane. The pressure and temperature dependence of the intramolecular kinetic isotope effect was used as evidence in establishing the inverse nature of the effect. The isotope effect observed was explained in terms of competing equilibrium and kinetic isotope effects in which the equilibrium isotope effects dominate. It was concluded on the bases of these results that an acyclic intermediate is involved in the fragmentation of methylenecyclobutane to ethylene and allene. The results also support the notion that deuterium prefers to accumulate at the methylene group with the greatest p charater in the carbon–hydrogen bond.

The thermolysis of methylenecyclobutane is a reaction which has been studied in great detail both experimentally and theoretically in the past few years.[1-5] The experimental data are supportive of the presence of an intermediate which is responsible (at least in part) for the automerization observed in methylene-d_2-cyclobutane and for the subsequent fragmentation to allene and ethylene observed at higher temperatures. This reaction, if analyzed as described above, offers an excellent opportunity to investigate the nature of long range isotope effects often ignored or assumed unimportant in the absence of sufficient data. In addition, the small molecular size permits investigation of the kinetic isotope effects into the falloff region, not often experimentally accessible.[5]

We would like to report the results of our experiments on the intermolecular and intramolecular kinetic isotope effect of methylenecyclobutane-d_2 and to describe some experiments which take advantage of the pressure dependence of the kinetic isotope effect. In addition, we wish to present evidence which suggests that the precursor to ethylene and allene is an acyclic intermediate, and as such the possibility of extensive bonding in interactions between the termini of the radical centers is precluded.

A kinetic analysis of the thermolysis of methylenecyclobutane-d_2 is given in Scheme I. The equilibrium constant, K, and the kinetic expression for formation of ethylene were derived from the steady-state approximation for D by requiring that the rate of automerization (k_{-1}, k_{-2}) is much faster than the rate of fragmentation (k_5). A similar expression for C gives the rate of formation of ethylene-d_2. Equation 2 gives the ratio of these rates in terms of the concentration of A. Equation 3 is valid provided that the relative concentrations of A and B remain invariant (i.e., equilibrium is rapidly established and maintained). Such a condition is satisfied by noting that the activation energy for automerization is approximately 50 kcal compared to 63.3 kcal for fragmentation, while the frequency factors for both processes are comparable.[1,2] At 500 °C the ratio of isomerization/fragmentation is approximately 500:1.

Scheme I. Kinetic Analysis of the Intramolecular Isotope Effect in Methylenecyclobutane

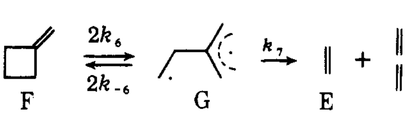


$$K = [\mathrm{A}]/[\mathrm{B}] = \frac{2k_{-1}k_2}{k_1k_{-2}} = 2.0 \qquad (1)$$

$$\frac{\mathrm{d}[\mathrm{E}]/\mathrm{d}t}{\mathrm{d}[\mathrm{E}\text{-}d_2]/\mathrm{d}t} \cong \frac{2k_5k_1k_{-3}[\mathrm{A}]}{k_4k_{-1}k_3[\mathrm{A}]} \qquad (2)$$

$$[\mathrm{E}]/[\mathrm{E}\text{-}d_2] \cong \frac{4k_5k_2k_{-3}}{k_4Kk_{-2}k_3} = \frac{2k_5k_2k_{-3}}{k_4k_{-2}k_3} \qquad (3)$$

Scheme II. Kinetic Analysis of the Intermolecular Isotope Effect in Methylenecyclobutane



$$\mathrm{d}[\mathrm{E}]/\mathrm{d}t \cong (k_7k_6[\mathrm{F}])/k_{-6} \qquad (4)$$

$$\frac{[\mathrm{d}[\mathrm{E}]/\mathrm{d}t]_{\mathrm{F}}}{[\mathrm{d}[\mathrm{E}]/\mathrm{d}t]_{\mathrm{A}}} \cong \frac{k_7k_6k_{-1}[\mathrm{F}]}{k_5k_{-6}k_1[\mathrm{A}]} = \frac{k_7k_6k_{-2}[\mathrm{F}]}{k_5k_{-6}k_2[\mathrm{A}]} \qquad (5)$$

The kinetic description used for the intermolecular kinetic isotope effect is given in Scheme II. Using a similar steady-state approach, the relative rate of formation of ethylene from A can be compared to ethylene formation from F (eq 5).

