# The gas-phase thermal decomposition of cyclobutanol<sup>1</sup>

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The thermal decomposition of cyclobutanol has been studied in the gas phase in a static system at pressures from 3–6 Torr and temperatures from 250 to 450°C. The major products observed were ethylene and acetaldehyde, while *n*-butyraldehyde was a minor product. First-order rate constants based on ethylene formation in a Pyrex vessel conditioned by carbon deposition gave Arrhenius parameters of A = 2.14 ( $\pm 0.2$ ) × 10<sup>14</sup> s<sup>-1</sup> and E = 57.3 ( $\pm 1$ ) kcal/mol. Under the same conditions, the ratio *n*-butyraldehyde/ ethylene increased with decreasing temperature, corresponding to an activation energy of about 50 kcal/mol for butyraldehyde formation and a frequency factor about 10<sup>4</sup> times lower than that for ethylene production. In an untreated Pyrex vessel that both ethylene and *n*-butyraldehyde are formed from a common  $\dot{CH}_2CH_2CH_2CHOH$  biradical by cleavage and by hydrogen transfer through a 6-membered cyclic transition state respectively. The thermal decomposition is thus the reverse of the Type II and II' processes observed in the photolysis of *n*-butyraldehyde.

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On a étudié la décomposition thermique du cyclobutanol en phase gazeuse dans un système statique à des pressions variant de 3 à 6 Torr et à des températures allant de 250 à 450°C. Les produits majoritaires observés sont l'éthylène et l'acétaldéhyde tandis que le butyraldehyde est le produit secondaire. Les constantes de vitesse d'ordre un, évaluées à partir de la formation d'éthylène dans un récipient en pyrex traité au noir de charbon, permettent de déterminer les paramètres d'Arrhénius  $A = 2,14(\pm 0,2) \times 10^{14} \text{ s}^{-1}$  et  $E = 57,3(\pm 1)$  kcal/mol. Dans les mêmes conditions, le rapport *n*-butyraldehyde/éthylène augmente lorsque la température diminue; ceci correspond à une énergie d'activation d'environ 50 kcal/mol pour le butyraldehyde.

[Traduit par le journal]

#### Introduction

The thermal decompositions of cyclobutane and its derivatives have been very extensively studied (1). Simple unimolecular decomposition into two ethylene molecules (or substituted ethylenes) is the usual mode of decomposition, generally believed to proceed through a biradical intermediate formed by ring opening:

1]  $\longrightarrow$  --CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- $\rightarrow$  2C<sub>2</sub>H<sub>4</sub>

In a few systems, alternative reactions of the biradical (other than isomerization) can compete with reaction [1]. In cyclobutanone, for example, minor products are cyclopropane and CO, although it is not clear whether they are formed from the same biradical which decomposes to yield ethylene and ketene, the main products, or by a totally different pathway (2). A better example is isopropenylcyclobutane, which forms 1-methylcyclohexene with a yield almost 80% of the normal fragmentation products by ring closure of an allylic resonance structure of the biradical (1, 3). A third and especially interesting example is the decomposition of *cis*-1,2-dimethylcyclobutanol. A brief account by Feit (4) reports two pairs of decomposition channels at 381°C, each pair proceeding

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through a common biradical and yielding not only the substituted ethylenes expected from fragmentation, but also the hexanone isomers formed by transfer of the O—H hydrogen through a cyclic six-membered transition state. The latter process is exactly the reverse of the biradical formation step postulated in the Norrish type II photochemical decomposition of these same ketones, and the fragmentation products are those observed in the latter processes in the gas phase (4). In the photolysis of the appropriate aldehydes and ketones (5, 6) isomeric cyclobutanols are produced, and it is clear that these photolyses and the thermal decomposition of the cyclobutanols are intimately related, and warrant further investigation.

No comparable studies of the thermal decomposition of cyclobutanol itself have been reported in the open literature, although a Ph.D. thesis on the subject was submitted to the University of Rochester in 1967 by P. M. Stacey, from the laboratory of the late W. D. Walters (7). Fragmentation to ethylene and acetaldehyde was the main decomposition path, and Arrhenius parameters based on carefully calibrated  $\Delta p$  measurements were reported for the temperature range 405–445°C. *n*-Butyraldehyde was also observed to be a very minor product, but was not measured systematically. The present paper describes a more thorough study of the thermal decomposition, with measure-

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ment of both product channels based on product analysis and covering a much wider range of temperature.

