Secondary Deuterium Isotope Effects in the Thermolysis of 2,2-Dimethyl-1-vinylcyclobutane

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Secondary deuterium isotope effects for the thermolysis of 2,2-dimethyl-1-vinyl-3,3,4,4-tetradeuteriocyclobutane are reported. A value of k_H/k_D (262.2 °C) for the overall decomposition of the starting material of 1.018 ± 0.008 was determined and values of 1.06 ± 0.04, 0.95 ± 0.04, 0.95 ± 0.08 and 0.98 ± 0.1 are reported for fragmentation to butadiene and 2-methylpropene, and for rearrangement to 4,4-dimethylcyclohexene, *cis*-2-methylhepta-1,5-diene, and 2-methylhepta-1,6-diene, respectively. The isotope effects are discussed in terms of the potential energy surfaces proposed for 1,4-diradicals. It is concluded from these results and the isotope effect observed in thermolysis of [$^2H_8$]cyclobutane that most of the effect in [$^2H_8$]cyclobutane results from cleavage of the first bond, and that the subsequent surface for fragmentation is relatively flat.

The thermolysis of cyclobutane is believed to occur by way of the tetramethylene diradical. Recent experimental results clearly indicate that the lifetime of the species is appreciable as compared with internal bond rotation.[1] Whether this is attributable to entropic factors[2] or a minimum in the potential energy surface is not at present known.[3]

The effect of deuterio-substitution on the thermolysis of cyclobutane is expected to be normal. Since the overall process converts four sp^3 centres into four sp^2 centres, an overall weakening of the out-of-plane bending force constant is expected in the transition state and k_H/k_D should exceed unity regardless of whether the potential energy surface of tetramethylene is flat or contains local minima. Indeed an intermolecular kinetic isotope effect of 1.41 at 449 °C has been reported for the thermolysis of [$^2H_8$]cyclobutane.[4] How much of the overall effect is attributable to cleavage of each of the two carbon–carbon bonds is not known, but this should reflect to some degree the nature of the surface for fragmentation. Results from kinetic studies of 1,1,2,2-tetradeuteriocyclobutane have not offered additional insight into this question.[5]

From an empirical and perhaps oversimplified perspective, treating tetramethylene as a shallow minimum in the potential energy surface with comparable barriers for recombination and fragmentation leads to an expectation that the transition state for ethylene formation should reflect the hybridization changes previously mentioned for cleavage of each bond, and that a significant portion of the overall k_H/k_D measured should be attributable to cleavage of the second bond. Alternatively, if the potential energy surface for tetramethylene is relatively flat and energy decreases monotonically as the second carbon–carbon bond is elongated, as predicted by theoretical calculations,[2,6] then the transition state for ethylene formation should reflect tetramethylene formation. A very uneven contribution to k_H/k_D overall is expected from the sequential breaking of each carbon–carbon bond, with the breaking of the first bond contributing significantly more than the breaking of the second (see Figure). Such an expectation, of course, assumes that the isotope effect originates mainly in changes in the out-of-plane bending force constants of the CH_2 groups.

Recently we have examined the kinetic behaviour of 2,2-dimethyl-1-vinylcyclobutane.[7] Effects of the vinyl and *gem*-dimethyl group combined to produce a sequential regiospecific cleavage of the cyclobutane ring, which is well suited for an investigation of the effect of deuterio-substitution on terminal bond cleavage of the cyclobutane ring. The thermolysis reaction has been shown to be a homogeneous unimolecular process producing the products shown in the Scheme.

