Figure 8. Proposed structure of HP_3^+, $3P \cdot H_9O_4^+$.

into solutions of TBP in inert solvents. They suggest that when the concentration of TBP in the inert solvent is low, the extracted species is $3TBP \cdot H_3O^+ \cdots ClO_4^-$, and when the concentration of TBP is high, the extracted species is $3TBP \cdot H_9O_4^+ \cdots ClO_4^-$.

It is proposed that in the highest concentration of 1,10-phenanthroline, 1,10-phenanthroline competes with

and replaces the water molecules in the secondary hydration sphere about the hydronium ion. Hence, the HP_n^+ species would be represented by $HP_n^+ = nP \cdot H_9O_4^+$. The proposed structure for $3P \cdot H_9O_4^+$ is shown in Figure 8.

It is also possible that the replacement of the water molecules by 1,10-phenanthroline could take place in the primary hydration sphere instead of the secondary hydration sphere. In this case the HP_n^+ species would be represented by $HP_n^+ = nP \cdot H_3O^+(3 - n)H_2O$. A Fisher–Taylor–Hirschfelder model of the hydronium ion was constructed, and a molecule of 1,10-phenanthroline could be arranged about each of the hydrogen atoms of the hydronium ion.

However, this latter proposal seems to be less favorable than the former proposal. The type of bonding in the $nP \cdot H_9O_4^+$ proposal would seem to fit in better with the type of bonding proposed in the 1,10-phenanthroline monohydrate studies.[27,33,34]

The Hydrogen Isotope Effect in the Thermal Decomposition of Cyclobutane[1]

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Abstract: The thermal decomposition of mixtures of cyclobutane and cyclobutane-d_8 has been studied at pressures from 100 to 0.005 mm at 449° and over the temperature range from 419 to 460° at pressures near 100 mm. The value of the isotope effect (k_H/k_D) for pressures in the neighborhood of 100 mm was observed to be 1.41 ± 0.02 at 449°. The temperature dependence of the isotope effect near 100 mm could be expressed as $k_H/k_D = 0.75 \exp(900/RT)$. It was found that k_H/k_D decreases with decreasing initial pressure and reaches a value of unity near 0.08 mm at 449°. At lower pressures an inverse isotope effect was observed, C_4H_8 reacting about 0.83 times as fast as C_4D_8 at 0.005 mm.

Previous investigations of kinetic isotope effects in gas-phase, unimolecular reactions of cyclic molecules have provided a number of interesting results. Weston[3] showed that in the isomerization of cyclopropane-t_1 the isotope effect decreased with decreasing pressure until it had almost disappeared at 0.4 mm. Blades[4] observed that the isotope effect in the isomerization of a mixture of cyclopropane-d_6 and cyclopropane decreases with a lowering of the initial pressure, k_H/k_D reaching a value of 1.35 at 0.178 mm. Rabinovitch, Setser, and Schneider[5] published a theoretical treatment of the isotope effect in the isomerization of cyclopropane-d_6. Their calculated values showed a

decrease with decreasing pressure in agreement with experimental results of Blades[4] and at pressures below those reached by Blades showed an inverse intermolecular isotope effect. Subsequently, in an experimental study of the cyclopropane system, Rabinovitch, Gilderson, and Blades[6] found values of k_H/k_D less than unity at pressures below 10^{-2} mm. A marked inverse isotope effect has been observed at low pressures also in the thermal isomerization of a mixture of CD_3NC and CH_3NC to the corresponding nitriles.[7]

Langrish and Pritchard[8] measured k_D/k_H for a mixture of cyclobutane-d_8 and cyclobutane at 449° from 36 to 0.7 mm. In this region where the first-order constants for light cyclobutane are pressure dependent,[9]

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

(2) Union Carbide Corporation Fellow in Chemistry, 1961–1962.

(3) R. E. Weston, Jr., J. Chem. Phys., 23, 988 (1955); 26, 975 (1957); see also R. H. Lindquist and G. K. Rollefson, ibid., 24, 725 (1956).

(4) A. T. Blades, Can. J. Chem., 39, 1401 (1961).

(5) B. S. Rabinovitch, D. W. Setser, and F. W. Schneider, ibid., 39, 2609 (1961).