### Experimental

The decomposition was studied in a conventional static system, using a cylindrical Pyrex vessel about 3 cm in diameter and 10 cm long, with rounded ends, of about 55 cm3 volume, mounted in a tube furnace controlled to  $\pm 0.5^{\circ}$ C. In the first series of experiments no special treatment was given to the surface of the reaction vessel. In the second series, a light carbon coating was deposited on the surface by the pyrolysis of about 100 Torr of isobutene for 10 h at 450°C. To test for surface effects a similar vessel was used, packed with lengths of 5 mm od Pyrex tubing which increased the surface/volume ratio by a factor of 3. The reaction vessels were attached through a metal valve to a grease-free vacuum line. Pressure was measured by a quartz spiral gauge or a mercury manometer, and because the vacuum line was at ambient temperature, pressures of cyclobutanol were limited by its vapor pressure. The reaction was started by admitting the cyclobutanol vapor to the hot reaction vessel and terminated by opening the valve leading through a cold trap (77 K) to a Toepler pump. The entire sample, reagent and condensible and noncondensible products, was then transferred by Toepler pump to the pickup of a gas chromatograph for analysis. One of two columns was usually employed, either 6 m of Durapak phenylisocyanate on Porasil-C for hydrocarbon analysis, or 3 m of squalane on Celite for analysis of aldehydes and ketones, and duplicate experiments were made to obtain complete product analysis.

Cyclobutanol of stated purity 99+% was purchased from Aldrich Chemical Co. and used after rigorous degassing and simple trap-to-trap distillation. Very small amounts of ethylene and several other hydrocarbons remained, and traces of acetaldehyde and butyraldehyde were present. These impurities were all also products of the pyrolysis and small corrections were made to measured product yields.

# **Results and discussion**

#### Reaction products

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The major products of the decomposition under all conditions were ethylene and acetaldehyde, as found by Stacey (7). Vinyl alcohol would be expected from the simple decomposition analogous to reaction [1], but would not have been directly detected in the present experiments as it would have been strongly retained on the columns employed. In the untreated vessel ethylene and acetaldehyde were observed in approximately equal amounts except at the lowest temperature (250°C) where acetaldehyde was about 80% of the ethylene. In the conditioned vessel acetaldehyde was consistently less than the ethylene, ranging from 65 to 85%. Very recently it has been shown by mass spectrometry that vinyl alcohol is a major primary product of the pyrolysis of cyclobutanol vapor in a quartz tube at 950°C and about 1 mTorr pressure (8). The stability of vinyl alcohol has been a subject of some controversy, the isomerization being apparently very surface sensitive. It seems probable that vinyl alcohol was formed initially in the present experiments but mostly isomerized to acetaldehyde before analysis, more efficiently in the untreated vessel than in the conditioned one. Careful analysis on a  $\beta$ , $\beta'$ -phenylnaphthylamine column showed that ethylene oxide, another possible isomer of vinyl alcohol, was not a product.

The only other product of any importance was *n*-butyraldehyde, which ranged in yield in the untreated vessel from about 15% of the ethylene at 250°C to about 4% at 450°C, and was rather less in the conditioned vessel.

Other minor products were CH<sub>4</sub> (0.2–0.9%),  $C_2H_6$  (~0.1%), propylene (0.3–2.5%), butadiene (1.5–3.2%), and cyclobutanone (1–5%); yields in parentheses are ranges of initial values in the untreated vessel, relative to ethylene, between 250 and 450°C. Yields in the conditioned vessel were much less.

#### Kinetics of the decomposition

Production of ethylene and butyraldehyde can be described by two parallel first-order unimolecular reactions,

2] 
$$\bigcirc$$
 OH  $\xrightarrow{k_2}$  C<sub>2</sub>H<sub>4</sub> + CH<sub>3</sub>CHO (or CH<sub>2</sub>CHOH)  
3]  $\bigcirc$  OH  $\xrightarrow{k_3}$  C<sub>3</sub>H<sub>7</sub>CHO

Rate constants based on yields of  $C_2H_4$  and  $C_3H_7$ -CHO were independent of conversion up to about 10% and independent of pressure over the relatively narrow range of pressures employed (3–6 Torr). (A series of experiments in sealed untreated Pyrex tubes of ~ 10 cm<sup>3</sup> volume at higher pressures (~110 Torr) gave product yields and rate constants similar to those in the untreated fixed vessel.) At higher temperatures and higher conversions secondary decomposition of the aldehydes set in and yields of minor products increased.

