[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Cyclobutane-1,1,2,2-d_4[1,2]

BY R. SRINIVASAN AND STEPHEN M. E. KELLNER[3]

RECEIVED JUNE 2, 1959

The thermal decomposition of cyclobutane-1,1,2,2-d_4 containing 6.5% of cyclobutane-1,1,2-d_3 has been studied over the temperature range from 404.9 to 450.0°. The principal product was ethylene which was made up of: C_2D_4, 100.0; C_2D_3H, 6.9; $C_2D_2H_2$, 209.1; C_2DH_3, 6.9; C_2H_4, 109.8. The isotopic composition of the product did not change detectably with temperature in the 45° range over which the decomposition was studied. The relative rates of decomposition of cyclobutane and cyclobutane-d_4 have been obtained by the mass spectrometric analysis of the ethylene formed in the thermal decomposition of a mixture of the two compounds. These results have been interpreted to mean that the thermal decomposition of cyclobutane-1,1,2,2-d_4 leads mainly to C_2D_4, $C_2D_2H_2$ and C_2H_4 in the ratio of 1:2:1 within experimental error.

Introduction

A considerable volume of evidence exists in the literature which indicates that the thermal decomposition of cyclobutane to give two molecules of ethylene is a homogeneous unimolecular reaction.[4,5] The chief interest in the present study of the thermal decomposition of cyclobutane-1,1,2,2-d_4 was the isotopic composition and the relative rates of formation of the various species of ethylenes produced. It was felt that this information would be helpful in evaluating the various mechanisms which have been proposed for the thermal decomposition of cyclobutane.

Experimental

Materials.—Cyclobutane-d_4 was prepared by photolyzing cyclopentanone-2,2,5,5-d_4 in the vapor phase. The cyclopentanone-d_4 was prepared by repeated exchange of cyclopentanone (K and K laboratories; "research" grade) with deuterium oxide (Stuart Oxygen Co.; 99.5% purity) in the presence of potassium carbonate. The yield of cyclopentanone-d_4 was very poor as most of the ketone was lost as high-boiling material.

Photolysis of the ketone gave carbon monoxide, ethylene-d_2, cyclobutane-d_4 and 4-pentenal-d_4. Cyclobutane-d_4 was removed from the products at −78° after the more volatile products had been pumped off at −130°. It was purified by successive contact with fuming sulfuric acid, KOH pellets and phosphorus pentoxide.

Ethylenes with three or four deuterium atoms were not found in the products of the photolysis of cyclopentanone-2,2,5,5-d_4, so that hydrogen migration may not have occurred during the photolysis. Since the ketone was photolyzed almost completely, it was assumed that the cyclobutane-d_4 obtained was deuterated only on the adjacent carbon atoms and that its isotopic purity was that of the ketone itself.

Two samples of cyclobutane-d_4 were prepared in this manner. The first sample which was found to be 72% -d_4 and 28% -d_3, was used for some control experiments. The second sample, which was 93.5% -d_4 and 6.5% -d_3, was used in all the quantitative studies. It was found to be essentially free from impurities by gas chromatography.

The cyclobutane used was a sample prepared by Genaux and Walters.[4] It was purified by gas chromatography.

Apparatus.—The apparatus, including the equipment for the measurement and control of the reaction temperature, has been described before.[6] The control runs were made in a vessel of 359-ml. volume. Both vessels were of Pyrex and were seasoned before use. Kinetic data were obtained from pressure changes measured with the help of a mercury manometer of wide bore and a cathetometer. The uncertainty in reading the pressure was ± 0.02 mm.

Procedure.—The extent of reaction was usually ~10%. To conserve material, the unreacted cyclobutane-d_4 from each run was freed from ethylene by prolonged distillation and used in the succeeding run. The accuracy of the general procedure was checked by the use of cyclobutane as a standard.

The thermal decomposition of a mixture of cyclobutane-d_4 and cyclobutane in the ratio 0.309:1.000 was followed by the analysis of the ethylene formed in the process, by mass spectrometry. The same mixture of the cyclobutanes was used at the three temperatures at which runs were carried out.

