[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y.]

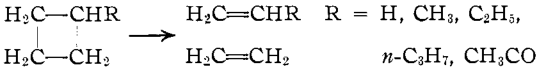
The Thermal Decomposition of Cyclobutanecarboxaldehyde[1,2]

BY B. C. ROQUITTE AND W. D. WALTERS

RECEIVED JULY 24, 1962

The pyrolysis of cyclobutanecarboxaldehyde in the gas phase has been investigated over the temperature range 360–400° and mainly at initial pressures of 9–35 mm. In the early stages of the reaction, ethylene and acrolein are found to be the only important products, and they are formed in equal amounts within the experimental error. The decomposition is a first-order homogeneous reaction not inhibited by nitric oxide, propylene or toluene. From the temperature dependence of the rate constant for initial pressures of 9–12 mm. the energy of activation was found to be 53.3 ± 0.5 kcal./mole, and the first-order rate constant for the decomposition may be expressed as $k = 2.7 \pm 0.1 \times 10^{14} \exp(-53{,}300/RT)$ sec.$^{-1}$.

The thermal decompositions of a number of derivatives of cyclobutane proceed by homogeneous first-order processes of the type



$$\begin{array}{l} \mathrm{H_2C{-}CHR} \\ \;|\qquad\;\; | \\ \mathrm{H_2C{-}CH_2} \end{array} \longrightarrow \begin{array}{l} \mathrm{H_2C{=}CHR} \\ \mathrm{H_2C{=}CH_2} \end{array} \quad \mathrm{R = H, CH_3, C_2H_5,}\ n\text{-}\mathrm{C_3H_7, CH_3CO} \qquad (1)$$

For methyl cyclobutyl ketone ($R = CH_3CO$) it has been found[3] that the activation energy (54.5 kcal./mole) is significantly lower than the activation energies for the pyrolyses of compounds where R is hydrogen or an alkyl substituent (61.2–62.5 kcal./mole).[4] Likewise, an appreciable change in pre-exponential factor was observed. The present work was undertaken to compare the kinetics of the cyclobutanecarboxaldehyde pyrolysis with the results obtained for methyl cyclobutyl ketone and the cyclobutane hydrocarbons. It has been observed[5] that cyclobutanecarboxylaldehyde when passed over glass chips at 350–450° gives acrolein and ethylene, but the kinetics of the reaction under conditions comparable to the earlier studies on cyclobutane derivatives were not reported.

Experimental

Materials.—The cyclobutanecarboxaldehyde was prepared by two different methods. Samples I and II were obtained from the oxidation of cyclobutylcarbinol with sodium dichromate and sulfuric acid as described below. Sample III was prepared earlier in this Laboratory by Dr. H. R. Gerberich by means of a catalytic reaction[6] between formic acid and cyclobutanecarboxylic acid. The cyclobutylcarbinol was prepared from cyclobutanecarboxylic acid by lithium aluminum hydride reduction.[7] The cyclobutanecarboxaldehyde fraction distilling from the oxidizing solution was subjected to further purification and drying. The final purification of both samples I and II involved passage of the vapor over a chromatographic column packed with diisodecyl phthalate on a Celite base. Prior to the chromatographic treatment sample II was purified by fractionation in a distillation column with 85 cm. of Lecky–Ewell packing. In gas chromatographic analyses in two separate columns packed with different materials the purified samples I and II showed only one peak and gave no evidence of impurities (in excess of 0.1%). Sample III was also purified by means of gas chromatography. The infrared spectra of the purified samples from the two different methods of preparation were the same. The trimer which formed from the aldehyde on standing melted at 119–120° (lit.[8] 118.5–120.5°). The 2,4-dinitrophenylhydrazones of various samples of the aldehyde had melting points in the range 152–155° (lit. 153–154°,[8] 156–159°[5]). Carbon-hydrogen analysis[9] were carried out in the aldehyde: II, C, 71.67, 71.16; H, 9.75, 9.41; III, C, 71.46; H, 9.73 (Calcd.: C, 71.39; H, 9.59). On account of the small quantities of purified samples available, an accurate boiling point was not obtained, but it appeared to be about 108.5–110.5° at 749 mm. The boiling points obtained by Becker[5] for four samples of aldehyde prepared in four different ways were 113.5–115°, 107–112°, 108–110 and 107–109°. A value of 113–115° has been reported also.[8] The lack of reproducibility of the boiling point may be the result of a reaction producing water during the distillation which Becker has observed.[5] The refractive index, n^{20}D, was 1.4310 for II and III (lit. 1.4357[8]; n^{25}D 1.4326–1.4333[5]). As an additional check on the purities of the samples after gas chromatographic purification they were analyzed by the hydroxylamine procedure of Bryant and Smith.[10] With the reagents and method standardized against vacuum-distilled Baker C.P. analyzed reagent furfural the average purity of samples I and III was found to be 100.1 ± 0.5%. Standardizations against purified butyraldehyde were within three parts per thousand of those with furfural.