Rates of decomposition were very much faster in the untreated reaction vessel, and less temperature dependent. Arrhenius plots of  $k_2$ , based on ethylene formation, are shown in Fig. 1. The Arrhenius parameters in the untreated vessel (E = 32 kcal/mol,  $A = 10^7 \text{ s}^{-1}$ ) are much too low for a homogeneous reaction and the decomposition is obviously occurring on the surface. Values for the carbon-coated vessel of  $E = 57.3 \pm 1 \text{ kcal/mol and}$  $A = 2.14 (\pm 0.2) \times 10^{14} \text{ s}^{-1}$  on the other hand, are compatible with those observed for other homogeneous cyclobutane decompositions; the reduction in E by about 5 kcal/mol from that for the parent cyclobutane seems reasonable for hydroxyl substitution. Experiments in a packed, conditioned reaction vessel with S/V increased by about a factor of 3 showed no significant change (Fig. 1) and

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FIG. 1. Arrhenius plot of first-order rate constant  $k_2$  for the thermal decomposition of cyclobutanol based on formation of  $C_2H_4$ . Stacey's data (Table XIV, ref. 7) =  $\Box$ .

it appears that the decomposition in the carboncoated vessel was almost entirely homogeneous. Although alcohols are notoriously surface sensitive, the magnitude of the surface effect in cyclobutanol seems unusually large, with the rate of decomposition at 600 K almost 600 times faster in the clean vessel than in the carbon-coated one. Stacey (7) also found a large surface effect in the decomposition, which could be eliminated by seasoning the vessel by repeated prolonged pyrolysis of cyclobutanol or olefins. In such a seasoned vessel, Arrhenius parameters of E = 60.1 kcal/mol and  $A = 1.28 \times 10^{15} \text{ s}^{-1}$  were obtained, independent of surface/volume ratio. While these values are substantially higher than ours, the actual rate constants on which they are based (plotted in Fig. 1) are in excellent agreement with the present data. Low Arrhenius parameters are generally suspect, since a variety of systematic errors (residual surface reaction, for example) tend in that direction. On the other hand, Stacy's data cover a narrow temperature range and depend on  $\Delta p$ measurements at fairly high conversions, and on balance, our present Arrhenius parameters are probably more reliable.

Figure 2 shows Arrhenius plots of the product ratio  $C_3H_7CHO/C_2H_4$  (i.e.,  $k_3/k_2$ ) for the treated and untreated reaction vessels; the ratio increases with decreasing temperature and is consistently higher and less temperature-dependent in the latter.

# Mechanism of the reaction

The present observations point to a mechanism analogous to that suggested for 1,2-dimethylcyclobutane (4), shown in Fig. 3, which also shows the energetics of the decomposition. If the isomerization of the biradical is assumed to proceed with little or no activation energy, as seems probable,

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FIG. 2. Arrhenius plot of  $k_3/k_2$ , based on relative yields of *n*-butyraldehyde and ethylene.

the value of  $E_2 - E_3 = 7.3$  derived from Fig. 2 for the conditioned vessel can be approximately equated to the activation energy for the decomposition of the biradical; from the value of  $E_2 = 57.3$ , the heat of formation of the biradical from cyclobutanol then becomes 50 (all energies in kcal/mol). These values are in reasonable accord with those calculated for similar systems by Benson et al. (1), making allowance for the effect of OH substitution. The value of  $A_2/A_3 = \sim 10^4$  is at least 10 times larger than can reasonably be predicted from simple estimates of entropies of activation. The dashed line in Fig. 2 has been drawn to give  $A_2/A_3 = 10^3$ , and results in  $E_2 - E_3 = 4.3$  kcal/mol. This seems a rather low activation energy for dissociation of the biradical, and perhaps a small barrier of 2 or 3 kcal/mol to the formation of the transition state for reaction [3], leaving 6 or 7 kcal/mol for dissociation, would be a happier solution. It is unfortunate that the low yields of *n*-butyraldehyde, its secondary decomposition, and possible surface effects, make the measurements of  $k_2/k_3$  rather uncertain. The present system is a somewhat unusual example of a two-channel system in which the highenergy channel, reaction [2], predominates despite its higher energy requirements, because of a favourable frequency factor.

