the greater freedom in the outer shell. Owing to the mutually compensating character of the ΔH and ΔS values, one finds that the ΔG values change much less than the ΔH values.

As was mentioned in the introduction, there is considerable evidence that positive ions are solvated better by aprotic solvents than negative ions. It should be noted that the negative end of the dipole in all aprotic solvents is located at a much more accessible place than the positive end. Thus, as mentioned earlier, the negative charge in acetonitrile is on the nitrogen

atom. Better solvation of positive ions is to be expected on this basis. The difference between positive and negative ions should be particularly noticeable in first-shell solvation. Some measurements[15] of the equilibria $M^+ + CH_3CN = M^+CH_3CN$ confirm this view. For $M^+ = K^+$, $\Delta H_{1,0} = 24$ kcal/mol. This is about 80% higher than $\Delta H_{1,0}$ for Cl^-, the isoelectronic negative ion which is of similar size. $\Delta H_{1,0}$ for K^+ is also considerably larger than $\Delta H_{1,0} = 18$ kcal/mol for the same ion solvated by a water molecule.

(15) W. R. Davidson and P. Kebarle, unpublished work.

Pyrolysis of Cyclobutane[1a]

Peter C. Beadle,[1b] David M. Golden,* Keith D. King, and Sidney W. Benson

Contribution from the Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California 94025. Received August 17, 1971

Abstract: The pyrolysis of cyclobutane has been studied by the VLPP technique between 969 and 1280 K. It was found that the Arrhenius parameters which give best agreement between the present results and those of previous workers are log $(k_\infty, sec^{-1}) = 16.5 - 65.5/\theta$. Estimates consistent with the above parameters have been made of the Arrhenius parameters for reactions 2, -2, and 3, c-$C_4H_8 \rightleftharpoons \cdot C_4H_8 \cdot \rightarrow 2C_2H_4$ (2, forward; -2, reverse). Studies on the pressure dependence of the rate constant in the 22,400-collision reactor indicate a gas-collision efficiency of about 0.1 relative to the wall, while the good agreement expressed above indicates approximately unit efficiency. By lowering the high-pressure Arrhenius parameters, we can reconcile such a low collision efficiency with the falloff data of other workers. However, such low parameters would not fit our other VLPP data, and there appears to be no way to reconcile the discrepancy.

The thermal decomposition of cyclobutane has been shown to be a homogeneous, unimolecular reaction.[2-6] Although ethylene is the major product, there have been reports of the formation of small amounts of other alkenes.[2b,4,5] Between 693 and 740 K, the high-pressure rate constant[2b] has been given by

$$\log k_\infty = 15.6 - 62.5/\theta$$

where $\theta = 2.303RT$ (R in kilocalories per degree per mole). The rate constant has been shown to be independent of pressure above approximately 20 Torr.[2b-4] Because of the apparent simplicity of the reaction, it has been used several times to test unimolecular reaction rate theories. Butler and Ogawa[4] measured the rate constant between 1.7×10^{-4} and 43 Torr at 722 K. Using the parameters $A_\infty = 2 \times 10^{-15}$ sec^{-1}, $k_\infty = 4.9 \times 10^{-4}$ sec^{-1}, $s = 14$, $E_\infty = 61,700$ cal mol^{-1}, and collision diameter $\sigma = 5.5$ Å, they found that RRK theory fitted the data well down to 10^{-3} Torr. Slater theory was found to give just as good a fit when n was taken to

be 16. Below 1 μ, the experimental rate constant was greater than the calculated one. A similar effect was noted by Vreeland and Swinehart[5] below about 20 μ. They used rather different parameters ($A_\infty = 7.02 \times 10^{15}$, $E_\infty = 63,200$ cal mol^{-1}, $s = 18$, and $\sigma = 5.8$ Å), but obtained a curve very similar to that of Butler and Ogawa. It was suggested[5] that this strange behavior at low pressures could be due to competition between the alternative pyrolysis routes, simultaneous rupture of two bonds or consecutive rupture (tetramethylene biradical mechanism). These deviations, however, are much more likely to be due to a wall-promoted reaction which would be caused by the limiting low collision frequency determined solely by the geometry of the reaction vessel. Maloney and Rabinovitch[7] have discussed this effect in relation to the ethyl isocyanide thermal isomerization, and it has been shown to be important in the thermal decomposition of methylcyclobutane.[8] Swinehart and his coworkers,[3] who demonstrated this, also emphasized that there was no evidence for chemical reactions occurring on the wall and that the only process important at the wall was the transfer of vibrational energy. The most extensive theoretical study of the reaction's falloff behavior has been made by Lin and Laidler,[9] who studied several small ring compounds. Using the reaction scheme

(1) (a) This work was supported in part by Grant No. AP 00353-07 from the Environmental Protection Agency, Air Pollution Control Administration; (b) Postdoctoral Research Associate.