Methylenecyclobutane-d_2, in which the deuterium was equilibrated at both vinylic and allylic positions, was prepared by reduction of cyclobutanecarboxylic acid with lithium aluminum deuteride (98%), acetylation with acetyl chloride, and pyrolysis at ~500 °C.[2] The methylenecyclobutane isolated was purified by preparative gas chromatography. Thermolysis was conducted in a flow system, a static system, and a diffusion stirred flow apparatus.[6,7] The ethylene produced was separated from allene and methylenecyclobutane by standard vacuum line techniques and analyzed by mass spectroscopy at 20 eV. The raw data were corrected for the P − 2 peak arising from ethylene-d_2 and for 2% methylenecyclobutane-d_1 (assumed from $LiAlD_4$ 98% isotopic purity). For additional details, see the Experimental Section.

The data for the intramolecular kinetic isotope effect measured under conditions of high pressure are given in Table I. Runs 1–5 summarize the results obtained at 515 °C at a pressure of approximately 13 cm of N_2 in a flow reactor. Equating the observed ethylene/ethylene-d_2 ratio of 1.79 to eq 3 and substituting the experimentally measured equilibrium constant K = 2.0[1,2,8] require the combination of rate constants $k_5k_2k_{-3}/k_4k_{-2}k_3$ to numerically equal 0.895. If long

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Table I. High-Pressure Kinetic Isotope Effects in Methylenecyclobutane-d_2

run[a]	pressure added N_2, cm	temp, °C	methylenecyclobutane initial, mmol	ethylene recovered, mmol	% reaction	raw data m/e			ethylene composition		k_H/k_D
						28	29	30	E	E-d_2	
1	20	518	0.099	0.049	49	0.617	0.075	0.308	0.646	0.354	0.91
2	13.2	518	0.109	0.046	42	0.618	0.072	0.311	0.644	0.356	0.90
3	12.8	515	0.054	0.015	28	0.612	0.075	0.313	0.639	0.361	0.89
4	13	515	0.086	0.033	38	0.614	0.072	0.314	0.640	0.360	0.89
5	13.3	515	0.077	0.033	43	0.615	0.073	0.312	0.642	0.358	0.90
6	17.9	470	0.043	0.018	42	0.615	0.077	0.308	0.644	0.355	0.91
7	17.9	436	0.051	0.043	86	0.603	0.093	0.305	0.643	0.357	0.90
8	17.9	413	0.050	0.034	68	0.602	0.087	0.310	0.638	0.362	0.88
9	18.3	392	0.054	0.017	31	0.610	0.067	0.322	0.631	0.369	0.86

[a] Runs 1–5 were performed in a flow system; 6–9 were performed in a static system.

range isotope effects are ignored, then $k_2/k_{-2} = k_3/k_{-3}$ and $k_4 > k_5$, a result totally inconsistent with what is generally observed for secondary deuterium isotope effects in a reaction where the carbon atom containing the isotopic label undergoes a change in hybridization from sp^3 to sp^2 during the rate-determining step.[9,10] Alternatively, taking long range isotope effects into consideration and making the reasonable assumption that $k_5 > k_4$ lead to the conclusion that the net isotope effect observed is dominated by an equilibrium isotope effect which favors the formation of C.[25]

One of the main difficulties in measuring intramolecular isotope effects is the necessity of establishing the isotopic composition of both reactant and product. Unlike the intermolecular case, where analysis of reactant or product at different time intervals ($t = 0, t = \infty$) is sufficient to establish the effect, comparison of two independent analyses in the intramolecular case can compound the difficulty encountered with experimental errors. Consequently, any experimental technique which could be used to amplify the magnitude of an observed intramolecular isotope effect, while of no mechanistic value in itself, could be of substantial value in conclusively demonstrating the presence or absence of an isotope effect in cases (both heavy atom and hydrogen) when the effect is small or the experimental error large.

