It seems that alkali metal compounds of low solubility with large neutral anions should follow Debye–Hückel eq 1 and should provide a simple method of investigating specific and mixed ion effects at ionic strengths in the range 0.1–0.3 M.[17]

Acknowledgment. The volumetric results for $RbClO_4$ were obtained by Jonathan Fletcher supported by an undergraduate research participation grant from the National Science Foundation in the summer of 1967.

---

(17) A paper on the solubility of $RbClO_4$ and $CsClO_4$ in aqueous $HClO_4$ by S. M. Arkhipov and N. I. Kashina, *Z. Neorg. Khim.*, **14**, 1114 (1969), was listed in *Chemical Titles* in May 1969. It was not available at the time this paper was written.

Thermal Decomposition of 1,1,3,3-Tetramethylcyclobutane[1,2]

Thomas A. Babcock

Contribution from the Department of Chemistry, University of Rochester,
Rochester, New York 14627. *Received May 5, 1969*

Abstract: The thermal decomposition of 1,1,3,3-tetramethylcyclobutane has been studied in the pressure region 7.65–42.8 mm at 435.7° and over the temperature range 415–455°. The reaction yielding two molecules of isobutylene as the primary product is a first-order process which occurs homogeneously, and the rate does not seem to be affected significantly by the addition of nitric oxide or propylene. Experiments near 10-mm pressure in the 40° temperature range indicate that the activation energy for the decomposition is 64.8 ± 0.3 kcal/mole. The first-order rate constant may be expressed as $k = (1.74 \pm 0.02) \times 10^{16} \exp(-64{,}800/RT)\ \mathrm{sec}^{-1}$. Occurring simultaneously with the decomposition, there is a slow structural isomerization to yield 2,4,4-trimethyl-1-pentene. When the results of this study are compared with previous data for the decomposition of cyclobutane, it is found that 1,1,3,3-tetramethylcyclobutane reacts about 0.83 times as fast as cyclobutane.

In recent years much interesting information concerning the homogeneous, vapor-phase pyrolyses of alkyl-substituted small-ring hydrocarbon compounds has been obtained. From the results of earlier studies of thermal decompositions of alkyl-substituted cyclobutanes,[3–6] it has been possible to make some comparison of the effect of the substitution upon the kinetics of the first-order reaction such as for the monoalkylcyclobutanes.

(1)

The activation energies and preexponential factors for the reactions of alkylcyclobutanes are not far apart, but a comparison of the calculated first-order rate constants taken at 450° indicates definite differences in the influence of the alkyl groups. For the series (cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane) the relative rates are 1.0:1.5:3.4. This observation seems to be in good agreement with the results observed in the cyclopropane series where the addition of each methyl group results in approximately a doubling of the rate. In order to study further the effects of methylation on the decomposition of the cyclobutane ring, it was of interest to investigate the kinetic behavior of 1,1,3,3-tetramethylcyclobutane.

Experimental Section

Materials. 1,1,3,3-Tetramethylcyclobutane was prepared by a Wolff–Kishner reduction of 2,2,4,4-tetramethylcyclobutane-1,3-dione according to the procedure suggested by Herzog and Buchman[7] and with modifications suggested by Lautenschlaeger and Wright.[8] The disemicarbazone was formed from the diketone by a method described by Wedekind and Weisswange.[9] The 1,1,3,3-tetramethylcyclobutane which was formed upon the reduction of the disemicarbazone was fractionated in a spinning-band column at a reflux ratio of about 15:1. The fraction obtained in the range 85–86° at 748 mm appeared to contain the desired compound. The literature reports that the pure compound boils at 86–87° at 748 mm.[7] For the kinetic study this fraction was further purified on a Perkin-Elmer Model 154D gas chromatograph with a 2-m R-X column (13% by weight UCON LB-550-X oil on a GC-22 base supplied by the Coast Engineering Laboratory) heated to 78°. The purity was found to be at least 99.8% on eight different gas chromatographic columns.

