of equation VI are shown in Table I, along with the corresponding temperatures. When these values are fitted in an Arrhenius plot, the slope is $E_0/2.3R$ where $E_0 = E_2 + E_4 - E_5$.

The least squares fit for the slope gives a value of $E_0 = 41.1 \pm 3.6$ kcal. (std. deviation). We have shown[10] previously that $E_2 = 9.3$ kcal., and it follows that $E_4 = 31.8 \pm 3.6$ kcal. (std. deviation), assuming $E_5 = 0$. The value of 9.3 is within a tenth of a kcal. of the value previously obtained by us for the abstraction of the secondary H in butane.[11] There is probably little or no strain in the ring. The strength of the C–H bond in cyclopentane is thus about 94 kcal. Sehon and Szwarc[11] have obtained a value of 77 kcal. for the H–CH_2CHCH_2 bond. The minimum activation energy for abstraction of H from cyclopentane by the allyl radical is thus 17 kcal. However, it should be remembered that the abstraction reactions of methyl radicals, which are all exothermic, proceed with activation energies of about 10 kcal., so that for the allyl radical the energy can reasonably be expected to be somewhat greater than 17 kcal.

The value for the difference in E_{act} for abstraction of D from acetone-d_6 and H from cyclopentane by allyl radical and by methyl radical may be obtained from an Arrhenius plot of the $CH_3CH{=}CH_2/CH_2DCH{=}CH_2$ and CD_3H/CD_4 ratios, respectively. The values are 1.9 ± 0.52 kcal. (std. deviation) for the allyl radical and 2.4 ± 0.23 kcal. for the methyl radical. The two values are the same within experimental error, showing that the discrimination barrier is the same for both radicals. It should be noted that our present value for the E_{act} difference for methyl radical abstraction is within 0.3 kcal. of the value we reported for the same system at a somewhat lower temperature.[10] The standard deviation shows that our present values are not as precise as the previous values.

Pyrolysis of Mixtures of Cyclopentane and A*d*$_6$.—Mixtures of Ad_6 and cyclopentane were pyrolyzed in quartz and Pyrex vessels and packed in Pyrex vessels with glass wool which increased the surface/volume by a factor of 100 over the unpacked vessels. In the temperature range of 500° the rate of pyrolysis is about the same in quartz and in Pyrex vessels of the same dimensions. The hundredfold increase in s/v increased the pyrolysis rate by a factor of three. However, the isotope distribution of the methanes and propylene in pyrolysis is different than for photolysis and much less reproducible. In our experiments the photolysis rate at 500° is nine times that for pyrolysis. From this ratio of rates and the values of the methane and propylene isotope ratios for photolysis and pyrolysis, we estimate that error in the photolysis ratios is about 10% at this temperature. At temperatures of 490° and lower, the pyrolysis rate is insignificant compared with the photolysis.

CHINA LAKE, CALIFORNIA

[10] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **79**, 825 (1957).

[11] A. Sehon and M. Szwarc, *Proc. Roy. Soc. (London)*, **A202**, 263 (1950).

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

The Photochemical Type II Process in 2-Hexanone-5,5-d_2 and 2-Hexanone[1]

BY R. SRINIVASAN

RECEIVED APRIL 18, 1959

The photolysis of 2-hexanone-5,5-d_2 at 3130 Å. and room temperature was found to give mainly C_3H_5D and acetone which was a mixture of CH_3COCH_2D (45%) and CH_3COCH_3 (54%). Since the course of the photolysis and the nature of the minor products were similar to that of 2-hexanone, it was surmised that acetone-d_1, which may have been formed in the type II primary process, was subsequently exchanging the odd deuterium atom for a hydrogen atom. Such an exchange was not found to take place after the photolysis and the exchanging molecule was most probably not any impurity in the parent ketone or the parent ketone itself. The photolysis of 2-hexanone in a cell that had been left in contact with D_2O vapor and then evacuated, gave rise to C_3H_6 and acetone which was made up of CH_3COCH_2D (25%) and CH_3COCH_3 (75%). Pure acetone did not exchange with the D_2O on the walls under the same conditions. These results can be explained on the basis of the formation of propylene and the enolic form of acetone in the primary process, and the subsequent rearrangement of the enolic form to the ketonic form on the walls, the latter step often involving the exchange of one hydrogen (or deuterium) atom.

Introduction

The photochemical process by which aliphatic ketones with at least one hydrogen atom on the carbon in the γ-position to the carbonyl group give rise to a methyl ketone and an olefin is classified[2] as type II to distinguish it from the primary processes which lead to free radicals. There is a considerable amount of indirect evidence that a γ-hydrogen is transferred to the α-carbon in the type II process.[3] Davis and Noyes[4] suggested that direct evidence might be obtained by replacing the γ-hydrogen atoms with deuterium in a ketone such as 2-hexanone and analyzing for the isotopic content of the photoproducts. The present study was undertaken with this in view.

The photolysis of 2-hexanone has been studied by Norrish and co-workers,[5] by Davis and Noyes,[4]

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[1] This work was supported in part by Contract AF18(600)1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government.