The surprising results obtained on the intramolecular isotope effect in methylenecyclobutane prompted us to try to independently confirm their authenticity. Our approach was to examine the pressure dependence on the magnitude of the kinetic isotope effect. Blades, Gilderson, and Wallbridge have reported the pressure dependence of the intramolecular kinetic isotope effect in the thermolysis of ethyl-*1,1,2,2-d*$_4$ chloride.[11] They observed that k_H/k_D increased from 2.05 at roughly 10 cm of pressure to 2.45 at 1 mm of pressure. If the observed effect in our experiments was real, we reasoned that the ratio of ethylene/ethylene-d_2 should decrease as the pressure is decreased. Runs 10–14 in Table II contain results of our experiments performed in a diffusion stirred flow apparatus at a pressure range of approximately 30 to 70 μm. As is evident from Table II, the high-pressure value of 0.9 decreases to 0.86 and 0.78 at approximately 70 and 30 μm.[24] This "amplification" of the intramolecular isotope effect is consistent with the results expected of an inverse isotope effect and is to the best of our knowledge the first report of the pressure dependence on an inverse intramolecular isotope effect.[13] Although the pressure dependence of the kinetic isotope effect has both theoretical and experimental justification,[11,12,23] the novelty of these results can hardly be used to conclusively establish the inverse nature of the effect. These results, however, are consistent with expectations.

Additional support reinforcing these conclusions was obtained from the temperature dependence observed for the intramolecular isotope effect (runs 6–9 in Table I, Figure 1). The observed isotope effect appears to be well-behaved with regard to temperature, and the effect appears more pronounced at the lower temperatures, exactly as expected. A least-squares treatment of the data gave the temperature dependence shown in eq 6. The correlation coefficient was 0.97. These results were obtained for experiments performed at constant volume. The isotope effects obtained at constant pressure, runs 1–5 in Table I, although included in Figure 1, were not included in the calculations.

$$(k_H/k_D)_{\text{intra}} = 1.48\, e^{-361/RT} \qquad (6)$$

Our attention was next focused on locating the position of deuterium substitution in methylenecyclobutane (B or A) mainly responsible for the inverse effect observed. Examination of eq 5 in Scheme II suggests that if long range isotope effects in B are unimportant, then this equation would be expected to reduce to unity since k_7/k_5, k_6/k_2, and k_{-2}/k_{-6} should cancel. Examination of runs 16–19 in Table III suggests that such is the case. The raw data obtained for experiments conducted at approximately 10, 20, and 80% reaction are identical within experimental error. These results are consistent with the interpretation that there is very little disturbance at the isotopically labeled site in B during the course of the reaction. A similar assumption was made by Dolbier and Dai in their study of a related reaction, the dimerization of allene.[14]

Table II. Low-Pressure Kinetic Isotope Effects in Methylenecyclobutane-d_2[a]

run	total pressure, μm	temp, °C	methylenecyclobutane initial, mmol	total ethylene recovered, mmol	% reaction	raw data m/e			ethylene composition		k_H/k_D
						28	29	30	E	E-d_2	
10	70	521	0.127	0.0041	3	0.609	0.070	0.321	0.632	0.368	0.86
11	70	521	0.123	0.0027	2	0.609	0.072	0.319	0.634	0.366	0.86
12	70	520	0.110	0.004	4	0.593	0.096	0.311	0.633	0.367	0.86
13	~50	520	0.10	0.003	3	0.577	0.086	0.337	0.606	0.394	0.77
14	~30	520	0.113	0.003	3	0.575	0.095	0.330	0.612	0.388	0.79

[a] Experiments were performed in the diffusion stirred flow apparatus.

