Table IV. Temperature Variation of the Rate Constants

Temp, °C	394.5	404.1[a]	405.7	415.6	421.4[a]	423.0
10^4k_1, sec^{-1}	1.26	2.09 (2.06)[b]	2.30	3.75	5.35 (4.96)	5.35
Temp	431.4	439.7	440.5[a]	447.8	455.7	
10^4k_1, sec^{-1}	7.70	12.0	13.3 (12.4)	17.0	25.6	

[a] Packed vessel. [b] The values in parentheses are calculated from the Arrhenius equation.

Experimental Section

A commercial sample (Eastman) of α-chloro-*o*-xylene was purified by vacuum distillation. The fraction with boiling point 120–121° (75 mm) was used. Identification of the compound was confirmed by mass spectral and nmr analysis. The glpc analysis of the sample showed the detectable impurities as being in total less than 0.2%. Benzocyclobutane was prepared by a modification of the method of Cava and Deana[12] and later in larger scale synthesized by pyrolysis of α-chloro-*o*-xylene in a flow system.[13]

The apparatus was essentially the same as previously described;[14] the reaction vessels were seasoned with allyl bromide.[14] The identification of products was done by mass spectral and glpc analysis. Because of the further reactions of the benzocyclobutane formed in the pyrolysis, the extent of reaction was not followed by pressure change but (a) determined by analysis of the hydrogen chloride produced and (b) by glpc analysis of the disappearance of the substrate. For case (a), in order to overcome the hydrolysis of the unreacted substrate in aqueous sodium hydroxide solution, the reaction products were trapped in acetone at −197°. The hydrogen chloride was then estimated by titration with an ethanolic solution of sodium ethoxide using lacmoid as indicator. For case b a Perkin-Elmer F.11 chromatograph with flame ionization detector was used with mesitylene as an internal standard. The following calibration factors (*f*) defined by the equation (subscript c stands for compound; s, for standard)

$$\frac{(\text{pressure})_c}{(\text{pressure})_s} = \frac{(\text{moles})_c}{(\text{moles})_s} = f\,\frac{(\text{glpc area})_c}{(\text{glpc area})_s}$$

were determined and used: for α-chloro-*o*-xylene, 1.13; benzocyclobutene, 1.15; *o*-xylene, 1.10; styrene, 1.12.

Three columns were mostly used in this work, namely 4-ft 10% Apiezon L, 6-ft 8% Antarox CO-990, and 2.5-ft 10% Apiezon L in series with 2.5 ft of 8% Antarox CO-990.

Acknowledgments. One of us (S. K. W.) acknowledges the award by the SRC of a research assistantship. A. M. acknowledges a Visiting Professorship in the Department of Chemistry of the University of Western Ontario, during the tenure of which the presentation of this work was completed.

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Pyrolysis of Ethylcyclobutane in the Gas Phase at High Pressures[1a]

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Abstract: The pyrolysis of ethylcyclobutane in nitrogen diluent gas was studied in the pressure range 100–2500 psi at 410°. In this pressure range, well into the high-pressure limiting region for this unimolecular reaction, the rate constant is given by $\log K = \log (4.54 \pm 0.03) \times 10^{-5}\ \text{sec}^{-1} - (3.54 \pm 0.64) \times 10^{-5}\ (\text{psi})^{-1}P$, where *P* is the total pressure in pounds per square inch. From these results the volume of activation of the reaction is found to be $\Delta V^{\ddagger} = 28.2 \pm 5.3$ ml/mole. This is in reasonably good agreement with a lower limit theoretical estimate of 21 ml/mole.