The refractive index $n^{25}\mathrm{D}$ of the purified sample was found to be 1.3915 (lit.[7] $n^{25}\mathrm{D}$ 1.3930). Duplicate carbon–hydrogen analyses yielded the following percentages: C, 85.7, 85.7; H, 14.4, 14.3 (theoretical, C, 85.63; H, 14.37). The synthesized compound gave a nuclear magnetic resonance spectrum on a Varian A-60 instrument and a mass spectrometric fragmentation pattern at 70 eV which would be expected for 1,1,3,3-tetramethylcyclobutane. A gas-phase infrared spectrum of a 60-mm sample in a cell with a 7.5-cm path length was determined on a Perkin-Elmer Model 421 spectrophotometer. Major absorption peaks were observed at 1155, 1265–1270, 1365–1372, 1430–1465, and 2860–2970 cm^{-1} with smaller absorptions at 950, 1200, 1650–1720, 2645, 2720, and 3240 cm^{-1}. This spectrum agrees with what Lautenschlaeger and Wright observed for 1,1,3,3-tetramethylcyclobutane.

Isobutylene (99.8%, Matheson), propylene (99.9%, Phillips), and 2,4,4-trimethyl-1-pentene (99.9%, Chemical Samples) were purified on the gas chromatograph prior to analytical use. Nitric oxide (99.0%, Matheson) was subjected to low-temperature distillation from trap to trap. All samples were degassed and dried before use.

---

(1) This work was supported in part by a grant from the National Science Foundation.

(2) Abstracted in part from the M. S. thesis submitted to the University of Rochester by T. A. Babcock, 1968.

(3) S. M. E. Kellner and W. D. Walter, *J. Phys. Chem.*, **65**, 466 (1961); in this paper references to earlier studies are given.

(4) M. Zupan and W. D. Walters, *ibid.*, **67**, 1845 (1963).

(5) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

(6) Work of P. C. Rotoli in this laboratory.

(7) H. L. Herzog and E. E. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

(8) F. Lautenschlaeger and G. F. Wright, *Can. J. Chem.*, **41**, 863 (1963).

(9) E. Wedekind and W. Weisswange, *Ber.*, **39**, 1631 (1906).

Apparatus and Procedure. The vacuum system and the apparatus for temperature control were similar to those used in a previous study.[10] Most of the experiments were carried out in an unpacked 355-ml cylindrical Pyrex glass reaction vessel (U). In order to study surface effects, a 276-ml packed vessel (P) was filled with thin-walled Pyrex glass tubes and had a surface-to-volume ratio seven times greater than the unpacked vessel. The pressure increase was measured to ±0.01 mm on a wide-bore mercury manometer with a 100-mm Gaertner cathetometer. The temperature was measured at the center of the reaction vessel with a platinum—platinum-13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer. The thermocouple was standardized at the melting point of zinc (419.5°).

In order to prevent the absorption of the reactant into the stopcock grease and to facilitate the volatilization of the sample into the reaction vessel, the tubing adjacent to the furnace was heated. Pure isobutylene was kept in the reaction vessel for at least 1 hr before each experiment in order to deactivate the surface. The vessel was then evacuated to about 10^{-5} mm. The extent of reaction was usually about 30%. In experiments with added propylene and nitric oxide, the added substance was introduced into the vessel before 1,1,3,3-tetramethylcyclobutane.

Analysis of the Products. After the decomposition had been allowed to proceed for the desired time, the reaction mixture was condensed into the analytical section of the line, and a separation of the components was generally made according to volatility. The fractions separated were (a) material not condensable at −196°, (b) material condensable at −196° and not condensable at −95° and, (c) material condensable at −95°. Fraction a was always found to be less than 0.4% of the reaction products obtained up to one-third decomposition and was not identified. The other components of the reaction mixture were identified by gas chromatography, mass spectrometry, and infrared absorption spectrometry.

The mass spectrum of fraction b from a 30% decomposition compared quite well with the mass spectrum of pure isobutylene determined on the same instrument and with literature values.[11] An infrared absorption analysis with 60 mm of fraction b was determined in a 7.5-cm gas cell. The spectrum agreed with an absorption curve of pure isobutylene taken on the same instrument, and both spectra corresponded closely to that of isobutylene in the literature.[12] Fraction b, when analyzed on a 2-m Perkin-Elmer R-X gas chromatographic column, showed the same retention time as pure isobutylene and the absence of any peak corresponding with 1,1,3,3-tetramethylcyclobutane. Analysis with a 3-m Perkin-Elmer D column (tetraisobutylene on a Celite base) at room temperature showed the presence of two minor components in fraction b with retention times shorter than isobutylene. The amounts of these minor components at 30% decomposition were 0.08 and 0.02 vol. % relative to the isobutylene. Reactions taken to 50 and 75% decomposition showed increased amounts of these components.