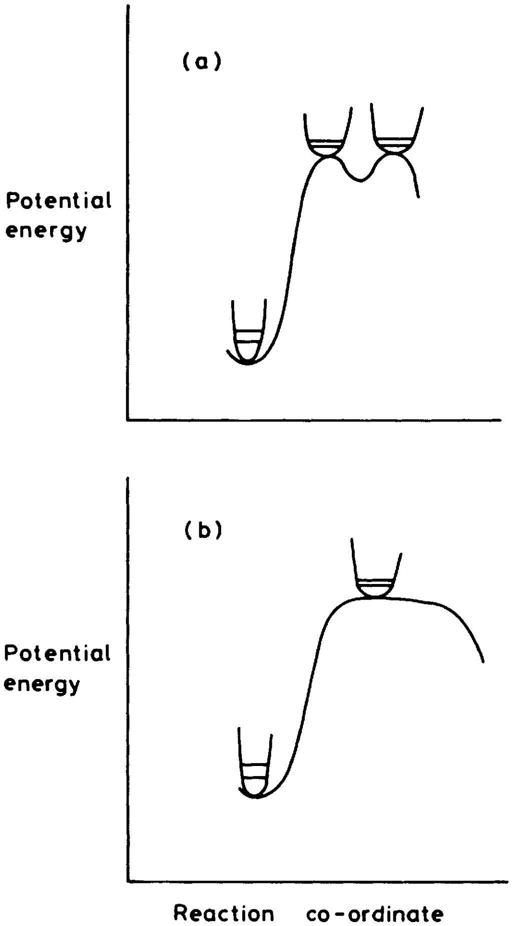

Figure. Potential energy surface for tetramethylene: (a) intermediate; (b) twixtyl (see ref. 6)

According to the product analysis, *ca.* 74% of the reactions can be described as proceeding through 2-methylhept-6-ene-2,5-diyl, with fragmentation accounting for over 90% of the fate

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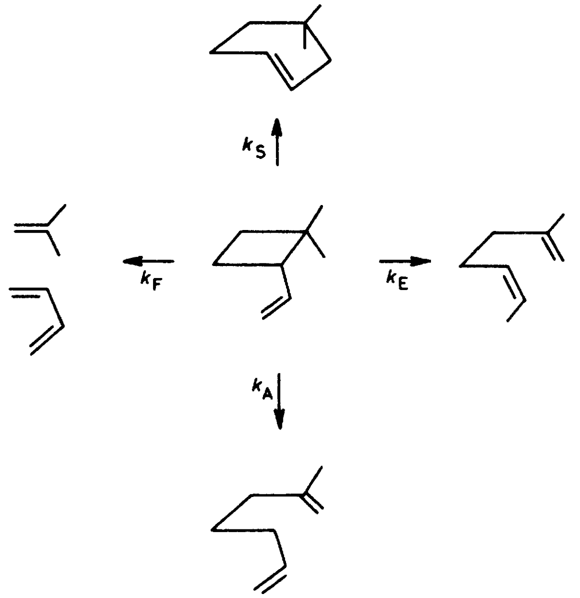
Table 1. Thermolysis of 2,2-dimethyl-1-vinylcyclobutane[a]

Butadiene + 2-methylpropene (k_F)	4,4-Dimethylcyclohexene (k_S)	*cis*-2-Methylhepta-1,5-diene (k_E)	2-Methylhepta-1,6-diene (k_A)	Starting material	Time (s)
2,2-Dimethyl-1-vinylcyclobutane (262.2 °C)					
0.177	0.0124	0.0632	0.003	0.742	5 161
0.281	0.0223	0.114	0.0063	0.574	9 871
0.380	0.0287	0.151	0.0085	0.432	14 760
0.536	0.0423	0.219	0.0123	0.189	29 641
0.648	0.0480	0.253	0.0148	0.0341	60 420
2,2-Dimethyl-1-vinyl-3,3,4,4-tetradeuteriocyclobutane (262.2 °C)					
0.162	0.0136	0.0715	0.004	0.748	5 161
0.262	0.0242	0.123	0.0067	0.583	9 721
0.370	0.0311	0.152	0.0085	0.438	14 760
0.540	0.0411	0.216	0.0120	0.189	29 641
0.617	0.0508	0.279	0.0147	0.0361	60 420
2,2-Dimethyl-1-vinylcyclobutane (288.0 °C)					
0.215	0.0275	0.0708	0.0085	0.681	960
0.362	0.0182	0.106	0.0056	0.492	1 800
0.480	0.0355	0.137	0.0111	0.333	2 790
0.578	0.0405	0.153	0.0124	0.211	3 720
2,2-Dimethyl-1-vinyl-3,3,4,4-tetradeuteriocyclobutane (288.9 °C)					
0.246	0.0164	0.0647	0.0050	0.665	990
0.341	0.0293	0.120	0.0094	0.498	1 800
0.471	0.0364	0.146	0.0117	0.334	2 800
0.542	0.0438	0.180	0.0141	0.218	3 720