(6) B. S. Rabinovitch, P. W. Gilderson, and A. T. Blades, J. Am. Chem. Soc., 86, 2994 (1964).

(7) F. W. Schneider and B. S. Rabinovitch, ibid., 85, 2365 (1963).

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

(9) (a) F. Kern and W. D. Walters, Proc. Natl. Acad. Sci. U. S., 38, 937 (1952); (b) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, Proc. Roy. Soc. (London), A218, 416 (1953); (c) J. N.

the isotope effect (calculated in terms of k_H/k_D) at about 1 mm was 1.18 and increased with increasing initial pressure. Over the temperature range 431–485° at 1.25 mm, the isotope effect could be expressed as $k_H/k_D = 0.435 \exp(1400/RT)$. Srinivasan and Kellner[10] studied the pyrolysis of cyclobutane-1,1,2,2-d_4 at 405–450° for initial pressures near 7 mm and determined the isotope effect relative to cyclobutane. At 449° they found $k_H/k_{D_4} = 1.10$. Benson and Nangia[11] have reported their calculations for the isotope effects in the isomerization of cyclopropane and in the decompositions of cyclobutane-d_8 and -d_4.

It was of interest to investigate further the isotope effect in the pyrolysis of cyclobutane-d_8, particularly at pressures lower than those used previously. Another object of the present study was to measure the isotope effect and its temperature dependence at somewhat higher pressures where the first-order rate constant for the cyclobutane decomposition is nearly constant for changes in the pressure.

Experimental Section

Materials. A small sample of cyclobutane-d_8 (kindly supplied by Professor R. C. Lord) was purified on a Perkin-Elmer 154B vapor fractometer with a column containing tetraisobutylene on 60–80 mesh firebrick. The purified sample was degassed at −130°, followed by trap-to-trap distillation from −78 to −130° and by drying with Linde Molecular Sieve 4A. Gas chromatographic analysis indicated that the sample was better than 99.9% pure cyclo-C_4 hydrocarbon. Mass spectrometric analysis on the Consolidated 21-620 instrument used in this work showed that the sample contained about 12% cyclobutane-d_7 and might contain a maximum of 2% cyclobutane-d_6.[12] Samples of ethylene-d_4 which were supplied by Dr. R. Srinivasan and Dr. L. M. Dorfman were used in the preliminary experiments. Later, ethylene-d_4 with a stated isotopic purity of at least 99% was obtained from Merck Sharp and Dohme of Canada. Gas chromatographic analysis showed no peak other than that attributable to an ethylene fraction. Mass spectrometric analysis indicated that the sample could contain about 1% C_2D_3H. The treatment of the ordinary cyclobutane and ethylene used has been described in a previous publication.[13]

Apparatus and Procedure. The experiments were performed in two different electrically heated furnaces. The furnace for most of the experiments above 0.05 mm contained a cylindrical iron core (o.d., 12.5 cm; i.d., 7.5 cm) and various Pyrex reaction vessels could be placed in the core. A spherical vessel (27 ml) was used for runs above 20 mm. It was situated in a spherical cavity in an aluminum cylinder of 7.4-cm o.d. At 0.05–10 mm pressure cylindrical bulbs (450 and 938 ml) were also used in this furnace. The temperature was measured with a Pt—Pt-13% Rh thermocouple and could be controlled to ±0.1°. The 938-ml vessel (25 cm long) was twice as long as the vessel for which the furnace was designed. Because of the extra length a noticeable temperature gradient existed along the longitudinal axis. For the front 20 cm of the vessel, the temperature was within ±1°, but over the last 5 cm the temperature averaged 1.5° lower. Since the isotope effect is only slightly temperature dependent, the use of this vessel for some of the pressure dependence experiments at 449° was regarded as satisfactory. Temperature gradients with the other vessels were negligible.