Methyl cyclobutyl ketone from the previous study[3] was further purified by the use of a chromatographic column with diisodecyl phthalate on Celite. Acrolein (Eastman Kodak Co. white label) was fractionally distilled, dried over anhydrous calcium sulfate, and then distilled under vacuum. Ethylene (Ohio, 99.5%) and propylene (Ohio, 99.5%) were subjected to vacuum distillation before use. By gas chromatography the ethylene sample was found to be 99.9% pure. Toluene (Mallinckrodt, anal. reag.) was degassed and dried over 4A Linde molecular sieve. Nitric oxide (Matheson, 98.7%) was purified by four distillations from −160 to −196°.

Apparatus and Procedure.—The reaction vessels were cylindrical Pyrex bulbs with volumes close to 300 ml. Vessel U was unpacked; vessel P was packed with thin-walled Pyrex tubes to increase the surface to volume ratio about 28-fold; vessel C was an unpacked vessel with the inner walls coated with potassium chloride. The temperature at the center of each vessel was measured by the use of a platinum, platinum–13% rhodium thermocouple which agreed to the nearest 0.1° with the temperature of melting (419.5°) of an N.B.S. sample of zinc. The pressure was determined by means of a wide-bore mercury manometer read with a Gaertner cathetometer. Pressure readings could be estimated to 0.001 mm. and were found reliable to 0.01 mm. External tubing connected to the reaction vessel was heated electrically and tests showed that no detectable condensation or absorption in stopcock grease occurred during an experiment. A preliminary pyrolysis was carried out each day to ensure a deactivated condition of the surface of the reaction vessel. Experiments with added gas were conducted with introduction of the added gas (a) before and (b) after the introduction of the aldehyde.

---

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

(2) Abstracted from the Ph.D. thesis submitted by B. C. Roquitte who held a Sherman Clarke Fund fellowship during the summer of 1958.

(3) L. G. Daignault and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 541 (1958).

(4) For references to the various studies see S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961).

(5) M. Becker, *Dissertation Abstracts*, **18**, 391 (1958); Ph.D. thesis, Ohio State University, 1952.

(6) Similar to the method of B. A. Kazanskii and M. Yu. Lukina, *Doklady Akad. Nauk S.S.S.R.*, **65**, 693 (1949).

(7) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

(8) Ya. M. Slobodin and M. V. Blinova, *Zhur. Obshch. Khim.*, **23**, 1994 (1953).

(9) Performed by W. Manser, Zurich, Switzerland.

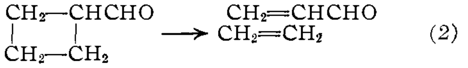
(10) W. M. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, **57**, 57 (1935).

Analysis of Products.—The reaction mixture was removed usually after about 35% decomposition and separated into different fractions according to volatility. The fractions were: (1) substances volatile at −196°; (2) substances condensable at −196°, but volatile at −112°; and (3) substances not volatile at −112°. Fraction 1 was less than 0.01% of fraction 2 and was not analyzed. In preliminary 10-mm. experiments carried to 60% decomposition at 390° the infrared spectrum of fraction 2 was obtained by the use of a Perkin–Elmer 21 instrument with a 1-liter gas cell having a 1-meter path length. Fraction 2 showed absorption maxima at 3.3, 5.26, 5.31, 5.38, 6.84, 6.95 and 7.0 μ and a strong absorption in the region 9.1–11.9 μ with the principal maximum at 10.54–10.56 μ. These observed peaks were in good agreement with the infrared absorption of pure ethylene determined in this Laboratory and with that reported in the literature.[11] In other experiments it was observed that on an average 98–99% of fraction 2 could be absorbed in sulfuric acid activated with 0.6% silver sulfate, indicating that it was composed of ethylene or other unsaturates. Fraction 2 from a 12-mm. experiment at 400° was analyzed on a Consolidated model 21–620 mass spectrometer and ethylene was found to be essentially the only component. With a silica gel column (J) in a Perkin–Elmer 154B chromatograph the retention time of fraction 2 was identical with that for pure ethylene. Quantitative gas chromatographic analyses showed that 99.9% of fraction 2 was ethylene. Therefore, for the present experimental conditions it was regarded as satisfactory to designate the amount of fraction 2 measured in a gas buret as ethylene.