Cyclobutane and many of its derivatives undergo quite clean, well-characterized unimolecular decompositions in the gas phase; these have been studied intensively by Walters and his collaborators and by others,[2] and their pyrolyses by simple unimolecular mechanisms can be regarded as almost certainly established. These systems therefore provide an ideal testing ground for unimolecular rate theorists who wish to avoid interpreting data on reactions which are subsequently found to be heterogeneous or complex free-radical processes. One of these systems is ethylcyclobutane, studied by Wellman and Walters[3] over the pressure range 7–400 mm at 450° and over the range 10–200 mm over the temperature range 420–460°. The decomposition (to ethylene and 1-butene) is homogeneous and first order, and is not inhibited by propylene, toluene, or nitric oxide. The rate constant is given by $k = 3.6 \times 10^{15}/\exp(-62{,}000/RT)$ sec^{-1}. The rate constant was found to be independent of total pressure, indicating that the high-pressure limiting rate constant of the reaction has been reached; this is quite reasonable in view of the complexity of the molecule.

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[1] (a) This work was supported by a grant from the Air Force Office of Scientific Research; (b) send correspondence to this author at Department of Chemistry, Vanderbilt University, Nashville, Tenn. 37203.

[2] A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, **4**, 136 (1967).

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Some years ago Baetzold and Wilson suggested[4] that the high-pressure limit of the rate constant, k_∞, might not be truly independent of pressure, as is predicted by most current theories of unimolecular reactions.[4–7] Their argument was based upon the possibility of nonrandom lifetime distributions of activated molecules, and the argument was not rigorous. Still, this work suggested that it might be worthwhile to reinvestigate the existence of the high-pressure limit for some very clean, well-characterized unimolecular reaction.

An argument based on transition state theory also indicates that values of k_∞ may not be truly constant; it is as follows

$$k_\infty = (kT/h)\exp(-\Delta G^{\ddagger}/RT) \qquad (1)$$

from which we deduce that

$$\left(\frac{\partial \ln k_\infty}{\partial P}\right)_T = -\Delta V^{\ddagger}/RT \qquad (2)$$

where $\Delta G^{\ddagger}$ is the free energy of activation, P is the pressure, $\Delta V^{\ddagger}$ is the molar volume change on activation, and the other terms have their usual significance. Equation 2 does depend on what might be regarded as an "over-interpretation" of transition state theory, but if one is willing to accept eq 1, it is surely reasonable to accept eq 2. This equation has been used extensively to interpret rates of chemical reactions and other processes in the liquid and solid phases,[8–11] but we know of no case in which it has been applied to gas-phase unimolecular reactions.

Experimental Section

Ethylcyclobutane from Chemical Sample Co. was purified by vapor phase chromatography (vpc) on a 2 m × 0.25 in. o.d. column packed with Perkin-Elmer packing R, the required peak being trapped out with liquid nitrogen. The collected material was distilled under vacuum into a reservoir on the sample-handling line. Subsequent vpc analyses on 8 m × $^1/_8$ in. o.d. columns with various packings showed only one peak with a detection level of better than one part in 50,000. Infrared analysis of the starting material indicated that it was of the order of 98–99% ethylcyclobutane.[12] Ethylcyclobutane was then introduced from the sample-handling line to stainless steel flask V_1 (Figure 1) at a pressure of about 50 mm.

Matheson prepurified nitrogen was slowly passed through approximately 1 ft of bright copper turnings at 500° to remove the last traces of oxygen. Subsequent mass spectrometric analysis did not detect oxygen, nor were unexpected reaction products observed after the nitrogen was treated in this manner. This nitrogen was introduced into stainless steel flasks V_1 and V_2 to yield a pressure of about 1400 psi. By placing a dewar of liquid nitrogen around V_1 we could collect most of the gas in V_1; valve 9 was then closed and V_1 allowed to warm to room temperature. This generated a pressure of about 5000 psi in V_1. Gentle uneven warming and a 3–4-day interval permitted adequate mixing of the ethylcyclobutane and the nitrogen.