A second furnace[14] containing a spherical 12-l. reaction vessel was used at pressures from 0.3 to 0.005 mm. The vessel was surrounded by a 1-in. thick spherical aluminum shell. Temperature control in this vessel for the duration of an experiment was ±0.1°. Temperature measurement was accomplished with five standardized Pt—Pt-13% Rh thermocouples, four of which touched the outer surface of the reaction vessel, and the fifth extended to the center of the vessel (in a glass well). The five measured temperatures were generally within 1° and the temperature of an experiment was taken as the average of the readings. Outside the reaction vessel the sections of the vacuum system used in sample handling were equipped with mercury float valves. To the tubing from the 12-l. vessel was attached a float valve immediately adjacent to the furnace in order to keep the dead space small. The pressure in the vessel was calculated from the quantity of sample introduced.

The times of reaction in the various vessels were measured with a stopwatch periodically checked for accuracy. The time for introduction and removal of samples in experiments with vessels from 27 to 938 ml were small enough to be negligible compared to the reaction time. With the 12-l. vessel the reaction mixture was removed by condensation into a trap immersed in nitrogen cooled considerably below its normal boiling point by pumping with a mechanical, oil-type vacuum pump. The time of removal was determined in experiments with n-butane-ethylene samples simulating the reaction mixtures, and corrections for the reaction during removal were applied (amounting to about 0.03 × the measured reaction time).

To compare the rate of reaction of cyclobutane-d_8 with that of cyclobutane, a mixture containing approximately equal amounts of both was prepared and pyrolyzed so that both compounds would be decomposing under the same conditions. Care was taken to have all reaction vessels seasoned before starting a series of experiments. Samples were kept in grease-free Pyrex containers until they were analyzed on the mass spectrometer. The most satisfactory method of treating the mass spectral data was found to be by the use of the relationship

$$(k_D/k_H) = \frac{\ln [(R_0^{64}/R_0^{56})(R_t^{56}/R_t^{64})]}{tk_H} + 1$$

where (k_D/k_H), the reciprocal isotope effect, is the ratio of the first-order rate constants for cyclobutane-d_8 and cyclobutane, respectively, and k_H is the constant for cyclobutane under similar conditions. R_0^{64}/R_0^{56} and R_t^{56}/R_t^{64} are the ratios of the mass spectrometric responses at the indicated values of m/e for the reaction mixture at time zero and t. The sample pressure in the mass spectrometer was kept roughly the same for all samples except those from the lowest pressure experiments. Tests showed that over a tenfold range of sample pressures (covering the range used in routine analysis) there was no significant trend in R_0^{64}/R_0^{56}. This ratio for the starting mixture was determined on the mass spectrometer frequently during the study. A small correction to m/e 56 for the contribution of deuterated cyclobutanes was made. The presence of cyclobutane-d_7 and -d_6 did not affect the kinetic results, since under the circumstances used for the experiments and treatment of the data, their small contributions to the m/e ratios would essentially cancel.

In the second method the mass spectrometer was calibrated with ethylene-cyclobutane and ethylene-d_4-cyclobutane-d_8 mixtures of known composition. The 27/56 and 30/64 peak height ratios (after suitable corrections) were taken to be proportional to the relative amounts of ethylenes and cyclobutanes in the two types of mixtures. Plots of these ratios vs. calculated per cent decomposition were made and used to find the percentage decomposition of reaction product mixtures. Since more than one substance contributed to the 27, 30, and 56 peaks and appreciable corrections had to be applied, the second method was not considered to be as reliable as the first. The results from the two methods, however, were found usually to be in good agreement. Tests simulating low-pressure experiments in the 12-l. and 938-ml vessels showed that isotopic fractionation did not occur as the reactant mixture was introduced into a reaction vessel heated to a temperature below the decomposition range.

Product Composition. In several experiments at 100 mm over the temperature range 430–450° the reaction mixture after about 25% decomposition was separated into two fractions, one of which

Butler and R. B. Ogawa, *J. Am. Chem. Soc.*, **85**, 3346 (1963); (d) R. W. Vreeland and D. F. Swinehart, *ibid.*, **85**, 3349 (1963).

(10) R. Srinivasan and S. M. E. Kellner, *ibid.*, **81**, 5891 (1959).

(11) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1963).

(12) According to a private communication from Dr. B. P. Stoicheff, National Research Council, Ottawa, a mass spectrometric analysis of a sample from the same source as the present sample indicated 83% C_4D_8, 13 ± 1% C_4D_7H, and 3 ± 1.5% $C_4D_6H_2$. In a private communication from Professor Lord, it was mentioned that infrared absorption measurements on the same sample indicated approximately 12% C_4D_7H.