Analysis.—The analysis of the ethylenes was made with a Consolidated Engineering Co. type 21-620 mass spectrometer. Standard patterns for C_2D_4,[7] $C_2H_2D_2$ and C_2H_4, which were the major products, were obtained independently on the same instrument. The patterns for C_2HD_3 and C_2H_3D, which amounted to only about 2% each of the total ethylene, were interpolated from the cracking pattern for these compounds on a type 21-103 instrument.[8]

Results

(1) The mass spectrum of the mixed ethylenes obtained by the pyrolysis of cyclobutane-d_4 containing 6.5% of cyclobutane-d_3 was found to be as follows: (mass 32, 100.00) 33, 2.20; 31, 12.46; 30, 262.6; 29, 93.78; 28, 247.5; 27, 151.2; 26, 96.78; 25, 15.78 after correcting for the instrumental background.[9] The corresponding composition of the various isotopic species of ethylenes is given in Table I.

TABLE I

COMPOSITION OF THE ETHYLENE OBTAINED BY PYROLYSIS OF CYCLOBUTANE-1,1,2,2-d_4 CONTAINING 6.5% OF CYCLOBUTANE-1,1,2-d_3

C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4
109.8	6.9	209.1	6.9	100.0

(2) The isotopic composition of the ethylene from cyclobutane-d_4 did not change detectably within the temperature range from 404.9 to 450.0°.

(3) The mass spectral pattern of the cyclobutane-d_4 did not change after a fraction of it had been decomposed thermally.

(4) The mass spectrum of the mixed ethylene product did not change on being left in the reaction vessel at the decomposition temperature for the duration of a run.

(5) At 7 mm. pressure, the over-all rate of decomposition of cyclobutane-d_4 containing 6.5% of

---

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

[2] Abstracted in part from the Ph.D. thesis submitted by Stephen M. E. Kellner.

[3] E. H. Hooker Fund Fellow.

[4] C. T. Genaux and W. D. Walters, THIS JOURNAL, **73**, 4497 (1951); F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci.*, **38**, 937 (1952); C. T. Genaux, F. Kern and W. D. Walters, THIS JOURNAL, **75**, 6196 (1953).

[5] H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **218A**, 416 (1953).

[6] E. R. Johnson and W. D. Walters, THIS JOURNAL, **76**, 6266 (1954).

[7] The authors are indebted to Dr. C. Trumbore of this Laboratory and to Argonne National Laboratory for the gift of a sample of C_2D_4.

[8] V. H. Dibeler, F. L. Mohler and M. de Hemptinne, *J. Research Natl. Bur. Standard*, **53**, 107 (1954).

[9] Only the *m/e* values from 33 to 25 are reported here.

cyclobutane-d_3 was about 10% slower than the rate of decomposition of cyclobutane under the same experimental conditions.

(6) The plot of log k_D^* vs. $1/T$, where k_D^* is the first-order rate constant for cyclobutane-d_4 containing 6.5% of cyclobutane-d_3 and T is the absolute temperature, did not differ from the corresponding plot for cyclobutane at the same initial pressure by more than the combined experimental uncertainty (± 1.5 kcal.). This is shown in Fig. 1.