(2) (a) C. T. Genaux and W. D. Walters, *J. Amer. Chem. Soc.*, 73, 4497 (1951); F. Kern and W. D. Walters, *Proc. Nat. Acad. Sci. U. S.*, 38, 937 (1952); (b) C. T. Genaux, F. Kern, and W. D. Walters, *J. Amer. Chem. Soc.*, 75, 6196 (1953).

(3) H. O. Pritchard, R. A. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc., Ser. A*, 218, 416 (1953).

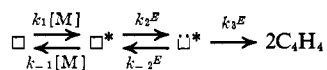(4) J. N. Butler and R. B. Ogawa, *J. Amer. Chem. Soc.*, 85, 3346 (1963).

(5) R. W. Vreeland and D. F. Swinehart, *ibid.*, 85, 3349 (1963).

(6) R. W. Carr and W. D. Walters, *J. Phys. Chem.*, 67, 1370 (1963).

(7) K. M. Maloney and B. S. Rabinovitch, *ibid.*, 72, 4483 (1968).

(8) T. F. Thomas, P. J. Conn, and D. F. Swinehart, *J. Amer. Chem. Soc.*, 91, 7611 (1969).

(9) M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, 64, 927 (1968).

$$\square \underset{k_{-1}[M]}{\overset{k_1[M]}{\rightleftharpoons}} \square^* \underset{k_{-2}{}^E}{\overset{k_2{}^E}{\rightleftharpoons}} \sqcup^* \overset{k_3{}^E}{\longrightarrow} 2C_4H_4$$

where k^E denotes the specific rate constant at energy E to $E + dE$. They performed RRKM calculations on three different cases, assuming (a) that $k_{-2}{}^E \gg k_3{}^E$ and splitting of the tetramethylene biradical is rate determining; (b) that $k_3{}^E \gg k_{-2}{}^E$, i.e., that ring opening is the rate-determining step; and (c) that $k_{-2}{}^E = k_3{}^E$, as proposed previously.[10,11] However, they found that the rate constants obtained by the RRKM theory were sensitive only to the imposed high-pressure Arrhenius parameters and not to the model. They pointed out that use of the Arrhenius parameters of Vreeland and Swinehart,[5] which are somewhat higher than those previously accepted,[2b] leads to a better fit of the data without assuming the low collision efficiency needed previously.[12]

Because of the relatively high Arrhenius parameters, it was decided to study the pyrolysis under VLPP conditions to further validate the technique.

Experimental Section

The reaction was carried out in a triple-aperture quartz reactor in an apparatus which has been described previously.[13,14]

Cyclobutane (supplied by H. M. Frey, University of Reading, England) was thoroughly degassed and fractionated under vacuum. Equimolar gas mixtures of cyclobutane with argon and cyclobutane with ethylene were used to calibrate the mass spectrometer. The cyclobutane-argon mixture was used to measure the rate constant for decomposition in the temperature range 958–1205 K.

Flow rates were measured by observing the pressure drop per unit time, through the flow-setting capillaries, from a calibrated volume.

Results

The reaction rate was measured both by ethylene formation and by cyclobutane decay. Cyclobutane was monitored by the 41-amu mass spectral fragment peak, and ethylene was monitored by the 27-amu fragment peak. Argon (parent peak, 40 amu) was used as an internal standard, and the relative sensitivities of cyclobutane, argon, and ethylene were determined from calibration runs.

In Tables I, II, and III, some recent results are shown for comparison, as well as some in Table II, which were obtained in a completely different system. The unimolecular rate constants are shown for each aperture setting in Tables I–III, and the mean rate constant is shown as a function of temperature in Figure 1.