Fraction c produced a mass spectrum and a vapor-phase infrared absorption spectrum in fairly good agreement with the pure starting material 1,1,3,3-tetramethylcyclobutane. A gas chromatographic analysis of fraction c with a Perkin-Elmer R-X column showed the main component to have the same retention time as the starting material. Also observed on the gas chromatogram was the presence of a small amount of isobutylene (less than 2 vol. %). A third peak was observed in fraction c which appeared to be less than 2% of the mixture at 30% decomposition. On six gas chromatographic columns the retention times of this minor component corresponded with a pure sample of 2,4,4-trimethyl-1-pentene. A small amount of this third peak was separated gas chromatographically and its mass spectrum agreed well with a pure sample of 2,4,4-trimethyl-1-pentene run on the same instrument. This would be the expected product if an isomerization of the starting material were to take place during reaction. Reactions taken to 50 and 75% decomposition showed additional minor components in fraction c which comprised less than 0.1 vol. % of the mixture. Thus, the products are in accord with a major reaction similar to eq 1 forming two molecules of isobutylene with a simultaneous slow isomerization to yield 2,4,4-trimethyl-1-pentene. Several experiments with isobutylene and 2,4,4-trimethyl-1-pentene indicated that the minor components observed at 50 and 75% decomposition in fractions b and c were due primarily to the subsequent reaction of 2,4,4-trimethyl-1-pentene. However, the extent of any subsequent reaction taking place up to 30% decomposition was not great enough to necessitate a correction to the ΔP.

Table I. Gas Buret Measurements of Fractions a and b from the Thermal Decomposition of 1,1,3,3-Tetramethylcyclobutane

Temp, °C	P_0,[e] mm	ΔP, mm	P_{NC},[f] mm	P_{IB},[f] mm
415.0	12.34	3.18	0.021	6.27
425.0	11.64	3.08	0.025	6.08
425.6[a]	12.02	1.66	0.004	3.33
425.6[a]	11.50	1.58	0.000	3.12
430.2	8.28	2.30		4.59
435.0	10.56	2.83	0.014	5.56
435.0	8.28	2.30		4.60
435.7	13.79	3.66	0.017	7.32
434.9[b]	10.45	5.46	0.063	10.76
435.1[c]	13.29	10.08	0.182	19.75
434.6[d]	8.57	2.26		4.49
439.5[d]	8.57	2.32		4.63
445.2	12.50	3.34	0.016	6.01
455.1	12.22	3.56	0.020	7.04

[a] Taken to about 14% decomposition. [b] Taken to about 50% decomposition. [c] Taken to about 75% decomposition. [d] Reaction in packed vessel. [e] Initial pressure of 1,1,3,3-tetramethylcyclobutane. [f] P_{NC} and P_{IB} mean pressures of noncondensable and isobutylene in the reaction mixture.

After separation as mentioned at the beginning of this section, fractions a and b were measured in the gas buret. The results for several typical experiments calculated as millimeters of pressure in the reaction vessel at the reaction temperature are shown in Table I. On the basis of the occurrence of a reaction such as eq 1 to form isobutylene, the pressure increase ΔP (observed pressure change with a 6–7% correction for dead space) should equal one-half the pressure of isobutylene formed. For the ten experiments taken to about 30% decomposition, the average value of the ratio $0.5P_{\mathrm{IB}}/\Delta P$ was 0.99 ± 0.01, indicating that pressure readings were a good measure for the extent of decomposition. The size of P_{NC} (fraction a) averaged only 0.006 times the pressure increase (ΔP) for the runs to 30% decomposition. Fraction a may be a measure of any subsequent reaction of the primary products which as determined from these results must be very small.

Since fraction c absorbed in the stopcock grease of the gas buret system, a gas chromatographic analysis of the entire reaction mixture was made using a Perkin-Elmer Golay R column. The results from eight analyses are presented in Table II. The pressures of isobutylene (P_{IB}), 1,1,3,3-tetramethylcyclobutane (P_{TMCB}), and 2,4,4-trimethyl-1-pentene (P_{TMP}) have been determined as fractions of the pressure of the final reaction mixture corrected for dead space. The average value of the ratio $0.5P_{\mathrm{IB}}/\Delta P$ for these experiments was 1.00 ± 0.02, giving further indication that the pressure increase during the reaction was primarily due to the formation of isobutylene. The importance of a simultaneous reaction forming 2,4,4-trimethyl-1-pentene can be determined by the ratio of $P_{\mathrm{TMP}}/\Delta P$. The average value of this ratio, 0.037 ± 0.001, might indicate that approximately 3.7% of the starting material is undergoing a structural isomerization. Since the ratio of $P_{\mathrm{TMP}}/P_{\mathrm{IB}}$ seemed to remain relatively constant over the temperature and pressure range studied, it was possible to make a small constant correction to the rates determined from the observed pressure change to obtain actual rates of decomposition to form two molecules of isobutylene.