(13) (a) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963); (b) R. W. Carr, Jr., Ph.D. Thesis, University of Rochester, 1962.

(14) (a) Described by A. Pataracchia, M. S. Thesis, University of Rochester, 1961; (b) A. Pataracchia and W. D. Walters, *J. Phys. Chem.*, **68**, 3894 (1964).
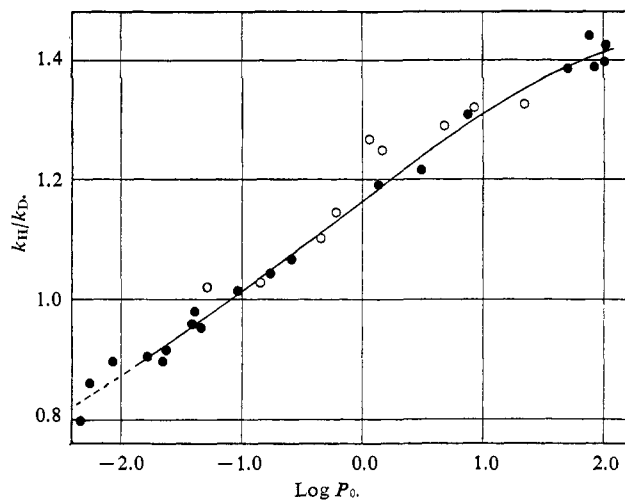
Figure 1. Change of the value of the isotope effect with pressure at 449°. Open circle denotes a run with a single value of R_t^{56}/R_t^{64} and less favorable signal-to-noise ratio.

was volatile at $-130°$ and the other condensable at $-130°$. Mass spectrometric analysis of the volatile fraction revealed that it contained C_2H_4, C_2D_4, and C_2D_3H. Mixed ethylenes such as $C_2D_2H_2$ or C_2DH_3 which might be formed by intermolecular hydrogen exchange or from deuterated cyclobutanes with less than seven D atoms were not detected. Mass spectrometric analysis of the fraction condensable at $-130°$ showed that it contained only the starting compounds. For experiments at the lowest pressures in the 12-l. vessel, mass analysis data did not indicate any products other than those which were found at 100 mm. In experiments over a wide range of pressures, measurements were made of the gas not removed by condensation at the end of an experiment, and the amount was found not to exceed 0.1% of the initial pressure. Thus, the quantity of noncondensable gases formed is not signifiant, and the composition of the sample removed for analysis is representative of the entire reaction mixture.

Kinetic Results. The relative rates of the thermal decomposition of cyclobutane and cyclobutane-d_8 were studied at pressures from 107 to 0.005 mm at 449° and at pressures near 100 mm over the temperature region 420–460°. The data which are shown in Figures 1 and 2 are values of k_H/k_D which were obtained by taking the reciprocal of the quantity calculated according to eq 1. In the calculations the values of k_H used on the right-hand side of the expression were based on the previous work.[9a,d,13a,14] Values of k_H in the region below 100 mm were taken from a plot of log k_H vs. log P_0, which showed good accord among the various investigations. The type of agreement can be seen in curve 4 of Figure 2 in a previous publication[14b] where log k/k_∞ against log P_0 is shown for a portion of the pressure range.

The results of the present study of the pressure dependence of the isotope effect are shown in Figure 1. There is a marked decrease of k_H/k_D with decreasing initial pressure, and a value of unity is reached at about 0.08 mm. At lower pressures cyclobutane-d_8 reacts faster than cyclobutane, the value of k_H/k_D reaching a value of about 0.83 at 0.005 mm. Thus, in the pressure region where there is a falloff in the first-order rate constant, the falloff for the C_4D_8 rate constant is more gradual than that for C_4H_8. The lower end of the curve (empirically drawn) in Figure 1 is shown as a broken line to indicate that its trend is not certain on the basis of the experimental points available.