The dependence of reaction rate on the gas pressure was investigated at 969 K, in the 22,400-collision reactor, by varying the flow rates up to about 10^{17} molecules sec^{-1} (see Table IV and Figure 2). Gas–wall and gas–gas collisions are equal at flows of ca. 4.1×10^{15} molecules sec^{-1} (5×10^{-3} Torr) with this reaction. Mixtures of sulfur hexafluoride, cyclobutane, and argon were also used in an attempt to observe the relative collision efficiencies of different gases.

RRK and RRKM calculations were carried out using the parameters shown in Table V. These pa-

(10) S. W. Benson and P. S. Nangia, J. Chem. Phys., **38**, 18 (1963).
(11) S. W. Benson and H. E. O'Neal, NSRDS-NBS 21, Feb 1970, p 18.
(12) G. M. Wieder and R. A. Marcus, J. Chem. Phys., **37**, 1835 (1962).
(13) S. W. Benson and G. N. Spokes, J. Amer. Chem. Soc., **89**, 2525 (1967).
(14) K. D. King, D. M. Golden, G. N. Spokes, and S. W. Benson, Int. J. Chem. Kinet., **3**, 411 (1971).

Table I. Rate Constants for the Cyclobutane Pyrolysis; 280-Collision Reactor, Gas Flow 6 × 10¹⁵ molecules sec⁻¹

Temp, °K	% decomposition Cyclobutane decay	Ethylene formation	Av rate constant, k, sec⁻¹
1136ᵃ	18.8	24.4	17.9
1142ᵇ	18.6		15.0
1165ᵃ	22.2	27.1	21.6
1175ᵇ	29.6		28.0
1186ᵃ	29.4	36.8	32.8
1188	35.9	33.8	35.5
1209	38.8	35.9	39.9
1211	40.5	43.2	48.3
1231	46.7	48.8	61.8
1243	47.9	50.3	66.8
1259	53.8	51.8	76.8
1277	56.5	60.4	97.0
1282	54.2	57.7	87.7
1285	56.5	61.0	98.5
1287	55.9	60.0	95.4

ᵃ Gas flow 1 × 10¹⁶ molecules sec⁻¹. ᵇ Gas flow 3 × 10¹⁵ molecules sec⁻¹ (experiments carried out in Sept 1971, 9 months after other data in the table).

Table II. Rate Constant for the Cyclobutane Pyrolysis; 1920-Collision Reactor, Gas Flow 1–2 × 10⁻⁶ molecule sec⁻¹

Temp, °K	% decomposition Cyclobutane decay	Ethylene formation	Av rate constant, k, sec⁻¹
1029	11.7	15.6	1.5
1058	14.5	10.1	1.9
1066	21.1	26.1	2.9
1066ᵃ	28.5	31.0	4.0
1076ᵇ	33.4		4.7
1088ᵃ	38.2	41.1	6.2
1101ᵇ	41.5		6.8
1102	32.1	38.0	5.2
1115ᵇ	49.2		9.4
1130ᵇ	45.8		12.3
1135	38.0	44.3	6.8
1140	41.6	49.7	8.2
1175	69.4	74.3	25.2

VLPP-II

	% decomposition	k, sec⁻¹ Exptl	RRKMᵈ
1058ᶜ	30.1	7.1	6.0
1068ᶜ	30.8	7.4	7.4
1099ᶜ	39.4	11.0	13.4
1112ᶜ	51.1	17.7	17.5

ᵃ Gas flow 6 × 10¹⁵ molecules sec⁻¹. ᵇ Experiments carried out Sept 1971, 9 months after other VLPP-I data reported here. Gas flow 3 × 10¹⁵ molecules sec⁻¹. ᶜ Experiments carried out in different system (VLPP-II, Sept 1971), where $\omega_S = (7.7 \times 10^3)(T/M)^{1/2}$. ᵈ Using $\log k_\infty = 16.5 - 65.5/\theta$.