Feit (4) reported a ratio of methylbutylketone/ propylene of about 8% for the decomposition of 1,2-dimethylcyclobutanol at 381°C; this is more than three times the analogous  $C_3H_7CHO/C_2H_4$ ratio at the same temperature in the conditioned vessel in the present experiments. No temperature dependence of this ratio was reported and surface conditions were not specified, although the activation energy of 58 kcal/mol, based on disappearance of the cyclobutanol, was close to that found in the present study; the frequency factor was about 5 times larger.

Dehydration, a major mode of decomposition of some alcohols (9), does not seem to be important with cyclobutanol. The expected product, cyclobutene, would have been unstable at the temperatures of the decomposition, isomerizing to butadiene. The latter was a product in the untreated vessel, rising from 1.5% of the C<sub>2</sub>H<sub>4</sub> at 250°C to 3.3% at 450°C; it was barely measurable in the conditioned vessel, less than 0.5% at the highest temperature. The other minor products, CH<sub>4</sub>,  $C_2H_6$ ,  $C_3H_6$ , and cyclobutanone were also almost negligible in the conditioned vessel. Their larger production in the untreated vessel probably came from free-radical reactions initiated at the surface; there was also a marked secondary formation of these products, probably from the decomposition of acetaldehyde and butyraldehyde.

The photolysis of *n*-butyraldehyde has been thoroughly studied, both in the gas phase and in solution, in a number of laboratories, most recently by Berces and co-workers (10). It was shown that both singlet and triplet excited states were precursors of ethylene, the type II photolysis product, and cyclobutanol, with both products presumed to arise from the  $\dot{C}H_2CH_2CH_2\dot{C}HOH$  biradical

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FIG. 3. Mechanism and energetics of the thermal decomposition of cyclobutanol.

formed by hydrogen transfer through a six-membered transition state (Fig. 3). The quantum yields of these products changed relatively little in going from the gas to the liquid phase, indicating that the biradical was formed directly from the excited singlet or triplet states rather than through a vibrationally excited ground state, and that vibrational excitation of the excited states was also not an important factor. In isooctane solution, the ratio  $C_2H_4$ /cyclobutanol (i.e., cleavage/ring closure) was 4.33, independent of temperature, while in the gas phase at 100 Torr the same ratio was 6.8 at room temperature. The difference between the gas phase and the solution, and a temperature dependence in the gas phase value, were attributed to a change in the singlet/triplet ratio, with the singlet yielding ethylene preferentially. The present study yields no information about ring closure in the cyclobutanol biradical, but Feit (4) in the thermal decomposition of cis-1,2-dimethylcyclobutanol at 381°C found appreciable *cis*-*trans* isomerization, indicating ring closure at a rate about one-third that of the cleavage to form propylene, i.e., cleavage/ring closure = 3.33. Making allowance for possible effects of methyl substitution, this value is close enough to those observed in the photolysis of n-butyraldehyde to support the contention that similar biradicals are intermediates in both systems.

- S. W. BENSON and H. E. O'NEAL. Kinetic data on gas phase unimolecular reactions. NSRDS-NBS 21, Washington. 1970.
- A. T. BLADES. Can. J. Chem. 47, 615 (1969); T. H. MCGEE and A. SCHLEIFER. J. Phys. Chem. 76, 963 (1972); 77, 1317 (1973); A. T. BLADES and S. SANDHU. J. Phys. Chem. 77, 1316 (1973).
- 3. R. J. ELLIS and H. M. FREY. Trans. Faraday Soc. 59, 2076 (1963).
- 4. E. D. FEIT. Tetrahedron Lett. 1475 (1970).
- N. C. YANG, S. P. ELLIOT, and B. KIM. J. Am. Chem. Soc. 91, 7551 (1969).
- 6. J. D. COYLE. J. Chem. Soc. B, 2254 (1971).
- P. M. STACEY. Ph.D. Thesis. University of Rochester, Rochester, NY. 1968; Diss. Abstr. B. 29, 1632 (1968).
- 8. F. P. Lossing. Private communication.
- 9. H. KNOZINGER. The chemistry of the hydroxyl group. Part 2. *Edited by* S. Patai. Wiley, Interscience. New York. 1971. p. 641.
- S. FÖRGETEG, T. BÉRCES and S. DÓBÉ. Int. J. Chem. Kinet. 11, 219 (1979); S. FÖGETEG and T. BÉRCES. Int. J. Chem. Kinet. 11, 239 (1979).

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