From Figure 1 it can be seen that the inverse isotope effect would not be in evidence at the lowest pressure (0.7 mm) used by Langrish and Pritchard.[8] However, for the pressure range of their study there seems to be satisfactory agreement between the present results and their data for the magnitude of the isotope effect and its change with pressure at 449°. For example, values taken from the curve in Figure 1 (k_H/k_D = 1.31 at 10 mm and 1.18 at 1.25 mm) may be compared with their values (1.28 at 10 mm and 1.18–1.19 at 1.25 mm) taken from the curve in Figure 1 of their paper.[8]

Since the rate constant for the cyclobutane decomposition does not change significantly in the region 100–1500 mm,[13] data obtained near 100 mm would appear to be close to the high-pressure value. In the present study the average value for k_H/k_D in four experiments in the pressure range 78–107 mm was found to be 1.41 ±
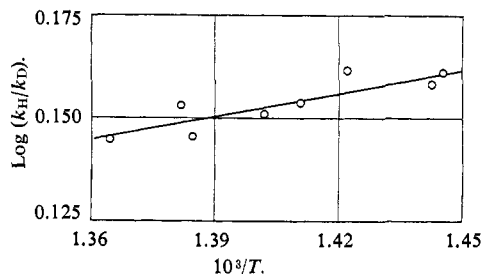

Figure 2. Dependence of the isotope effect upon the temperature.

0.02 at 449°. The reciprocal quantity k_D/k_H (0.71 ± 0.01) may be compared with the extrapolated high pressure value obtained by Langrish and Pritchard.[8] By means of a plot of (k_D/k_H) vs. $(1/P_0)$ for their data at 0.7–36 mm, they found upon extrapolation to $(1/P_0)$ = 0 a value of 0.73 ± 0.03.

From the experiments near 100 mm over the range 420–460°, a small temperature dependence was observed for k_H/k_D. With only a small difference between the activation energies for the decompositions of cyclobutane and cyclobutane-d_8 (which are in the range 62.5–64 kcal/mole), the experimental errors, due to variations in the analytical conditions, etc., make it difficult to evaluate the quantity $E_D - E_H$ with precision. For such an evaluation it seems best to use the data obtained in a series of experiments under closely controlled experimental and analytical conditions. In Figure 2 are shown the results of a series of unpacked bulb experiments in which (a) all samples were taken from the same C_4D_8–C_4H_8 mixture, (b) the signal-to-noise ratio of the mass spectrometer was favorable, and (c) for all experiments except one the ratio R_t^{56}/R_t^{64} was the average of at least three determinations.

By a least-squares calculation[15] the value of $E_D - E_H$ was found to be 0.9 ± 0.2 kcal/mole. On the basis of 900 cal/mole for $E_D - E_H$ together with k_H/k_D for each experiment shown in Figure 2, an average preexponential ratio (A_H/A_D) and its standard deviation were calculated, and the isotope effect could be expressed as

$$(k_H/k_D) = (0.75 \pm 0.01) \exp(+900/RT)$$

The line shown in Figure 2 represents this relationship.[16]

Discussion

The present observation that k_H/k_D for the decompositions of C_4H_8 and C_4D_8 decreases below unity at lower pressure has provided another example of an inverse secondary intermolecular isotope effect. Such inverse isotopic behavior at low pressures has been reported for other systems (CH_3NC–CD_3NC[7] and cyclo-C_3H_6–cyclo-C_3D_6[6]), and the results have been interpreted as a quantum statistical isotope effect on the basis of the Rice–Ramsperger–Kassel–Marcus formulation.[5] The isotope effect for the structural isomerization of cyclopropane has been studied at pressures down to 10^{-4} mm, but in the region below 7 × 10^{-3} mm there is a leveling-off of the k_H/k_D ratio at a value of about 0.8. Wall activation has been advanced as an explanation of this phenomenon.[6] It does not seem that the present data afford definite evidence for such behavior with C_4H_8–C_4D_8 in the pressure region used in this study; however, at lower pressures an approach to a limiting value may become unmistakably evident.

Comparison can also be made between the three- and four-membered ring compounds at the other end of the pressure region. For the cyclopropane reaction the limiting high-pressure values for the isotope effect

(15) Performed by Mr. L. Lowden.