[2] This classification was proposed by C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

[3] A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

[4] W. Davis, Jr., and W. A. Noyes, Jr., THIS JOURNAL, **69**, 2153 (1947).

[5] R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); C. H. Bamford and R. G. W. Norrish, *ibid.*, 1538 (1938).

by Nicholson[3] and by Brunet and Noyes.[6] The quantum efficiency of the type II process in this ketone is 0.45[6] and the value is independent of temperature[4] and the presence of oxygen.[6] At 3130 Å. and room temperature, the free radical processes are less than 5% of the type II process.

It may be mentioned that two recent studies[7,8] on the type II process in 2-pentanone-1,1,1,3,3-d_5 led to conflicting results with regard to the isotopic composition of the acetone formed. While these studies were made at intensities 50–100 fold greater than those used in the present instance, a possible explanation for the discrepancy has emerged based on variations in the experimental procedure. In view of this, the procedure used in this investigation is given in detail.

Experimental

Materials.—2-Hexanone-5,5-d_2 was prepared by condensing acetoacetic ester with 1-bromopropane-2,2-d_2 in the presence of sodium ethoxide, hydrolyzing and decarboxylating the resulting ester.[9] The procedure was as detailed by Vogel.[10] 1-Bromo propane-2,2-d_2 was obtained from Merck and Co. (Canada). The 2-hexanone-d_2 so made was found to contain ethyl alcohol as an impurity. Repeated distillation *in vacuo* gave about 50 mg. of a sample of 99.5% purity, as estimated by gas chromatography. The remaining 0.5% was ethyl alcohol.

The infrared spectrum of the product in chloroform, on comparison with 2-hexanone, showed two additional peaks at 2100 and 2175 cm.$^{-1}$ (C–D), while the peaks at 1354 (CH_3 adjacent to >C=O), 1372 (actually a shoulder; due to CH_3–), and 1410 cm.$^{-1}$ (–CH_2– adjacent to >C=O) were unchanged. The intensity of the peak at 1460 (–CH_2–) relative to the one at 1450 (–CH_3) had diminished. The deuterium atoms were presumably not in the two methyl groups or in the –CH_2– adjacent to >C=O.

The mass spectrum of the product showed that the sample was 92.7% –d_2; 6.1% –d_1 and about 1.2% –d_0 while the peak at 103 was wholly accounted for on the basis of the contribution of the C^{13} isotope. The important peaks of m/e ratio greater than 56 were at 87, 71, 59 and 58 as compared to 85, 71, 58 and 57 in 2-hexanone. If the fragment at 85 in 2-hexanone is due to the parent molecule less one methyl group and that at 71 is due to the parent molecule less –CH_2CH_3, then it can be inferred that 2-hexanone-d_2 gives rise to the fragments $CH_3COCH_2CH_2$ at 71 and CH_3-$COCH_2CH_2CD_2$ at 87, showing the position of the deuterium atoms. The ratio 71/102 was 0.820, whereas in 2-hexanone, the ratio 71/100 was 0.763. The shift of the prominent peak at 58 (CH_3COCH_3) in 2-hexanone to 59 in 2-hexanone-d_2 indicated that this fragment was richer by one deuterium atom.

The sample of 2-hexanone used was very kindly provided by Dr. W. D. Walters. It was the same as material (c) described by Barry and Walters.[11] The acetone used was an Eastman Kodak spectro-grade sample.

Apparatus.—Photolyses were carried out in a quartz cell 20.0 cm. long and 3.9 cm. in diameter at 27 ± 1°. A conventional vacuum line, where the reactants did not come in contact with stopcock grease was used. The light source was a Hanovia S-100 lamp. The radiation was filtered by 2 mm. of Pyrex glass. The useful radiation entering the cell, which was essentially the group of lines at 3130 Å., was 1.1×10^{16} quanta/sec. as measured by a diethyl ketone actinometer at 100° ($\Phi_{CO} \sim 1$). For the experiments with 2-hexanone the incident intensity was 3.3×10^{15} quanta/sec. The absorbed intensities were less than 8% of the incident intensities in all the experiments. The extent of photolysis was less than 4.5% in all the quantitative experiments.

In certain experiments with 2-hexanone, the cell walls were "conditioned" by exposure to D_2O vapor before each run. This was done by letting D_2O of 99.5% purity (Stuart Oxygen Co.) at a pressure of about 17 mm. come in contact with the walls of the cell for a short period. At the end of this time, the vapor was replaced by a fresh sample. Four successive treatments of 5, 8, 11 and 15 minutes duration were carried out followed by evacuation until the pressure was essentially 10^{-6} cm. (about 10 minutes). Immediately the cell was isolated from the pumps and ketone vapor was admitted.