The identification of another important decomposition product was accomplished by allowing the more volatile portion of fraction 3 to vaporize at −25° into the 1-meter infrared gas cell. At this temperature the undecomposed cyclobutanecarboxaldehyde has a very low vapor pressure. The infrared spectrum of the volatile part of fraction 3 showed absorption in the regions 2.95–3.05, 3.25–3.45, 3.55–3.85, 5.2–5.3, 5.6–6.05, 8.5–9.0, 10.1–10.2 μ with positions of the absorption maxima in general agreement with those for acrolein. Differences between the sample from fraction 3 and acrolein were noticeable at 3.4 and 3.75 μ where the sample showed stronger absorption, presumably due to some cyclobutanecarboxaldehyde which absorbs in these regions.

In addition to the infrared analysis, fraction 3 was subjected to polarographic[12] and ultraviolet absorption analysis. In the polarographic procedure, fraction 3 was dissolved in water and the supporting electrolyte, prepared by neutralizing phosphoric acid with lithium hydroxide, was added. The agreement between the polarogram of the sample and that for acrolein was good enough to show that fraction 3 contained acrolein. An aqueous solution of fraction 3 which was analyzed in a Beckman DU spectrophotometer showed strong absorption in the region 208 to 213 mμ with a maximum at 210. Acrolein was found to have a similar absorption. It was observed that the optical density at 210 mμ for an acrolein solution follows Beer's law and from analysis of standard solutions under the experimental conditions to be used in the subsequent work a molar extinction coefficient of 1.29×10^4 liter mole^{-1} cm.$^{-1}$ was obtained. By measurement of the optical density of fraction 3 from pyrolyses at various temperatures and pressures the amounts of acrolein present were calculated. A small correction (approximately 2%) was applied for the optical density of the undecomposed cyclobutanecarboxaldehyde present in fraction 3 of the reaction mixture. In the experiments with added inhibitors the analyses for both fractions 2 and 3 were not performed in every experiment on account of the interference from the inhibitors.

The product analyses indicate that the homogeneous thermal decomposition of cyclobutanecarboxaldehyde occurs as



(2)

In view of the formation of 2,3-dihydrofuran from cyclopropanecarboxaldehyde,[13] the possibility of the formation of 3,4-dihydro-2H-pyran from cyclobutanecarboxaldehyde was investigated. The infrared results in the present and earlier[5] work gave no indication of dihydropyran in the products. In gas chromatographic analyses of products from experiments with 10–15 mm. pressure at 360–400° a very small amount of a substance with a retention time either identical with or quite close to that of dihydropyran was found. By comparison with a standard sample, any dihydropyran present after 30% decomposition was found not to exceed 0.007 times the cyclobutanecarboxaldehyde and at 11% decomposition this component was only 0.0033 as large as the cyclobutanecarboxaldehyde. Rate measurements[14] with dihydropyran showed that during the first 25% reaction not more than 1 part per 100 of the acrolein and ethylene could have been formed *via* dihydropyran, and the effect on the calculated rate constants would be smaller. If the trace component were not dihydropyran, it might be a very minor side or subsequent product, but in any case the decomposition appears to occur essentially by reaction 2.