Table III. Rate Constants for the Cyclobutane Pyrolysis; 22,400-Collision Aperture

Temp, °K	% decomposition Cyclobutane decay	Ethylene formation	Av rate constant, k, sec⁻¹
958ᵃ	25.1	27.1	0.27
971ᵃ	30.0	37.1	0.39
994ᵃ	45.8	49.3	0.70
1012ᵇ	57.3	56.2	1.0
1020ᵇ	61.5	65.9	1.4
1036ᵇ	69.4	70.8	1.9
1047ᶜ	74.6		2.6
1050ᶜ	77.4		3.1
1068ᵇ	79.0	81.4	3.3
1068ᶜ	82.9		4.3

ᵃ Gas flow 4 × 10¹⁵ molecules sec⁻¹. ᵇ Gas flow 7 × 10¹⁵ molecules sec⁻¹. ᶜ Experiments carried out in Sept 1971, 9 months after other data shown here. Gas flow 3 × 10¹⁵ molecules sec⁻¹.

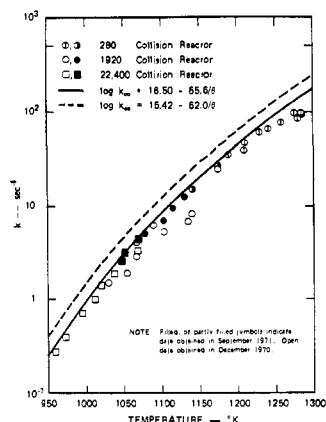Figure 1. VLPP data on the pyrolysis of cyclobutane.

Figure 2. Pressure dependence of the rate constants for cyclobutane pyrolysis in the 22,400-collision vessel at 969 K.

rameters give $S°_{298K} = 63.5$ eu, which is identical with the literature value.[15] The vibrational assignment for the molecule is based on that of Rathjens, et al.,[15]

Table IV. Rate Constants for the Cyclobutane Pyrolysis; 22,400-Collision Aperture, Pressure Dependence at 969 K

$10^{-15} \times$ flow rate, molecule sec^{-1}	% decomposition	k_C, sec^{-1}	r_d/λ^d
1.07[a]	24	0.24	0.26
2.83[a]	30	0.33	0.69
3.22[a]	38	0.46	0.79
7.03[a]	35	0.41	1.71
21.3[a]	37	0.45	5.03
61.8[a]	45	0.63	15.1
95.0[a]	57	1.07	23.2
202[a]	55	0.93	49.0
246[a]	55	0.92	60.0
2.62[b]	36	0.43	
17.8[b]	42	0.56	
135[b]	60	1.13	
1.08[c]	35	0.40	
17.8[c]	39	0.54	
145[c]	53	0.85	

[a] Reactant mixture, C_4H_8–Ar (1:1). [b] Reactant mixture, C_4H_8–Ar–SF$_6$ (1:1:3). [c] Reactant mixture, C_4H_8–Ar–SF$_6$ (1:1:10). [d] r_d = radius of reaction vessel = 2.40 cm. λ = mean free path = (9.86×10^{15})/flow rate, cm.

Table V. Molecular Parameters for the Pyrolysis of Cyclobutane

	Molecule	Complex 1	Complex 2[a]
Frequencies, cm^{-1}	2900 (8)	2900 (8)	
(and degeneracies)	1450 (4)	1300 (2)	
	1290 (4)	1450 (4)	
	1150 (4)	1290 (4)	
	1000 (1)	1150 (2)	
	930 (2)	890 (2)	
	890 (4)	430 (2)	610 (2)
	750 (1)	400 (2)	
	625 (1)	200 (2)	300 (2)
	95 (1)	90 (1)	240 (1)
$I_A \cdot I_B \cdot I_C$, (g cm^2)^3 $\times 10^{114}$	0.952	4.282	
σ/n	8.0	2.0	
Collision diameter, Å	5.0		
Log A_∞		16.5	15.45

[a] Complex 2 denotes alterations made to give log $A_\infty = 15.45$.

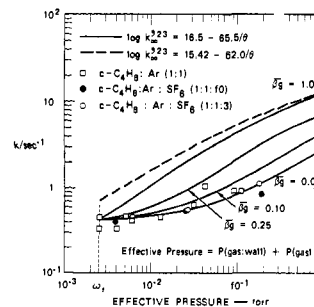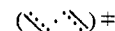(15) A. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, J. Amer. Chem. Soc., 75, 5634 (1953).

while that for the complex is based on the structure

$$(\text{structure}) \ddagger$$

Both RRK and RRKM theories gave essentially the same results, and the RRKM predictions are compared with experiments in Figures 1 and 2.