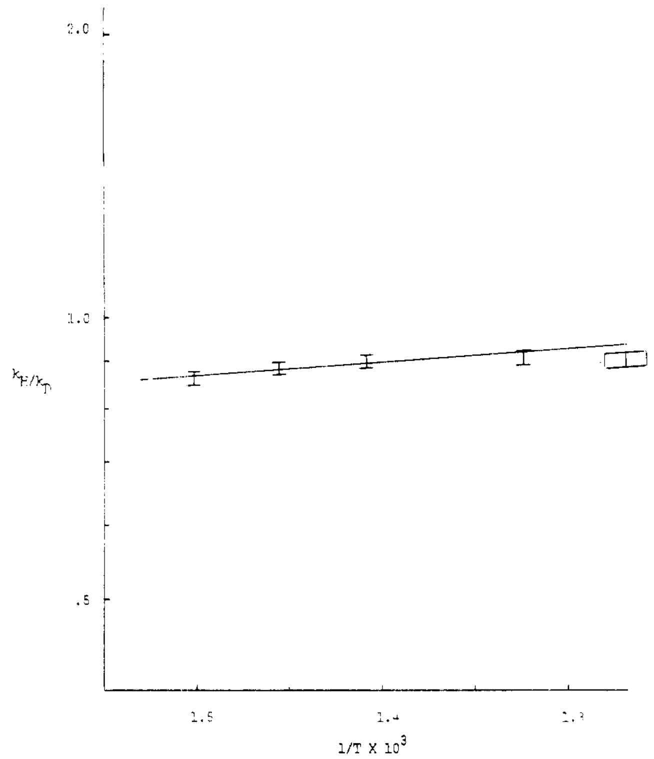
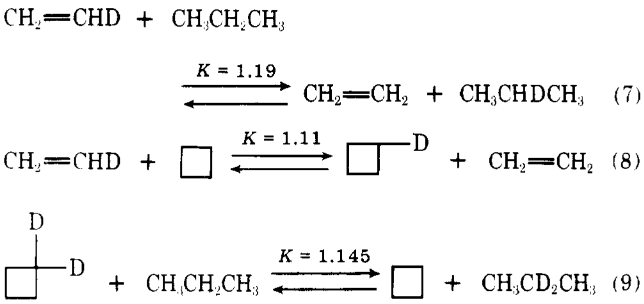


Figure 1. Temperature dependence of the intramolecular kinetic isotope effect in methylenecyclobutane-d_2: (I) single determination, static system; (□□) average of five determinations, flow system.

We now return to the problem of explaining why deuterium in A facilitates formation of ethylene-d_2. Secondary β-isotope effects are known and have generally been associated with hyperconjugation[16] since they show strong conformational dependence, at least in solvolytic reactions.[17] These isotope effects generally are observed to give rise to normal isotope effects, $k_H/k_D > 1$. Examples of equilibrium secondary β-isotope effects measured in the gas phase are to our knowledge not known. S. R. Hartshown and V. J. Shiner, Jr., however, have calculated equilibrium isotope fractionation factors for some hypothetical reactions.[18] Two of these reactions pertinent to this discussion are shown in eq 7 and 8 along with the calculated equilibrium constants. Equation 9 was derived by dividing eq 7 by eq 8 and by assuming the effect of two deuteriums on K to be multiplicative. The equilibrium constant for eq 9 clearly indicates that given a chance, deuterium substitutions at the methylene group favor the acyclic position. Comparing the equilibrium between D and B and G and F, deuterium substitution at the vinylic position, B, would not be expected to significantly perturb the position of equilibrium. Using cyclobutane and propane as models for methylenecyclobutane and the diradical C, deuterium substitution in A according to eq 9 should affect the position of equilibrium by shifting it in the direction of C. This shift is reflected by an enhancement of the concentration of C relative to D (and G). This apparently dominates the direction in which the subsequent fragmentation (k_4 vs. k_5) occurs. As a result, an overall inverse effect is noted.



Acceptance of this explanation of the observed effect requires the acceptance of a discrete acyclic intermediate in the thermolysis reaction. Within the framework of Gajewski's work, these results require the diradical to be the precursor of the allene and ethylene. This of course does not preclude the possibility of other (concerted) processes giving rise to rearrangement of the methylenecyclobutane.