Results

Homogeneity and Order of the Reaction. The pressure–time curves used to determine the rates of reaction seemed to obey a first-order law. These curves showed no induction period or any other anomaly which might indicate a marked deviation from a first-order reaction. Additional evidence helped to establish first-order behavior for the pyrolysis. As can be seen in Table III, the first-order rate constants for four experiments at 435.7° as determined from quarter-times are independent of the initial pressure for an approximately sixfold change in pressure. Likewise, linear behavior

---

(10) E. R. Johnson and W. D. Walters, *J. Am. Chem. Soc.*, **76**, 6266 (1954).

(11) American Petroleum Institute Research Project 44, Mass Spectra No. 28 and 70.

(12) Reference 11, Infrared Curves No. 23, 378, and 913.

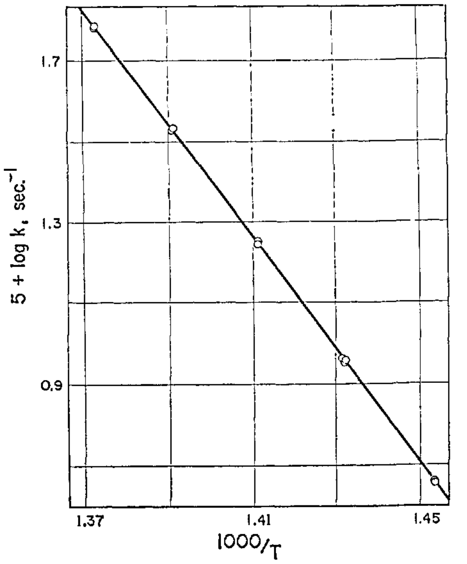


Figure 1. First-order rate constants for the decomposition of 1,1,3,3-tetramethylcyclobutane. Summary of 15 experiments (three runs at each of five temperatures) at approximately 10 mm initial pressure.

Table III. First-Order Rate Constants for the Decomposition of 1,1,3,3-Tetramethylcyclobutane under Various Experimental Conditions

Temp, °C	P_0,[a] mm	10^4k, sec^{-1}	Added gas,[b] mm	Reaction vessel[c]
435.7	7.65	1.79		U
	13.03	1.80		U
	29.30	1.77		U
	42.76	1.80		U
425.1	11.89	0.930	5.45, C_3H_6	U
	11.17	0.929	3.97, C_3H_6	U
	12.54	0.928		U
425.5	13.84	0.947	0.65, NO	U
	13.24	0.950	0.20, NO	U
	13.82	0.947		U
445.2	7.02	3.37		P
	9.02	3.36		U
440.9	6.43	2.64		P
	7.24	2.61		U
434.6	8.57	1.69		P
	11.49	1.68		U
430.1	6.76	1.30		P
	8.65	1.28		U

[a] P_0 corrected for "dead space." [b] C_3H_6 means propylene; NO means nitric oxide. [c] P refers to the packed vessel and U to the unpacked vessel.

was observed for plots of log $[P_0/(P_0 - \Delta P)]$ *vs.* time up to 20–25% decomposition. For the majority of the experiments without added gases, the ratio $t_{25}/t_{12.5}$ averaged 2.16 ± 0.02 which is in fairly good agreement with the expected value of 2.15 found for a first-order rate law.