[a] Data reported as fractions of total reactant. [b] The rate constant for decomposition was calculated from data prior to rounding off to three significant figures for inclusions in this table; each $k_{overall}$ calculation included a data point at $t = 0$.



Scheme. Thermal reactions of 2,2-dimethyl-1-vinylcyclobutane

of this intermediate. The remaining 26% of the reaction can be accounted for by an 'ene' reaction, k_E, of the starting material. The data in Table 1 summarize the results we obtained from thermolysis of 2,2-dimethyl-1-vinylcyclobutane and 2,2-dimethyl-1-vinyl-3,3,4,4-tetradeuteriocyclobutane* at 262.2 and 288.0 °C. Calculated inter- and intra-molecular isotope effects are summarized in Table 2.

The results clearly indicate that deuterio-substitution at the internal methylene positions does not significantly perturb fragmentation of the second bond in 2-methylhept-6-ene-2,5-diyl. This is particularly evident in k_H/k_D for fragmentation at 262.2 °C, which is 1.06 ± 0.04. This effect, 1.015 ± 0.01 per deuterium atom at 262.2 °C, can be contrasted with an isotope effect of 1.051 per deuterium atom observed for [$^2H_8$]cyclobutane a 449 °C.* The lack of a substantial k_H/k_D value for fragmentation of the second bond of 2-methylhept-6-ene-2,5-diyl is significant, since the minimum in the potential energy surface, if it exists, would be expected to be deeper for the stabilized diradical than for butane-1,4-diyl. Yet these results indicate that isotopic substitution causes very little perturbation in the cleavage of the second carbon–carbon bond of the stabilized diradical. These results can be accommodated by invoking either rate-determining formation of 2-methylhept-6-ene-2,5-diyl as an intermediate followed by rapid cleavage of the second carbon–carbon bond, or a surface which is relatively flat. The activation energies for the 1,3-sigmatropic rearrangement of 2,2-dimethyl-1-vinylcyclobutane (E_a 44.4 kcal)† and for fragmentation (E_a 47.7 kcal mol^{-1}) are comparable, and since both processes are believed to proceed by way of 2-methylhept-6-ene-2,5-diyl,[7] this precludes the former possibility. We therefore conclude from these results that most of the isotope effect observed in [$^2H_8$]cyclobutane thermolysis results from cleavage of the first carbon–carbon bond and that the surface for the subsequent fragmentation reaction remains relatively flat.

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* Extrapolation of the isotope effect of 1.41 ± 0.02 at 449 °C to 262.2 °C gives a value $k_H/k_D = 1.75$ which translates to an isotope effect of 1.093 per deuterium at this temperature.[4]

† 1 kcal = 4.184 kJ.

Table 2. Isotope effects in the decomposition of 2,2-dimethyl-1-vinylcyclobutane[a,b]