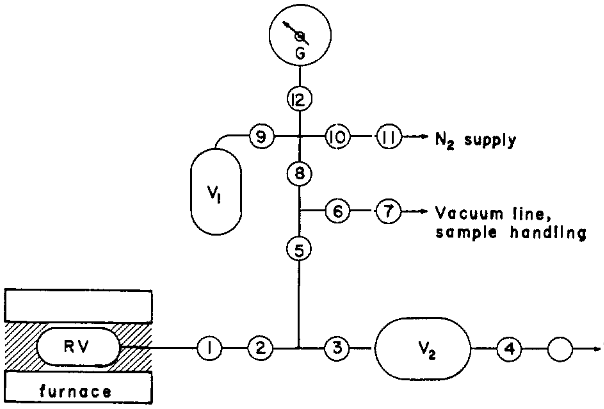

Figure 1. The apparatus: RV, reaction vessel, approximately 100-ml stainless steel (SS), packed with thin-walled SS tubes; V_1 500-ml SS vessel; V_2 1500-ml SS vessel; G, Helicoid pressure gauge, 50–5000 × 25 psi; circles numbered 1 through 12 are Whitey SS valves.

Aminco superpressure tubing, Swagelok fittings, and 66TS4-316 Whitey valves were used for the high-pressure line. The reaction vessel was a modified Aminco Catalog No. 41-9230 tank having a volume of 100 ml; it was packed with Type 304 stainless steel tubing to improve temperature uniformity at the beginning of the runs and "cured" with reaction mixture before use. The furnace consisted of an aluminum core around the reaction vessel which was lagged with asbestos tape, then noninductively wound with nichrome wire (main and control windings), lagged with more asbestos tape, and mounted horizontally in a metal can packed with firebrick. The control windings were operated by a precision temperature controller, Model 233, from the Bayley Instrument Corp.

Before each run the reaction vessel and the associated vacuum line were evacuated to less than 5 μ (McLeod gauge) by a mercury diffusion pump backed by a rotary pump. (The line was trapped at liquid nitrogen temperature at the diffusion pump.) The system was then isolated and a run started by slowly opening valve 9 (to avoid heating by compression in the reaction vessel by a sudden surge of gas). A stopwatch was started, valves 1, 2, and 9 were closed, and the temperature was measured (Leeds and Northrup Type K3 potentiometer and two Pt–Pt–Rh thermocouples); most runs were carried out at 410 ± 1°.

At the end of a run, normally after 2 hr, the contents of the reaction vessel were expanded into V_2. In early experiments this mixture was expanded into a 16-l. vessel, passed through liquid nitrogen traps to collect the organic materials, distilled from a 3-methylbutane slush cooled trap to remove ethylene, and transferred to a bulb which could be taken off the line and attached to a vpc for analysis for 1-butene and ethylcyclobutane. Despite precautions (use of mercury cut-off valves, employment of break-off seals, etc.), our results obtained by this method generally showed too much scatter. An "on line" vpc method was therefore developed (using a Varian Aerograph Hy-Fi instrument, Model 600-D, with flame ionization detection) which permitted us to analyze directly small aliquots of the contents of V_2.

To improve the accuracy further a column packing was developed such that the peaks to be measured had comparable retention times, thus minimizing errors due to peak distortion, flow, etc. On polypropylene glycol (PPG), 1-butene preceeded ethylcyclobutane; the order was reversed on diethylene glycol–$AgNO_3$ (DEG–Ag). In both cases the ratio of retention times was quite large. The retention times of both components were linear functions of the composition of the packing, however, and it was found that packings which were about 40% PPG (and 60% DEG–Ag) or 60% PPG (and 40% PEG–Ag) reduced the ratio of retention times adequately while still yielding good peak separations.