Table II. Gas Chromatographic Analysis of Reaction Components from the Decomposition of 1,1,3,3-Tetramethylcyclobutane

Temp, °C	P_0,[c] mm	ΔP, mm	P_{IB},[d] mm	P_{TMCB},[d] mm	P_{TMP},[d] mm
425.6[a]	11.50	1.58	3.12	9.87	0.061
425.6	12.30	3.17	6.26	9.05	0.119
425.4	12.83	3.38	6.94	9.15	0.121
425.4[b]	11.89	3.15	6.37	8.55	0.115
435.8	7.65	2.03	4.03	5.58	0.077
435.5	29.30	7.87	15.66	21.22	0.290
436.4	14.35	4.25	8.24	10.20	0.153
446.5	12.47	3.49	7.10	8.73	0.129

[a] Taken to about 14% decomposition. [b] Propylene added, 5.45 mm. [c] Initial pressure of 1,1,3,3-tetramethylcyclobutane. [d] P_{IB}, P_{TMCB}, and P_{TMP} stand for the pressures of isobutylene, unreacted 1,1,3,3-tetramethylcyclobutane, and 2,4,4-trimethyl-1-pentene in the reaction mixture.

In order to ascertain whether the thermal decomposition of 1,1,3,3-tetramethylcyclobutane takes place within the vapor phase as a homogeneous reaction, a number of experiments were done in a packed vessel having a surface-to-volume ratio about seven times the ratio of the unpacked vessel. The data in Table III indicate that the first-order rate constants obtained from the packed bulb experiments at four different temperatures were not more than 2% higher than the rate constants in the unpacked vessel. This difference is within the experimental error expected for measurements made in two different furnace systems.

There is a possibility that experiments in packed vessels may not reveal the presence of certain heterogeneous free-radical chain reactions if the chains start and stop at the walls. For this reason the rate of reaction was measured in the presence of propylene and nitric oxide which have been found to inhibit free-radical chain reactions. As can be seen from the data of Table III, no evidence for an appreciable amount of chain decomposition has been found.

Activation Energy. The influence of temperature upon the rate of decomposition of 1,1,3,3-tetramethylcyclobutane was based mainly upon a special series of 15 experiments performed in the unpacked Pyrex vessel. Rate constants were determined at 10° intervals over the temperature region 415–455° with initial pressures of about 10 mm. Using the integrated first-order rate equation, the rate constants were determined from the times of 12.5 and 25% pressure increase corrected for dead space. (Slight corrections were made to account for a small amount of side reaction.) An average of these two rates was also determined. These experimental data were then used to determine the activation energy from the Arrhenius equation $k = A \exp(-E/RT)$ in two ways: (1) as shown in Figure 1, by a plot of log k *vs.* $1/T$ to graphically determine the slope of the best straight line through the points; (2) by a least-squares analysis of the data with an IBM 650 computer. The graphical method yielded a value of the activation energy fo 64.9 kcal/mole for the averaged rate constants. The activation energy evaluated by a least-squares analysis of the rate constants determined at eighth-time was found to be 64.8 ± 0.3 kcal/mole; 0.3 is the standard deviation as determined from the program. Similarly, using the rate constants determined at quarter-time, an activation evergy of 64.9 ± 0.2 kcal/mole was found. It was evident from evaluation of the values of E resulting from various treatments of the results in this study that an activation energy of 64.8 ± 0.3 kcal/mole would cover the range of calculated values and their standard deviations. Using this activation energy and the known rate constants for this special series of experiments, the frequency factor, A, was calculated. The first-order rate constant can thus be expressed as

$$k = (1.74 \pm 0.02) \times 10^{16} \exp(-64{,}800/RT)\ \text{sec}^{-1} \quad (2)$$

Discussion

The thermal decomposition of 1,1,3,3-tetramethylcyclobutane over the temperature range 415–455° has been shown in this study to proceed primarily to form two molecules of isobutylene. This mode of decomposition seems to be in accord with other alkylcyclobutanes previously studied. In addition, the decomposition reaction is accompanied by a slow isomerization to form a small amount of 2,4,4-trimethyl-1-pentene. Within limits of the sizable analytical errors involved in the determination of small quantities of 2,4,4-trimethyl-1-pentene, the ratio of this isomerization product to isobutylene seems to stay within a narrow range for experiments at different initial pressures and temperatures. This information would lead one to speculate that its activation energy is not too far different from the reaction to form isobutylene.

Independence of the rate constant for decomposition to two molecules of isobutylene for a sixfold increase in the initial pressure and the linearity of a plot of log $[P_0/(P_0 - \Delta P)]$ *vs.* time shows that the reaction is first order. Packed vessel measurements indicate the reaction is homogeneous, and free-radical chain processes seem to be negligible since the reaction rate constants and the composition of the products are not changed significantly by the presence of propylene or nitric oxide. On the basis of these findings, it is concluded that the thermal decomposition to form isobutylene in the early stages of reaction proceeds as a unimolecular reaction or is dependent mainly upon a unimolecular step.