(16) For $E_D - E_H$ a value of about 1.6 ± 0.2 kcal/mole was reported in ref 13b, but that evaluation also included other experimental results, probably of lower reliability, and involving one or more of the following difficulties: lower signal-to-noise ratio, single determination of R_t^{56}/R_t^{64}, or different mass spectrometer attenuations for R_t^{56} and R_t^{64}.

$(k_H/k_D = 1.96$ at $482°$[4]; $k_H/k_D = 2.12$ at $511°$[6])
are larger than that found for the cyclobutane decomposition, presumably because the latter does not involve a primary isotope effect whereas the former does.

With respect to the cyclobutane isotope effect near 100 mm and its temperature dependence, it seems that the present value for k_H/k_D at $449°$ is in reasonable accord with the value which Langrish and Pritchard found earlier by extrapolation, but the temperature dependence of k_H/k_D at 100 mm (corresponding to $E_D - E_H = \sim 0.9$ kcal/mole) may be slightly smaller than that reported previously for 1.25 mm ($E_D - E_H = 1.4$ kcal/mole).[8] Several studies[9] have shown that at 1.25 mm the rate constant for C_4H_8 decomposition is in the falloff region and the present data indicate that the rate constant for C_4D_8 falls off less than that for C_4H_8 at a similar pressure. Therefore, any decrease in activation energy for C_4H_8 in going from a high pressure to 1.25 mm would be expected to be larger than that for C_4D_8, and this could result in a slightly greater value of $E_D - E_H$ at 1.25 mm than at 100 mm. However, the scatter of the data makes such a comparison uncertain.

On the basis of the fact that the value of 1.4 kcal/mole obtained by Langrish and Pritchard at 1.25 mm was similar to the value of 1.3 kcal/mole for $E_D - E_H$ found for the isomerization of cyclopropane at about 600 mm, Blades[4] suggested that the critical processes in the formation of the activated complexes for cyclobutane and cyclopropane are the same and that the cyclobutane decomposition involves a C–C bond rupture assisted by partial bonding of one hydrogen to its neighboring carbon atom. Since there is no intramolecular hydrogen exchange during the decomposition of cyclobutane,[10] a transition state without a special bonding role for hydrogen seems more likely. Also, if $E_D - E_H$ for cyclobutane is about 0.9 kcal/mole as the data in Figure 2 tend to indicate, there is less similarity in the values for cyclopropane and cyclobutane.

From various calculations Wolfsberg[17] has concluded that sizable secondary isotope effects can arise when the force constants (stretching, bending, and torsional) involving isotopically substituted positions are significantly different in the transition state from those in the reactant. Benson and Nangia[11] have pointed out that secondary isotope effects can have appreciable activation energies. On the basis that two twisting modes and one ring stretch–deformation mode of cyclobutane undergo marked decreases in the transition state, they have calculated 1.1 kcal/mole as the value for $E_D - E_H$ (C_4D_8 vs. C_4H_8) and half this value ($E_{D_4} - E_H = 0.55$ kcal/mole) for $C_4H_4D_4$ compared to C_4H_8.[11] Their calculated values, as well as the 2:1 relationship, for $E_D - E_H$ in the two systems are in accord with the 0.5 kcal/mole for $C_4H_4D_4$ vs. C_4H_8 found earlier by Srinivasan and Kellner,[10] and with ~ 0.9 kcal/mole for C_4D_8 vs. C_4H_8 indicated by the data shown in Figure 2.

Even if the model for the transition state is appreciably different from that postulated by Benson and Nangia,[11] it would appear that changes in the vibrational frequencies in going from the normal to the activated condition could be sufficient to explain the observed activation energy differences in terms of a secondary isotope effect. With respect to the preexponential factor, it is to be noted that if $E_D - E_H$ is 0.9 kcal/mole as calculated from the data in Figure 2, the magnitude of the kinetic isotope effect (k_H/k_D) at 100 mm would indicate that A_D may be about $1.33A_H$ instead of the larger value ($\sim 2.2A_H$) which would be computed if $E_D - E_H$ is in the neighborhood of 1.5–1.6 kcal/mole.

(17) M. Wolfsberg, *J. Chem. Phys.*, **33**, 2 (1960).