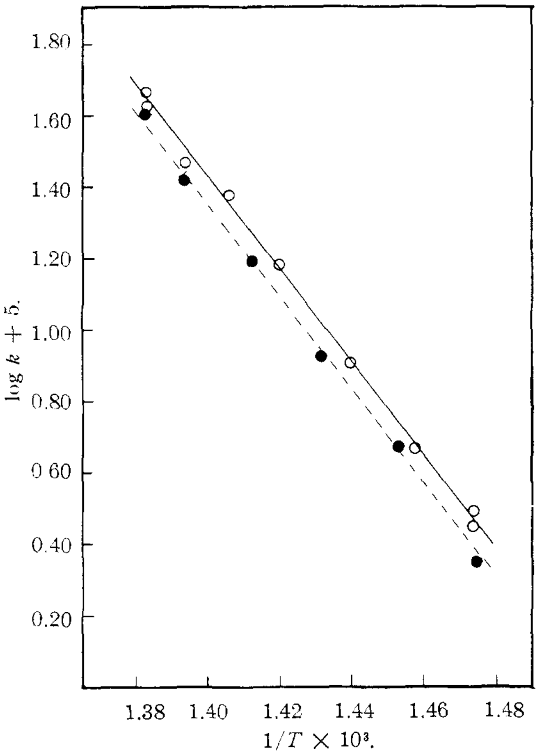


Fig. 1.—Dependence of first-order rate constant upon temperature: ○, cyclobutane; ●, cyclobutane-d_4 (containing 6.5% of cyclobutane-d_3); initial pressure 7 ± 1 mm. in all the cases.

(7) The ratios of the first-order rate constants for cyclobutane-d_4 corrected for cyclobutane-d_3 present (k_D) and cyclobutane (k_H) obtained from the decomposition of a mixture of the two at a total initial pressure of 7 mm. have been plotted against $1/T$ in Fig. 2. The slope of the line corresponds to an activation energy of 500 cal. The ratio of the pre-exponential factors A_D/A_H is 1.3.

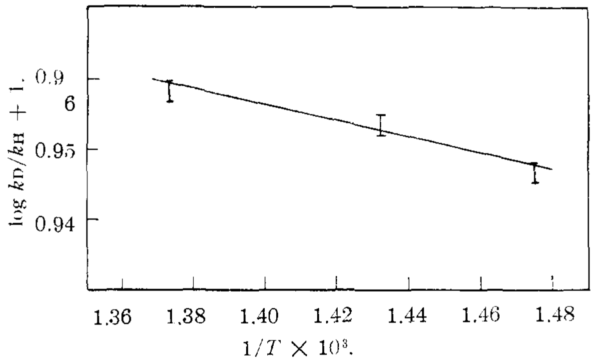
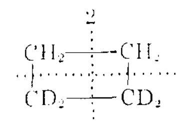
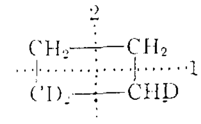


Fig. 2.—Dependence of k_D/k_H upon temperature.

Discussion

The results of the present study throw some light on the question of how the methylene groups in cyclobutane-d_4 pair off to give two molecules of ethylene. Since the thermal decomposition of a mixture of cyclobutane and cyclobutane-d_8 does not give rise to ethylene of the formula CH_2CD_2,[10] it follows that in the present instance, C_2D_4 could have come only from cyclobutane-d_4 by a unimolecular decomposition. Material balance requires that for every C_2D_4 produced, one C_2H_4 must also be formed from a cyclobutane-d_4. This would represent one mode of decomposition of the molecule (mode 1). The corresponding split in cyclobutane-d_3 would give rise to C_2HD_3 and C_2H_4 in equal amounts. Since the starting material contained 7 parts of cyclobutane-d_3 for every 100 parts of cyclobutane-d_4, this mode of decomposition will account for all the C_2D_4, C_2D_3H and 97.5% of the C_2H_4 in the products.[11] The C_2H_3D and an equivalent amount of $C_2H_2D_2$ could have come from cyclobutane-d_3 by a second mode of splitting (mode 2). The corresponding mode in cyclobutane-d_4 would give rise to $C_2H_2D_2$ only. After subtracting the contribution to the products made by cyclobutane-d_3, it is deduced that the products of the thermal decomposition of cyclobutane-d_4 are C_2D_4, $C_2H_2D_2$ and C_2H_4 in the ratio 1.00:2.02:1.03. The $C_2H_2D_2$ is believed to be only -1,1-d_2 and not -1,2-d_2 as an exchange of hydrogen (or deuterium) atoms between adjacent methylenes in cyclobutane-d_4 would be necessary for the formation of the latter.[12] The results suggest that the formation of ethylene from cyclobutane-d_4 by the pairing of two methylene groups placed diagonally in the molecule is relatively unimportant.