The frequency factor for the decomposition reaction of the present study is 1.74×10^{16} sec^{-1}. This value is somewhat above the values observed for other alkylcyclobutanes and much higher than the value of 10^{13} sec^{-1} often expected on the basis of the absolute theory of reaction rates for a unimolecular reaction. Nevertheless, other apparently unimolecular processes[13] also exhibit frequency factors in the region 10^{15}–10^{16} sec^{-1}. Using the experimentally determined frequency factor, the entropy of activation was evaluated at 450° from the relationship

$$A = \kappa e(kT/h) \exp(\Delta S^{\ddagger}/R)$$

The value of 12.0 eu obtained for $\Delta S^{\ddagger}$ is shown in Table IV together with the entropies of activation of various other alkylcyclobutanes. A positive value for $\Delta S^{\ddagger}$ is typical of the cyclobutane compounds where there is a ring-breaking reaction involving the loosening of some of the bonds in the formation of the transition complex.

Table IV. Kinetic Data for Pyrolysis of Some Alkylcyclobutanes at 450°

Derivative	$10^{-15}A$, sec^{-1}	$\Delta S^{\ddagger}$,[a] eu at 450°	E_{act}, kcal/mole	$10^4 k_1$,[b] sec^{-1} at 450°	Ref
Cyclobutane	4.0	9.2	62.5	5.18	*c*
	4.2	9.2	62.5	5.4	*d*
	7.0	10.2	63.2	5.6	*e*
Methylcyclobutane	2.4	8.1	61.2	7.75	*f*
1,1-Dimethylcyclobutane	4.8	9.5	61.0	17.7	6
1,1,3,3-Tetramethylcyclobutane	17.4	12.0	64.8	4.55	*g*

[a] Values calculated from preexponential factor (A) with $\kappa = 1$. [b] Values of k are calculated from the Arrhenius parameters. [c] C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 4497 (1951). [d] R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963). [e] R. W. Vreeland and D. F. Swinehart, *J. Am. Chem. Soc.*, **85**, 3349 (1963). [f] M. N. Das and W. D. Walters, *Z. Physik. Chem.* (Frankfurt), **15**, 22 (1958); A. F. Pataracchia and W. D. Walters, *J. Phys. Chem.*, **68**, 3894 (1964). [g] Present study.

Table IV also gives the kinetic parameters (A and E) and the rate constants at 450° of 1,1,3,3-tetramethylcyclobutane and some of the other alkylcyclobutanes. Sometimes it may be more significant to compare the rate constants for a series of related molecules rather than Arrhenius parameters. This seems to be the case with the alkylcyclobutanes since the reaction rates at 450° differ by as much as several hundred per cent. The cause of the changes in rate produced by methyl substitution, dimethyl substitution, and now of tetramethyl substitution may be difficult to determine and may not be the result of a single effect. It is of interest to note, however, that 1,1,3,3-tetramethylcyclobutane is found to be the first alkyl-substituted cyclobutane to have an observed rate of decomposition slower than cyclobutane. It has been considered for the pyrolysis of some alkylcyclobutanes that hyperconjugation may provide some stabilization and thus result in a lower energy for either an activated complex leading to a biradical or for an activated complex caused by the simultanoeus lengthing of two of the carbon–carbon bonds and the contraction of the other two. However, it is evident from the results of the decomposition of 1,1,3,3-tetramethylcyclobutane that the observed rate is not in accordance with the result expected if hyperconjugation were acting alone in affecting the rate of reaction.

It was observed from very early studies of the formation of ring compounds from acyclic precursors that the presence of alkyl substituents, especially when these were geminal, facilitated ring formation. According to the "Thorpe–Ingold effect,"[14,15] when the bond angle is distorted between one pair of substituents on a saturated carbon atom, the bond angle between the other pair of substituents will be distorted in the opposite manner. It has been more recently suggested by Arcus[16] that large substituents (X and Y) on one of the carbon atoms in a three- or four-membered ring tend to stabilize the ring since the trigonal bonding character of such a ring gives a wider XCY angle which allows less crowding of the substituents than occurs with the normal tetrahedral angle. Thus, the replacement of hydrogens by bulkier methyl groups in a geminal position should have some stabilizing effect upon a cyclobutane ring. Searles, *et al.*,[17] have suggested in studying 3,3-diethyloxetane that the *gem*-diethyl groups might be widening the external angle at position 3, thereby decreasing both the internal

---

(13) A. F. Trotman-Dickenson, *J. Chem. Phys.*, 21, 211 (1953); B. de B. Darwent and R. Roberts, *Proc. Roy. Soc.* (London), **A216**, 344 (1953).