Table I summarizes a portion of the quantitative determinations which were carried out in order to find out whether the reaction proceeds stoichiometrically according to eq. 2. The amounts of the individual products were computed as the pressures of gases which would have been present in the reaction vessel. These values may be compared with the measured pressure increases in the reaction vessel. Different samples of the reactant gave similar results. For the decomposition in an essentially constant volume system at 360–400° with pressures near 10 mm. the pressure increase (ΔP) in the unpacked vessel corresponds closely to the analyzed pressure of acrolein (p_A) or ethylene (P_E). For 21 experiments the ratio $P_E/\Delta P$ averaged 0.99 ± 0.01 and the ratio $P_A/\Delta P$ averaged 1.01 ± 0.02.[15] The fact that the ratio for ethylene tends to be slightly lower than unity may be due to the loss of some ethylene which dissolved in acrolein and cyclobutanecarboxaldehyde in the trap at −112°. Data obtained for pure acrolein at 400° by pres-

TABLE I

COMPARISON OF THE PRESSURE CHANGE IN THE DECOMPOSITION OF CYCLOBUTANECARBOXALDEHYDE WITH THE PRESSURES OF THE PRODUCTS

Conditions[a]	P_0,[b] mm.	ΔP,[c] mm.	P_A, mm.	p_E, mm.
		Temp., 360°		
II, U	9.44	2.53	2.51	2.51
II, U	11.95	3.33	3.34	3.30
		Temp., 370°		
I, U	9.55	2.85	2.93	2.81
		Temp., 380°		
I, U	10.35	2.95	3.02	2.94
I, U	9.88	2.87	2.91	2.84
		Temp., 390°		
I. U	9.71	2.89	2.95	2.93
I, U, C_7H_8	9.51	3.22	..	3.21
I, U, C_3H_6	8.77	2.95	3.03	..
I, U, NO	9.72	3.31	3.38	..
III, P	10.50	3.48	3.48	3.45
I, P	10.92	3.45	3.56	3.54
I, P	31.75	9.76	9.71	9.52
		Temp., 400°		
I, U	11.08	3.51	3.53	3.54
III. U	10.07	3.38	3.47	3.37

[a] Roman numeral designates the sample, letter gives the type of vessel, formula indicates any inhibitor which was added; C_7H_8 means toluene; C_3H_6 means propylene. [b] Initial pressure of reactant. [c] Pressure increase.

---

(11) "Infrared and Ultraviolet Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.; infrared curves 18 and 530 for ethylene; ultraviolet curve 330 for acrolein.

(12) The procedure was similar to that of R. W. Moshier, *Ind. Eng. Chem., Anal. Ed.*, **15**, 107 (1943).

(13) C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947).

(14) Performed by Dr. C. A. Wellington in this Laboratory.

(15) The ratio would be 0.995 if the absorptivity of acrolein for the data in A.P.I. ultraviolet curve 330, ref. 11, were used. In a private communication Dr. R. R. Brattain indicated that the absorbance at 210 mμ would give 1.306×10^4 liter mole^{-1} cm.$^{-1}$ for the absorptivity.

sure measurements and analysis indicated that any subsequent reaction of acrolein would be so slow that the effect on the present kinetic results would be negligible. Inspection of the results of the analyses (see Table I) reveals that the stoichiometry does not alter when the surface to volume ratio is increased 28-fold or when toluene, propylene or nitric oxide is added.

Results

Order and Homogeneity of the Reaction.—The analytical data indicate that the measurement of the pressure increase is satisfactory for following the reaction. The pressure–time curve which has no induction period has the general appearance of a first-order process. The times for 25% decomposition ($t_{1/4}$, corrected for dead space) were obtained from the pressure–time curves for a number of different experimental conditions. A sixfold variation in the initial pressure (from 6 mm. to 36 mm.) at 370° and variations in pressure of fourfold or greater at 360°, 380°, 390° and 400° revealed no dependence of quarter-time upon the initial pressure and thus gave evidence for first-order character. Some of the data for different pressures at 390° are shown in Table II. In a few experiments the ratio $t_{1/4}/t_{1/8}$ was calculated. The average value obtained was 2.13 which is close to the theoretical value of 2.15 for a first-order reaction. Over the portion of the reaction studied (about the first 35%) a plot of log $[P_0/(2P_0 - P_t)]$ *vs.* time gave a satisfactory straight line. Rate constants calculated from the slope of such lines were in agreement with those calculated from the quarter-times (within 1.6%, av.). Different methods of preparation or drying of samples of reactant produced no noticeable effect on the rate. To investigate the homogeneity of the decomposition, experiments were performed in a packed vessel with a 28-fold larger (S/V) ratio and in a KCl-coated vessel. Typical results are given in Table II. Since neither an increase in surface area nor a change in the nature of the surface had a significant influence on the rate, it appeared that in the unpacked bulb at least 99.5% of the decomposition of cyclobutanecarboxaldehyde takes place in the gas phase.