The ratio of C_2D_4 or C_2H_4 to $C_2H_2D_2/2$ is a measure of k_1/k_2 where k_1 and k_2 are the rate constants for the two modes of splitting of cyclobutane-d_4. Since 2 $C_2D_4/C_2H_2D_2$ is found to be equal to unity within 1%, $k_1 = k_2$.[13]

The ratio k_D/k_H at 449° at an initial pressure of 7 mm. can be interpolated from Fig. 2 and is found

---

(10) J. Langrish and H. O. Pritchard, *J. Phys. Chem.*, **62**, 761 (1958).

(11) The C_2HD_3 could have come from cyclobutane-d_4 it, in addition to mode 1, there was a second mode of splitting which involved the exchange of one hydrogen or deuterium atom among adjacent methylene groups followed by the splitting of the molecule into two ethylenes. In this instance, an equal amount of C_2H_3D would also have been formed, as is found to be the case. However, if the reasonable assumption is made that the same mode or modes of splitting are operative in both cyclobutane-d_4 and -d_3, then it would not be possible to account for the products that would arise from the latter by a split *not* preceded by a hydrogen or deuterium exchange.

(12) The mass spectra of ethylene-1,1-d_2 and ethylene-1,2-d_2 are not sufficiently different[8] to be picked up easily in a complex mixture such as the present one.

(13) The uncertainty in the analysis for C_2H_4 is greater than for C_2D_4 as all five species of ethylenes contribute to the peak at 28. Hence 2 $C_2D_4/C_2H_2D_2$ rather than 2 $C_2H_4/C_2H_2D_2$ was used in this calculation.

to be 0.91. This can be compared with the ratio k'_D/k_H, where k'_D is the rate constant for cyclobutane-d_8, as determined by Langrish and Pritchard.[10] Using their plot of k'_D/k_H (present notation) *vs.* 1/pressure at 449°, at 7 mm. pressure, the value for k'_D/k_H is 0.79. The change in the first-order rate constant caused by the replacement of hydrogen by deuterium appears to be almost linear.

In comparing the present values for A_D/A_H and $E_D - E_H$ with the corresponding quantities for cyclobutane-d_8 and cyclobutane as determined by Langrish and Pritchard,[10] it must be borne in mind that the temperature effect in the latter work was studied at an initial pressure of 1.25 mm., while in the present work a pressure of 7 mm. was used. At these pressures, the first-order rate constants for cyclobutane are known to fall off sharply.[4] Assuming that a comparison can be made, the ratio of the three pre-exponential factors are A_H:A_D:A'_D:: 1:1.3:2.3. The differences in the activation energies are $E'_D - E_H \sim 1400$ cal.; $E_D - E_H \sim 500$ cal. As Langrish and Pritchard have observed,[10] the trends in the A factor and the activation energy on substituting deuterium for hydrogen atoms in cyclobutane are qualitatively similar to the effects reported by Lindquist and Rollefson[14] and by Weston[15] on tritiated cyclopropane.

Acknowledgment.—The authors wish to thank Professor W. D. Walters for his helpful suggestions and encouragement during the course of this work.

[14] R. H. Lindquist and G. K. Rollefson, *J. Chem. Phys.*, **24**, 725 (1956).

[15] R. E. Weston, *ibid.*, **23**, 988 (1955); **26**, 975 (1957).

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE]

Ruthenium(III) Gluconate Complexes[1]