Experimental Section

Methylenecyclobutane-d_2. Methylenecyclobutane-d_2 was prepared by reduction of cyclobutanecarboxylic acid with lithium aluminum deuteride, acetylation with acetyl chloride, and pyrolysis.[2,19] The methylenecyclobutane-d_2 isolated was purified by preparative VPC at room temperature on a squalene column and characterized by comparison with reported spectra.[20] Integration of the NMR spectrum indicated complete equilibration of the deuterium between the methylene and vinyl positions. An equilibrium constant, $K = 2$, was calculated as previously reported.[2]

Thermolysis Experiments. Flow System. The flow system consisted of a 35-cm quartz tube (16 mm o.d.) jacketed with a brass sheath and controlled to ±4 °C. The temperature was monitored by an

Table III. Intermolecular Kinetic Isotope Effects in Methylenecyclobutane at High Pressure[b]

run	pressure added N$_2$, cm	temp, °C	total methylene-cyclobutane initial, mmol	total ethylene recovered, mmol	% reaction	raw data m/e 28	29	30	ethylene from methylene-cyclobutane	ethylene from methylene-cyclobutane-d_2[a]	k_H/k_D
15	13.1	511	0.109	0.089	82	0.714	0.075	0.211	0.318	0.682	
16	12.9	500	0.083	0.016	19	0.715	0.070	0.215	0.312	0.688	0.97
17	12.7	498	0.083	0.011	13	0.716	0.070	0.214	0.315	0.685	0.98
18	12.6	496	0.079	0.013	16	0.716	0.068	0.216	0.312	0.688	0.97
19	12.4	496	0.066	0.010	15	0.724	0.064	0.212	0.323	0.677	1.03

[a] Calculated by correcting for the ethylene produced by methylenecyclobutane-d_2 at high pressure by using the m/e 30 peak and the known m/e 28/30 ratio. [b] Experiments were performed in a flow system by competition.

Table IV. Raw Data for the Thermolysis of Cyclobutane-*1,1,2,2*-d_4 as a Function of Pressure

apparatus	temp, °C	total pressure	observed m/e[c] 28	30	32
flow[a]	460	>85 mm	0.832 ± 0.04	1.0	0.388 ± 0.006
diffusion stirred flow[b]	460	~40 μm	0.798 ± 0.03	1.0	0.383 ± 0.008

[a] Average of five runs, using nitrogen carrier gas pressures from 85 to 210 mm. [b] Average of three runs. [c] Errors reported as standard deviations.

iron–constantan thermocouple kept inside the tube. Flow rates were monitored as the exhaust of the vacuum pump and were kept at approximately 0.25 mL/s. All intermolecular isotope effects were measured by competition and calculated as previously described.[15]

Static and Diffusion Stirred Flow Apparatus. The vessel consisted of a 5-L Pyrex sphere with an outlet and inlet port consisting of 12-mm Pyrex tubing. The temperature was controlled to ±1.5 °C. The functioning of this apparatus in the diffusion stirred flow mode has recently been tested.[7] Low pressures of methylenecyclobutane were generated by using low temperature baths.

Analysis of Ethylene. The isotopic composition of the ethylene was analyzed on an AEI MS 12 mass spectrometer at 20 eV. The background was checked after each run by condensing out unused ethylene. Background corrections were generally not necessary. The fragmentation due to trace amounts of allene and methylenecyclobutane at *m/e* 28 and 30 was not significant. Ethylene exposed to vacuum for prolonged periods of time can be volatilized, even at −196 °C. The possibility that the low-pressure results are simply due to isotopic fractionation of ethylene can be discounted since isotopically labeled ethylenes are more volatile in condensed phase than is ethylene itself.[22]

Data Adjustments. The raw data were analyzed by correcting the *m/e* 28 peak for the P − 2 contribution from *m/e* 30. An authentic sample of ethylene-*1,1*-d_2 was prepared by reducing acetic-d_4 acid with lithium aluminum hydride, acetylation, and pyrolysis of the acetate at 500 °C. The ethylene-d_2 exhibited the following mass spectrum at 20 eV: *m/e* 30 (100%), 29 (16.4%), 28 (14.2%). In addition, 2% methylenecyclobutane-d_1 was assumed to be present (from 98% $LiAlD_4$).[21] Fragmentation of this material was assumed to be statistical. The experimental *m/e* 29 peak was not used in correcting the data. The data reproduced in Tables I and II were obtained from two samples of methylenecyclobutane-d_2 separately synthesized. Both samples gave identical results.

Control Experiments. The following control experiments, not necessarily reported in Tables I–III, were performed. The methylenecyclobutane recovered from both high- and low-pressure runs was reused to check to see if the ratio of ethylene/ethylene-d_2 varied with the extent of decomposition; it did not. The equilibrium constant for equilibration was measured after pyrolysis at low pressure to check for a pressure dependence on *K*. A value of 2.04 ± 0.1 was obtained.