Discussion

Tables I–III show that the per cent decomposition calculated from cyclobutane decay and ethylene formation agrees well within 10%, and the average discrepancy is more like 5–6%. The rate constant is obtained from the expression

$$k = k_{ea}f/(1 - f)$$

where k_{ea} is the unimolecular escape rate constant for the reactant and f is the fraction of decomposition. Thus, the relatively small error in f (which would seem to indicate a fairly good mass balance) is magnified in the "observed" rate constant. The mean values of the rate constants obtained plotted against temperature, in Figure 1, show the correlation between results obtained in different reactors. The agreement is generally good, although around 1140 K the discrepancies amount to about ±2 kcal mol^{-1} in activation energy at 0 K (E_0). We believe that these discrepancies in the 1920-collision reactor are due to imperfect seating of the aperture plate, leading to a higher escape rate constant. The curve, however, is well defined by the results obtained in the other reactors. The more recent results support this conclusion and show excellent agreement with the original data.

If log $A_\infty = 15.6$, as reported by Walters, et al.,[2b] is used with RRKM theory, then a high-pressure activation energy (E_∞) of 64.6 kcal mol^{-1} is needed to explain the data. This compares with 62.5 kcal mol^{-1} reported previously.[6] Use of the somewhat higher parameters of Vreeland and Swinehart[5] results in a similar, if slightly smaller, discrepancy. It would appear that in order to reconcile our data with those of previous workers, we should raise the A factor to provide greater falloff and raise the activation energy correspondingly to fit the high-pressure rate constants. Analysis of all previously reported data[2–6] reveals that most workers have studied the reaction at 722 ± 1 K. They have determined k_∞ at this temperature to be about 5×10^{-4} sec^{-1} (Figure 3), and so whatever parameters we decide on should agree with this value. The A factor was raised by lowering the skeletal deformations of the complex and good agreement (Figures 1 and 3) among all the data was found with
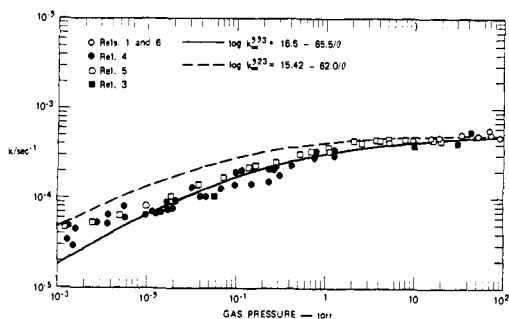
Figure 3. Pressure dependence of the rate constant for cyclobutane pyrolysis at 722 K.

Figure 4. Arrhenius plot for the pyrolysis of cyclobutane.

the parameters

$$\log k_\infty = 16.50 - 65.51/\theta$$

where $\theta = 2.303RT$ (R in kilocalories per mole per degree). The recent results obtained in another VLPP system (VLPP-II) agree well with these parameters (Table II). These parameters are well within the scatter of the available data on the temperature dependence of the rate constant (Figure 4), although a least-squares treatment gives the parameters

$$\log k_\infty = 15.42 - 62.0/\theta$$

The pressure dependence of the rate constant in the 22,400-collision vessel is shown in Figure 2. Individual RRKM curves have been calculated according to the relation

$$k = \int_{E_0}^{\infty} \frac{P(E)k(E)}{1 + k(E)/\omega_T} dE$$

where ω_T is the total collision efficiency. This can be written

$$\omega_T = \beta_s \omega_s + \bar{\beta}_g \omega_g$$

where β_s and $\bar{\beta}_g$ are relative collisional efficiencies for gas–wall and gas–gas collisions, respectively. β_s is assumed to be unity and $\bar{\beta}_g$ is the average value for the different species under study. The experimental data are best fitted by the value $\bar{\beta}_g = 0.1$–0.2, and there appears to be no difference in the effect of cyclobutane and SF_6. This value is in direct contrast to the fit obtained in Figure 3 assuming unit gas-collision efficiency, and there seems to be no obvious way of resolving the discrepancy.

The VLPP reactions performed at 969 K are much farther in the falloff than those performed at 723 K. At 10^{-1} Torr, k/k_∞ is about 0.08 under VLPP conditions, whereas it is 0.3 at 723 K. Thus we should detect a much greater change in rate constant between 10^{-2} and 10^{-1} Torr, but the observed factor of 2 is slightly less than that observed at the lower temperature.