	$k_{overall}$	k_F	k_S	k_E	k_A
T 262.2 ± 0.3 °C					
$10^5k_H/s^{-1}$	5.58 ± 0.01	3.74 ± 0.06	0.283 ± 0.01	1.48 ± 0.06	0.083 ± 0.008
$10^5k_D/s^{-1}$	5.50 ± 0.03	3.58 ± 0.08	0.295 ± 0.02	1.54 ± 0.07	0.084 ± 0.005
$k_H/k_D(0.77D_4)$	1.014 ± 0.008	1.044 ± 0.04	0.96 ± 0.04	0.96 ± 0.08	0.99 ± 0.1
k_H/k_D $(D_4)^c$	1.018 ± 0.008	1.06 ± 0.04	0.95 ± 0.04	0.95 ± 0.08	0.98 ± 0.1
T 288.0 ± 0.3 °C					
$10^5k_H/s^{-1}$	4.13 ± 0.1	2.99 ± 0.08	0.22 ± 0.012	0.851 ± 0.05	0.069 ± 0.003
$10^5k_D/s^{-1}$	4.03 ± 0.09	2.83 ± 0.08	0.22 ± 0.016	0.902 ± 0.08	0.071 ± 0.007
$k_H/k_D(0.77D_4)$	1.024 ± 0.04	1.057 ± 0.06	1.0 ± 0.1	0.944 ± 0.1	0.972 ± 0.11
k_H/k_D $(D_4)^c$	1.03 ± 0.04	1.074 ± 0.06	1.0 ± 0.1	0.927 ± 0.1	0.964 ± 0.11

[a] k_F, k_S, k_E, and k_A were calculated from the product of $k_{overall}$ and the fractional contribution of each product in Table 1; the mean of each fractional contribution was weighted by calculating the sum of the entries in each column divided by the sum of the total products. [b] Errors reported for k_F, k_S, k_E, and k_A are standard deviations of the mean calculated from each entry in Table 1. [c] Corrected for isotopic abundance.

Experimental

2,2-Dimethyl-3-vinylcyclobutane.—This compound was prepared as previously described.[7] 2,2-Dimethyl-1-vinyl-3,3,4,4-tetradeuteriocyclobutane was prepared by use of diethylene [$^2H_2$]glycol in the reaction of 2,2-dimethyl-3-vinylcyclobutanone semicarbazone with sodium in diethylene glycol. The sample was purified by g.l.c. on a squalane column. The 220 MHz ^{1}H n.m.r. spectrum indicated that exchange had occurred at both methylene positions of the cyclobutane ring. The residual protons observed at the characteristic chemical shift, δ 1.4, appeared to be statistically distributed. A parent ion was observed at m/z 110 in the non-deuteriated species. The deuteriated species exhibited peaks at m/z 114 ($^2H_4$), 113 ($^2H_3$), 112 ($^2H_2$), and 111 ($^2H_1$) in a 1:1.16:0.52:0.1 pattern, respectively. This distribution is consistent with a 77% overall deuterium incorporation at the ring methylene positions.

Thermolysis.—The thermolysis of 2,2-dimethyl-1-vinylcyclobutane and its deuteriated analogue was performed at 262.2 and 288.0 °C in a conventional high-vacuum static apparatus at a total pressure of *ca.* 3.3 kPa. Sample pressures in the thermolysis vessel were about 83 Pa, with the difference in pressure made up by nitrogen gas. The fall-off pressure, $P_{1/2}$, is estimated to be in the sub-Pascal region for a molecule of this size (22 atoms).[8] Sample transfer was achieved by sharing the contents of the reaction vessel with an evacuated glass vessel. The products were analysed by g.l.c. using a gas inlet system on 5% tris(cyanoethoxy)propane–oxydipropiononitrile columns in tandem. Each data point in Table 1 was obtained by sequentially alternating labelled and unlabelled sample.

The output of the detector was shown to be dependent on carbon count, and mass balance was confirmed by using cyclohexane as an internal standard. The composition of the cyclohexane was found to be reproducible to within ±1% of over the entire decomposition range studied. Previous studies[7] have shown the reaction to be insensitive to surface-to-volume ratio.

All products were stable to the reaction conditions with the exception of *cis*-2-methylhepta-1,5-diene. This material was shown to rearrange slowly to the corresponding *trans*-isomer and to 2,4-dimethylhexa-1,5-diene. Isomers of both products could be separated by the analytical system employed and the amount of *cis*-2-methylhepta-1,5-diene in Table 1 is appropriately corrected for formation of these two secondary products.

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