TABLE II

DECOMPOSITION OF CYCLOBUTANECARBOXALDEHYDE UNDER VARIOUS EXPERIMENTAL CONDITIONS

P_0, mm.	$t_{1/4}$, min.	Sample	P_0, mm.	$t_{1/4}$, min.	Sample
	Temp., 390°, unpacked vessel				
8.06	6.4	I	20.1	6.7	I
9.85	6.4	II[a]	23.1	6.4	I[a]
10.42	6.3	I[a]	32.4	6.2	I
10.55	6.5	III	43.5	6.5	I
	Temp., 390°, packed vessel				
10.92	6.5	I	27.7	6.3	I
10.50	6.1	III	31.8	6.1	I
	Temp., 390°, KCl-coated vessel				
10.04	6.4	I	29.3	6.2	I
	Temp., 360°, packed vessel				
9.57	43.5	I	33.8	41.6	I
9–38	43.5 average, in unpacked vessel				

[a] Sample dried over anhydrous calcium sulfate.

Activation Energy.—To determine the effect of temperature, the logarithms of the rate constants for thirty-eight experiments in the range 9–12 mm. were plotted against the reciprocals of the absolute temperatures. The rate constants had been calculated from the quarter-times by the use of the integrated first-order equation. The plot is shown in Fig. 1. It is seen that there is a linear relationship between log k and $1/T$ over the temperature range used. The value of the activation energy was found by least squares analysis on an IBM 650 computer to be 53.3 kcal./mole and from consideration of the standard deviation of 0.3 kcal./mole and possible sources of error it is estimated that the activation energy should be accurate within about ±0.5 kcal./mole. Evaluation of the activation energy from the slope of the line in the graph gave a value within this range. It is to be noted that a change in the pressure in the region 9–12 mm. produced no detectable change in rate constant within the experimental error. The value of A was determined by setting $k = A \exp(-53{,}300/RT)$ for each of the thirty-eight experiments. The average value of A and the average deviation were found to be $2.72 \pm 0.06 \times 10^{14}$ sec.$^{-1}$.

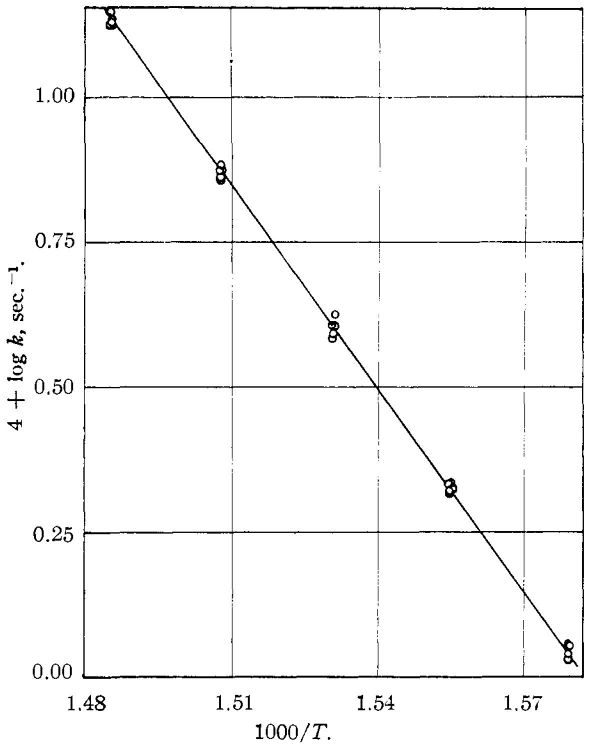


Fig. 1.—Change of the first-order rate constant for the decomposition of cyclobutanecarboxaldehyde with temperature; initial pressure, 9–12 mm.

Influence of Added Substances.—For the purpose of ascertaining whether the decomposition involves free radical chain processes, experiments were performed in the presence of nitric oxide, toluene or propylene. The pressure–time curves in such experiments were similar to those exhibited by pure cyclobutanecarboxaldehyde. Table III gives the quarter-times observed in the presence and absence of added inhibitor. Since the rate of the decomposition is not affected significantly by the addition of any of the substances, there is no evidence for a free radical chain reaction.