It would be possible to reconcile a low gas-collision efficiency with previous data by assuming low Arrhenius parameters such as those obtained by the least-squares method above. However, this would mean that the rate constants obtained in VLPP would be *too low* (an error of 2–3 kcal mol^{-1} in E_0). We must therefore conclude that, while it is possible to reconcile either set of VLPP data (temperature or pressure dependence of the rate constant) with the data of
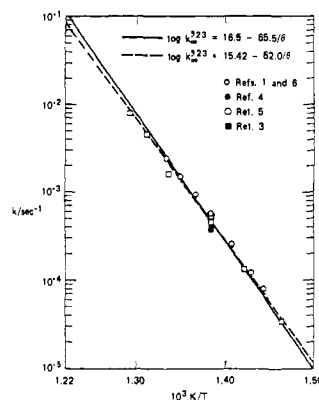
previous workers, it is not possible to make all three sets agree. This would at least tend to rule out any wall effect such as catalysis.

If we accept an A factor as high as $10^{16.5}$, we can effectively rule out reactions 2 and -2 as being the rate-determining steps. This is because the complex involved in the ring opening and closing process

$$(\underset{\ldots}{\square})^{\ddagger}$$

is too constrained a species to have sufficient entropy. Thus the complex which must be considered is that involved in reaction 3; *i.e.*

$$(\ddots \cdot \ddots)^{\ddagger}$$

$$\square^* \underset{-2}{\overset{2}{\rightleftarrows}} \square^* \xrightarrow{3} 2C_2H_4$$
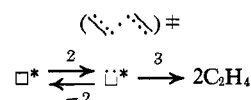
This implies that $k_{-2} > k_3$, and for this to be acceptable it must be consistent with a value of $E_{-2} \leq 6.6$ kcal mol^{-1}.[11,16]

We can check the internal consistency of our results by combining known thermochemistry, additivity methods, and assigned frequencies and molecular parameters as outlined in the Appendix. The results of these calculations are summarized in Table VI,

Table VI. Thermochemical and Kinetic Data for the Reactions

$$\square \underset{-2}{\overset{2}{\rightleftarrows}} \square \xrightarrow{3} 2C_2H_4$$

	$\square$	$(\square)^{\ddagger}$	$\square$	$(\ddots)^{\ddagger}$
S_f^{723}, cal deg^{-1} mol^{-1}	88.24[c] 87.73[a]	98.67[b]	103.22[b]	100.9[a]
ΔH_f^{723}, kcal mol^{-1}	18.88		78.48	

	Reaction i, $i =$		
	2	-2	3
$\Delta S_i^{\ddagger}$, cal deg^{-1} mol^{-1}	10.97	-4.55	-2.32
Log $(A_i^{\ddagger}$, sec$^{-1})$	15.56	12.30	13.07
E_i, kcal mol^{-1}	63.34	6.6	8.25

[a] Calculated from assigned frequencies and molecular structure. [b] Calculated from thermochemistry (see text). [c] Obtained from experimental values at 700 and 800 K.

and from them we can see that if $E_{-2} = 6.6$ kcal mol^{-1}, then $k_3 \approx k_{-2}$ within calculational uncertainty. If $k_{-2} = 10k_3$, this would imply a value of E_{-2} about

(16) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968).

3.3 kcal mol^{-1}, which seems a little low. These results would seem to bear out the previous assumption[11,16] that $k_{-2} \approx k_3$ although they do not disprove our estimate of the Arrhenius parameters, since there is considerable uncertainty in these values and only a slight change in activation energies is required to make ring closure considerably faster than splitting of the biradical.