Data Analysis. All entries in Tables I–III are single determinations. The average of runs 1–5, Table I, is 0.9, with a standard deviation of 0.008. Triplicate analysis at 70-μm total pressure, runs 10–12, gave $k_H/k_D = 0.86$, and results obtained at lower pressures, runs 13 and 14 at approximately 50 and 30 μm, gave values of 0.77 and 0.79, respectively. Direct comparison of runs 10–12 with runs 1–5 probably encompasses more risk than comparison with runs 13 and 14 since the former comparison is between experiments performed under vastly different conditions. We have previously shown that intermolecular isotope effects in the thermolysis of cyclobutane measured in flow and diffusion stirred flow apparatus give good agreement with literature values obtained in static systems.[7] To test whether we could reliably compare intramolecular isotope effects measured in flow and diffusion stirred flow systems, we decided to investigate the thermolysis of cyclobutane-*1,1,2,2*-d_4 prepared from dimethyl acetylenedicarboxylate.[7] This system was chosen because the intramolecular isotope effect, k_H/k_D, had been reported as 1[26] and as such should remain pressure independent. The results tabulated in Table IV indicate that within the reproducibility of our results, both flow systems give comparable results when $k_H/k_D = 1$, both in the high-pressure and falloff regions. Thus, comparison of runs 1–5, Table I, with runs 10–12, Table II, should be reliable. Comparison of runs 10–12 with runs 13 and 14 further substantiates the pressure dependence.[24] The approximate signs in runs 13 and 14, Table II, indicate difficulty in maintaining a constant pressure during the course of the experiments primarily because of the extended duration of these experiments. Pressure was maintained by the solid–liquid equilibrium of appropriate solvent baths.

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Registry No.—A, 14597-44-5; B, 14597-43-4; F, 1120-56-5; cyclobutanecarboxylic acid, 3721-95-7; ethylene-*1,1*-d_2, 6755-54-0; acetic-d_4 acid, 1186-52-3.

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(10) Exceptions have been noted for reactions proceeding in the reverse direction: J. E. Baldwin and J. A. Kapecki, *J. Am. Chem. Soc.*, **92**, 4974 (1970); K. E. von Gustorf, D. V. White, J. Leitch, and D. Henneberg, *Tetrahedron Lett.*, 3113 (1969); C. J. Collins, B. M. Benjamin, and G. W. Kabalka, *J. Am. Chem. Soc.*, **100**, 2570 (1978).

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(19) J. M. Conia and J. Gore, *Bull. Soc. Chim. Fr.*, 735 (1963).

(20) Infrared Spectral Data, Serial No. 561, Nuclear Magnetic Resonance Spectral Data, Serial No. 473, American Petroleum Institute, Research Project 44.

(21) Neglecting isotope effects, the composition of methylenecyclobutane should be 96% d_2 and 4% d_1 starting from 98% $LiAlD_4$. 2% d_1 was chosen because this amount, when considered in conjunction with P − 1 contributions from ethylene-d_2 and ^{13}C contributions from ethylene, generated the observed *m/e* 29 peak of approximately 7%.

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(24) As the pressure is decreased, energization of the molecule should shift from occuring homogeneous to occuring predominately on the surface of the wall. Consequently, there should be among other factors some limiting pressure below which no further pressure effect should be noted. Geometrical considerations of the reaction vessel should therefore be one factor influencing the magnitude of the limiting isotope effect. Such a consideration might explain the effect of pressure on the results of runs 13 and 14, Table II. This was not investigated further.

(25) An alternative mechanism for the thermolysis of methylenecyclobutane could involve two competing but separate processes occuring without similar or common intermediates (C and D): fast methylene equilibration ($A \rightleftharpoons D$) and slower fragmentation to ethylene and allene. Explanation of the regioselective fragmentation observed would require either an inverse isotope effect for formation of the olefins or a temperature dependence on the equilibrium constant, *K*. The former possibility has already been discussed, and the latter is unlikely in view of the fact that *K* values measured at 327 and ~500 °C were identical.[2]

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