BY DONALD T. SAWYER, RAYMOND S. GEORGE AND JOHN B. BAGGER

RECEIVED APRIL 23, 1959

An investigation of polarographic methods for the determination of ruthenium has led to a systematic study of the complexes of ruthenium(III) with the gluconate ion. A reversible polarographic wave, which is independent of *p*H and gluconate ion concentration, is obtained above *p*H 13 for the reduction of ruthenium(III). In 0.2 *F* sodium gluconate at *p*H 14 the reduction wave has a half-wave potential of −0.67 v. *vs.* S.C.E. and a diffusion current constant of 1.17. When an excess of ruthenium(III) is added to a basic gluconate solution, soluble polymers are formed initially which have a molar ratio of metal to gluconate of approximately 6. The polymers hydrolyze slowly to give ruthenium oxide and a stable complex with a molar ratio of one ruthenium(III) per gluconate ion. Spectrophotometric studies of this stable complex indicate that there are two forms, one from *p*H 3.5 to *p*H 7.5 and a second above *p*H 8. The second form of the complex follows Beer's law when a ten-fold excess of gluconate ion is present and the *p*H is 14. The molar absorptivity is 4170 at 337 mμ. In basic gluconate solutions ruthenium(II) and ruthenium(III) exhibit a complex set of equilibria which have been studied polarographically. Reaction mechanisms are proposed for the equilibria on the basis of the polarographic studies.

The solution chemistry of ruthenium has not been studied extensively. Almost all of the older literature is concerned with the chloride and amine complexes, and with the properties of solid compounds.[2–4] Although there has been renewed interest recently in the aqueous solution chemistry of ruthenium,[5–9] chelate studies have been restricted to the terpyridyl[10] and bipyridine[11] complexes. Additional knowledge of the effect of chelation on ruthenium ions is desirable and has led to the consideration of several chelating agents, *e.g.*, citric acid, ethylenediamine, ethylenediaminetetraacetic acid, salicylic acid and gluconic acid. Because gluconic acid is known to form strong complexes with iron(III),[12] similar complex formation might be expected for ruthenium ions.

The present study is concerned with the results of a systematic study of the complexes formed between ruthenium(III) and gluconic acid. Polarographic and spectrophotometric techniques have been used to ascertain the nature and stability of the glucono-ruthenium(III) system. Because of the complex nature of the system and the slow rate of equilibration for many of the solutions, many of the data are approximate. However, by considering many pieces of data obtained by independent methods, a general understanding of the system can be obtained.

Previous polarographic studies of ruthenium with a dropping mercury electrode have been restricted to ruthenium(IV) in perchloric acid media[7] and to ruthenocene in alcoholic perchloric acid–perchlorate media.[13] Two additional polarographic studies of ruthenium, using solid microelectrodes, have been made; the cyanide complex of ruthenium(II)[6] and ruthenium(VI, VII, VIII) in basic solutions.[9]

Experimental

Equipment.—Polarographic data were obtained with a recording polarograph which has been described previously.[14] A modified cell was used to prevent attack by strongly basic solutions on the agar in the salt bridge.[15] All measurements

---

[1] Presented before the Analytical Division of the American Chemical Society in Boston, Massachusetts, April, 1959.

[2] W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 228.

[3] "Gmelins Handbuch der anorganischen Chemie," Vol. 63, Verlag Chemie, G.m.b.H., Berlin, 1938.

[4] R. Charonnat, *Ann. chim.*, [10] **16**, 1 (1931).

[5] P. Wehner and J. C. Hindman, THIS JOURNAL, **72**, 3911 (1950).

[6] D. D. DeFord and A. W. Davidson, *ibid.*, **73**, 1469 (1951).

[7] L. W. Niedrach and A. D. Tevebaugh, *ibid.*, **73**, 2835 (1951).

[8] R. E. Connick and C. R. Hurley, *ibid.*, **74**, 5012 (1952).

[9] M. D. Silverman and H. A. Levy, *ibid.*, **76**, 3319 (1954).

[10] F. P. Dwyer and E. C. Gyarfas, *ibid.*, **76**, 6320 (1954).

[11] R. R. Miller, W. W. Brandt and S. M. Puke, *ibid.*, **77**, 3178 (1955).

[12] R. L. Pecsok and J. Sandera, *ibid.*, **77**, 1489 (1955).

[13] J. A. Page and G. Wilkinson, *ibid.*, **74**, 6149 (1952).

[14] D. T. Sawyer, R. L. Pecsok and K. K. Jensen, *Anal. Chem.*, **30**, 481 (1958).

[15] R. L. Pecsok and R. S. Juvet, *ibid.*, **27**, 165 (1955).