Conclusion

The results obtained by pyrolysis of cyclobutane under VLPP conditions have been shown to be compatible with previous data if high Arrhenius parameters are assumed. It has been shown that this assumption does not contravene any thermodynamic considerations. However, the VLPP data on gas-collision efficiency under these conditions cannot be reconciled with previous results, and at the present time we can suggest no valid reason for this discrepancy.[16a]

Appendix

The entropy (S_f^{723}) of cyclobutane at 723 K can be obtained from known values[15] at 700 and 800 K, and this agrees with the value obtained from the frequency assignment, as is shown in Table VI. The heat of formation (ΔH_f^{723}) can be calculated by adding the contribution due to $\int_{300}^{723} C_p dT$ to the known value at 300 K of 6.3 kcal mol^{-1}. S_f^{723} and ΔH_f^{723} for the biradical can be calculated by group additivity methods or from n-butane by making suitable corrections.[16,17] It must be remembered that since only singlet biradi-

(16a) Note Added in Proof. Some workers may conclude that the above results indicate that VLPP is not a useful technique. However, it must be emphasized that cyclobutane is the only species we have found to exhibit this behavior. The list of molecules studied by VLPP, for which the results agree with previously accepted (or expected) high-pressure parameters, now includes: isopropyl iodide, n-propyl iodide, ethyl acetate, azoisobutane, azoisopropane, azoethane, 2,3-dimethylbutane, 2,2,3,3-tetramethylbutane, *tert*-butyl peroxide, and *tert*-amyl peroxide.

(17) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969).

cals can participate in ring closure or ethylene formation, no correction for election spin degeneracy should be included in the above estimates. The results are shown in Table VI, and from these values we can obtain

$$\Delta H_2^{723} = \Delta H_f^{723}(\sqcup) - \Delta H_f^{723}(\square) = 59.60 \text{ kcal mol}^{-1}$$

and

$$\Delta S_2^{723} = S_f^{723}(\sqcup) - S_f^{723}(\square) = 14.96 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

These values lead to the value 1.3×10^{-14} for the equilibrium constant (K_2^{723}) for reactions 2 and -2.

The experimental value of the overall rate constant (k_∞) at 723 K is well known (Figure 3). If we assume $k_{-2} > k_3$ in the steady-state expression for k_∞, then we can make the approximation

$$k_\infty = \frac{(k_2/k_{-2})k_3}{1 + (k_3/k_{-2})} \cong K_2 k_3$$

and thus we can obtain an estimate of the upper limit for k_3. Since the entropy of the complex

$$(\ddots\ddots\ddots)^{\ddagger}$$
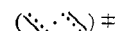
is defined by the parameters shown in Table V, we can calculate $\Delta S_3^{\ddagger}$ and so $\log A_3^{\ddagger}$.

Ring closure in 1,2-dimethylcyclobutane appears to have an activation energy of about 7.4 kcal mol,[11,16] and from this limits of about $4 < E_{-2} < 6.6$ kcal mol^{-1} can be set[11,16] for the ring closure in cyclobutane. This higher value leads to an entropy of 7.0 cal deg^{-1} mol^{-1} ($\Delta S_{-3}^{\ddagger}$) and, since $\Delta S_2^{\ddagger} = \Delta S_2 + \Delta S_{-2}^{\ddagger} + R \ln 4$, we can calculate $\Delta S_2^{\ddagger}$, and thus $\log A_2^{\ddagger}$. The activation energy for reaction 2 can be calculated from the heat of formation of the biradical and the activation energy for ring closure. Thus we can estimate $\log k_2^{723}$ to be -3.57 and by combining this value with K_2^{723} we can obtain k_{-2}^{723} and thus $\log A_{-2}^{\ddagger}$. The values of $\log A_{-2}^{\ddagger}$ calculated by this method, and from $\Delta S_{-2}^{\ddagger} = 7.0$ cal deg^{-1} mol^{-1}, differ by only 0.2 log unit, which is well within experimental uncertainty.

Quantitative Application of the Nuclear Overhauser Effect to the Determination of Molecular Structure

Roger E. Schirmer* and Joseph H. Noggle

Contribution from Eli Lilly and Company, Indianapolis, Indiana 46206, and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received May 3, 1971

Abstract: Procedures for obtaining relative internuclear distances from nuclear Overhauser effect measurements, particularly in three-spin systems, are described. Calculations for model systems and for real systems using literature data are given.

The nuclear Overhauser effect (NOE) is the change in the integrated intensity of one line in an nmr spectrum when a strong radiofrequency field is applied at the frequency of a second resonance in the spectrum.

In spin systems that relax primarily through intramolecular dipole–dipole interactions, the NOE has a $1/r^6$ dependence on the internuclear distance. Because of this dependence on internuclear distances, the NOE