TABLE III

DECOMPOSITION OF CYCLOBUTANECARBOXALDEHYDE IN THE PRESENCE OF VARIOUS SUBSTANCES AT 390°

P_C,[a] mm.	Added gas	P_1,[b] mm.	$t_{1/4}$, min.
9.72	Nitric oxide	0.39	6.5
9.14	Nitric oxide	0.22	6.5
9.30	Propylene	3.26	6.6
8.77	Propylene	4.72	6.7
8.75	Toluene	3.80	6.7
9.51	Toluene	4.57	6.5
8.5–9.9	None	...	6.5[c]

[a] Pressure of cyclobutanecarboxaldehyde. [b] Pressure of added gas. [c] Average of six experiments.

Discussions

The experimental results give evidence that the thermal decomposition of cyclobutanecarboxaldehyde is mainly a simple unimolecular reaction producing ethylene and acrolein. If a free radical chain reaction were occurring, it seems likely that products in addition to acrolein and ethylene would be observed. Moreover, the fact that the addition of propylene, toluene or nitric oxide does not alter either the rate or the composition of the products is in agreement with the absence of a free radical chain mechanism. The existence of a biradical intermediate of very short life which decomposes into molecular products cannot be excluded on the basis of the present experimental data. With regard to the type of ring cleavage, kinetics and mechanism, the decomposition of cyclobutanecarboxaldehyde appears to resemble the pyrolytic reactions previously observed for cyclobutane and its derivatives, especially methyl cyclobutyl ketone, and is not similar to the decomposition of a saturated aliphatic aldehyde, *e.g.*, propionaldehyde, whose decomposition involves free radical reactions and is of three-halves order.[16] Likewise the behavior of cyclobutanecarboxaldehyde is different from that of a higher aliphatic ketone since it has been observed that free radical processes occur in the pyrolysis of methyl *n*-butyl ketone and the rate is decreased in the packed vessel.[17] For the decomposition of cyclobutanecarboxaldehyde no decrease in first-order rate constant was observed down to 6 mm. initial pressure, but in comparison with other cyclobutane derivatives a fall-off would not be expected under such conditions for this type of molecule.

From the experimental value of the frequency factor one can estimate the entropy of activation ($\Delta S^{\ddagger}$) from the expression

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

when κ, the transmission coefficient, is assumed to be unity. The entropy of activation at 390° for the decomposition of cyclobutanecarboxaldehyde has been calculated to be +3.9 e.u. which is not far from the value reported for methyl cyclobutyl ketone (+4.3 e.u. at 400°).[3] The change in structure from methyl cyclobutyl ketone to cyclobutanecarboxaldehyde brings about a lowering of the activation energy from 54.5 to 53.3 kcal./mole with the result that the rate of decomposition of the aldehyde at 390° is about twice as fast as that for methyl cyclobutyl ketone. In the case of each of these compounds containing a carbonyl group the observed rate is considerably higher than the rates for cyclobutane and its alkyl derivatives. The fast rates for the carbonyl compounds are due to the lower activation energies (7.5–9 kcal./mole). Although the frequency factors are smaller for the carbonyl derivatives, the change is not sufficient to counterbalance the decrease in activation energies. The cause of the lowering of the activation energy has not been established, but if biradical formation is the rate-determining step, it would appear that a biradical which could be formed from cyclobutanecarboxaldehyde by ring opening would have more resonance energy than a biradical from an alkyl-substituted cyclobutane. Such an effect has been suggested already for methyl cyclobutyl ketone.[3] If a biradical is not involved, the lower activation energy may be due in part to greater resonance stabilization of acrolein[18] as a product compared to that for the corresponding product from an alkyl cyclobutane. Also, if there were some interaction in the activated complex between the oxygen atom of the carbonyl group and a hydrogen atom on the ring, the entropy of activation might be lower than for an activated complex without such interaction.[19]

Acknowledgment.—The authors wish to thank Mr. Carl Whiteman, Jr., for making the infrared measurements and the least squares analysis. They are also grateful to the Xerox Corporation for the use of the IBM 650 computer.

---

(16) A. Boyer and M. Niclause, *J. chim. phys.*, **49**, 354 (1952), and other references given in the article.

(17) W. T. Barry, Jr., and W. D. Walters, *J. Am. Chem. Soc.*, **79**, 2102 (1957).

(18) Concerning the resonance energy of an analogous compound crotonaldehyde, see M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.*, **60**, 440 (1938) and M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **79**, 4016 (1957).

(19) Suggestion of R. Carr of this Laboratory.