(14) R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 107, 1080 (1915).

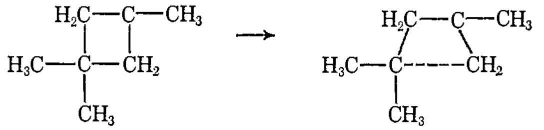
(15) C. K. Ingold, *ibid.*, 119, 305 (1921).

(16) C. L. Arcus, *Chem. Ind.* (London), 41, 646 (1947).

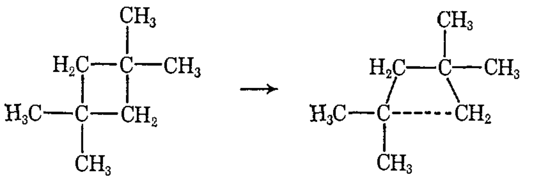
(17) S. Searles, E. F. Lutz, and M. Tamres, *J. Am. Chem. Soc.*, **82**, 2932 (1960).

angle there as well as the internal COC angle directly across the ring. Consequently, there may be a reinforced Thorpe–Ingold effect taking place for 1,1,3,3-tetramethylcyclobutane which stabilizes the cyclobutane ring.

The two types of ring cleavage which have been envisioned for the cyclobutane ring suggest the breaking of two of the original bonds in the ring either (a) simultaneously or (b) in succession. A preference to mechanism b has been given in the majority of the recent publication.[18] One of the important features of the biradical mechanism is that it may be used to account for the minor product, 2,4,4-trimethyl-1-pentene, as well as the major product, isobutylene. It is of interest that much more of the isomerization product is observed for the decomposition of 1,1,3,3-tetramethylcyclobutane than has been observed for the monoalkylcyclobutanes such as methylcyclobutane[19] where only a 1–2% yield was found. The explanation for this may be that the monosubstituted cyclobutanes form two different biradicals, only one of which will isomerize, while only one biradical would be formed for the compound in this study accounting for almost a doubling of the yield of the isomer.



(3)



(4)

Since there seems to be strong evidence that the decomposition reactions of the cyclobutane series proceed by a biradical mechanism, let us suppose that the rate-determining steps for 1,1-dimethylcyclobutane and 1,1,3,3-tetramethylcyclobutane go as shown in eq 3 and 4. A complex such as in eq 3 would be favored for 1,1-dimethylcyclobutane because of the alkyl substitution. As was mentioned in the discussion of the Thorpe–Ingold effect, in the reactant molecules the $H_3C–C–CH_3$ bond angle may be spread out. The orbitals used to form ring bonds have excess p character and the bonds used to form $C–CH_3$ bonds have excess s character. As the 1,1,3,3-tetramethylcyclobutane ring opens, the *gem*-dimethyl group not attached to the bond being broken begins to close up to a normal sp^3 bond angle. However, this would increase the methyl–methyl repulsion. On the other hand, this effect is absent if 1,1-dimethylcyclobutane proceeds as in reaction 3, because the $H_3C–C–CH_3$ bond angle is approaching 120° (sp^2) as the bond breaks. It must be conceded that this is just speculation, but an effect such as this could explain why the rate of decomposition of 1,1,3,3-tetramethylcyclobutane is so slow and, in particular, is so much slower than 1,1-dimethylcyclobutane.[20]

Acknowledgment. The author wishes to express his special gratitude to Dr. W. D. Walters for his guidance throughout the progress of this research. The advice and guidance of Dr. A. B. F. Duncan are also acknowledged. The author is also grateful to Mr. Carl Whiteman and Mr. Tom Weisflog for their assistance. Thanks to the General Railway Signal Company for the use of its computer are also extended.

---

[18] S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, **16**, 421 (1965).

[19] T. F. Thomas, Ph.D. Thesis, University of Oregon, 1964.

[20] NOTE ADDED IN PROOF: It has come to the author's attention that an article has just been published [A. T. Cocks and H. M. Frey, *J. Chem. Soc., A*, 1671 (1969)] which has results substantially in agreement with those recorded here. However, the isomerization product, 2,4,4-trimethyl-1-pentene, is not found in their study.