Results

The experimental results are given in Table I. The

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Table I

Pressure, psi	$k_1 \times 10^5$, sec^{-1}	Ln $10^5 k_1$
2525	4.14	1.4206
2100	4.19	1.4278
1850	4.25	1.4469
1575	4.26	1.4492
1350	4.24	1.4445
950	4.38	1.4770
295	4.38	1.4770
245	4.39	1.4792
205	4.40	1.4812
165	4.53	1.5107
135	4.60	1.5260
105	4.56	1.5172
660	4.51	1.5062
600	4.57	1.5195
375	4.67	1.5411
280	4.71	1.5496
255	4.60	1.5260
225	4.59	1.5237
1365	4.30	1.4574
1055	4.39	1.4795
805	4.38	1.4757
460	4.47	1.4973

least-squares fit to the expression

$$\log k(P) = \log k_\infty - aP$$

yields

$$k_\infty = (4.54 \pm 0.03) \times 10^{-5} \text{ sec}^{-1}$$

$$a = (3.54 \pm 0.64) \times 10^{-5} \text{ (psi)}^{-1}$$

from which we calculate $\Delta V^{\ddagger} = +28.2 \pm 5.3$ ml/mole.

Dead-space corrections were estimated and found to be negligible, due to the enormous excess of N_2 over ethylcyclobutane, the small-bore stainless steel high-pressure tubing used in the high-pressure line, and the extremely slow rate of diffusion at the high pressures involved.

The value obtained for $\Delta V^{\ddagger}$, 28 ml/mole, is substantially larger than typical solution work results. This is readily explained in terms of the relative freedom of rotational motion in the gas phase as compared to the liquid phase. In solution free rotation of the molecule is generally not possible, and $\Delta V^{\ddagger}$ can therefore be estimated as follows. We approximate the volume of a cyclobutane system as a rectangular solid of thickness 4 Å (the van der Waals "radius" of a CH_2 group is about 2 Å), and width and length 5.50 Å (1.5 + 2 + 2 Å). We approximate the volume of the transition state as a rectangular solid thickness 4 Å, width 5.33 Å (1.33 + 2 + 2 Å), and length 6.21 Å (2.21 + 2 + 2 Å). We assume the C–C bond length in the normal ring to be 1.50 Å, the shorter C–C distances in the transition state to be 1.33 Å (double bonds), and the longer C–C distances in the transition state to be 2.21 Å (bonds of order $^1/_{10}$).[13] The $\Delta V^{\ddagger}$ deduced from this approach is +15.9 ml/mole.

In the gas phase, however, the assumption of free rotation is probably a reasonable approximation even at these pressures at 410°. The volume effectively occupied by a molecule which is freely rotating can be roughly approximated by computing the volume of a sphere having as its diameter the longest distance measured across the molecule; we use the same approach on the transition state. The flexing of the ring and the bending and internal rotation of the ethyl group make it difficult to make assessments of these volumes which are at all precise; using the same dimensions for the ring as employed in the nonrotating model above and neglecting the ethyl group entirely lead to a $\Delta V^{\ddagger}$ of +21.1 ml/mole. This is a lower limit, because of our ignoring of the ethyl group. Considering the roughness of the approximations in the calculation and the uncertainty in our experimental value of $\Delta V^{\ddagger}$, we may regard this agreement as reasonably good. We conclude that our hypothesis that this pressure dependence of k_∞ is due to a volume of activation effect has not been disproved, and that the high experimental value of $\Delta V^{\ddagger}$ suggests that the molecules are undergoing free rotation.

Experiments with Ethylene

It is not known whether the pyrolysis of alkylcyclobutanes is a concerted process (as assumed above) or one involving a diradical intermediate. It was hoped that information could be obtained on this point by pyrolyzing ethylcyclobutane in the presence of high pressures of ethylene and then examining the products. Unfortunately, but not unexpectedly, it was found that pure, oxygen-free ethylene reacted extensively in the temperature and pressure ranges of interest. Pure ethylene at an initial pressure of 1 atm was kept in the reaction vessel for 124 min at 410° and then analyzed by vpc; 24 peaks were observed. A similar run made at 180 psi initial pressure and 432° for 121 min showed 26 vpc peaks from the product material. This aspect of the study was therefore not pursued further.

Acknowledgment. We are greatly indebted to the late Professor W. D. Walters whose encouragement, help, and sage advice up to the time of his death made this work possible.

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