Analysis.—From the photolysis products, two fractions were removed at –195 and –130° and measured volumetrically. The former, which consisted of carbon monoxide, ethane and methane, was not analyzed further. The latter was analyzed mass spectrometrically using a consolidated Engineering Co. Type 21–620 instrument and found to be exclusively propylene. A third fraction was distilled from the products at Dry Ice–ether temperature and condensed into a sample tube cooled in liquid nitrogen. It was analyzed mass spectrometrically and found to be mostly acetone with a small amount of n-pentane and traces of the parent ketone. While this procedure did not give a quantitative measure of acetone, it minimized the chances of an exchange reaction which would alter the isotopic composition of the acetone. In some experiments with 2-hexanone, acetone was separated from the products by gas chromatography and then analyzed by mass spectrometry. The isotopic composition of the acetones as found in this manner did not differ by more than 2.5% (total acetone = 100) from the results of a duplicate experiment in which the acetone had been separated by direct distillation. Even so, the procedure of direct distillation was adopted routinely.

Results

2-Hexanone-5,5-d_2.—1. The main products of the photolysis at 3130 Å. and room temperature were propylene and acetone. The minor products were carbon monoxide, ethane (C_2H_6), pentane ($C_5H_{10}D_2$) and biacetyl ($C_4H_6O_2$).

2. The propylene was chiefly C_3H_5D with a $C_3H_4D_2$ content of less than 3%. The deuterium content of the acetone fraction showed 54% CH_3COCH_3 and 45% CH_3COCH_2D.

3. The isotopic composition of the propylene was reproducible and did not vary on decreasing the wave length of the radiation, changing the intensity or increasing the extent of photolysis. The isotopic content of the acetone was reproducible over an interval of three runs but differed when the radiation from an unfiltered mercury arc was used. Further, in the first two runs, the acetone was nearly 80% CH_3COCH_3, the rest being CH_3-$COCH_2D$.

4. The isotopic analysis of the acetone fraction did not change significantly on letting the products stand in the cell for 17 hr. after photolysis as compared to a run in which the analysis was carried out in less than 1 hr.

5. In one set of three consecutive runs, the same sample of ketone was used, the volatile products being distilled off at the end of each run. The over-all decomposition was about 16%. The amount of CH_3COCH_3 produced was 10 mole %. The mass spectrum of the residual 2-hexanone-d_2 showed no more than 1.4 units at $m/e = 103$ (m/e of 102 = 100.0 units) after subtracting the contribution of the C^{13} isotope. Mass 101 was exactly as in the starting material.

6. At a higher (85%) conversion of 2-hexanone-d_2, the undecomposed ketone, which was separated by gas chromatography, showed the

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(6) V. Brunet and W. A. Noyes, Jr., *Bull. soc. chim.* (France), 121 (1958).

(7) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **80**, 261 (1958).

(8) P. Ausloos and E. Murad, *ibid.*, **80**, 5929 (1958).

(9) The technical assistance of J. L. Bass in carrying out this preparation is acknowledged.

(10) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 465.

(11) W. T. Barry, Jr., and W. D. Walters, THIS JOURNAL, **79**, 2102 (1957).

following mass distribution (m/e of 102 = 100.0 units) 103–7.1 (after subtracting the contribution of C^{13}); 101–40.5.

2-Hexanone.[12]—1. Control runs at 3130 Å. (and room temperature) agreed with the results of Davis and Noyes[4] in that the ratio of CO + C_2H_6 + CH_4 to propylene was $^1/_{22}$ compared to their average value of $^1/_{23}$; the quantum yield of propylene was 0.35 using a value of 0.42 for the logarithm of the molar absorption coefficient[13] compared to their value of 0.4–0.5 and 0.45 given by Brunet and Noyes.[6]

2. The course of the photolysis in a D_2O "conditioned" cell was identical except for the isotopic composition of the acetone fraction which changed from CH_3COCH_3 100% before conditioning, to CH_3COCH_3 75% and CH_3COCH_2D 25%.

3. The propylene formed in photolysis in a "conditioned" cell was entirely C_3H_6.

4. The residual 2-hexanone after photolysis in a "conditioned" cell did not show any detectable change in its mass spectrum.

5. The isotopic composition of the acetone fraction obtained when using a "conditioned" cell was reproducible and did not change in one run in which the photolysis was conducted in the presence of carbon dioxide at a pressure of 101 mm.

6. In a control experiment, acetone at a partial pressure of 0.48 mm. was allowed to stand in a D_2O "conditioned" cell for the period of a photolysis. At the end of this time its mass spectrum showed that it was entirely CH_3COCH_3, and the 59 peak was wholly accountable on the basis of the normal content of C^{13} isotope.

Discussion

The isotopic analysis of the propylene and the acetone from the photolysis of 2-hexanone-5,5-d_2 show a lack of balance of deuterium atoms.[14] The general nature of the photolysis does not indicate any fundamental difference from the results of Davis and Noyes,[4] and the control experiments in the present study on 2-hexanone. The minor products can be explained by the free radicals which can normally be expected from 2-hexanone-5,5-d_2, namely, $CH_3\cdot$, $CH_3CO\cdot$, $CH_3CD_2CH_2CH_2\cdot$.

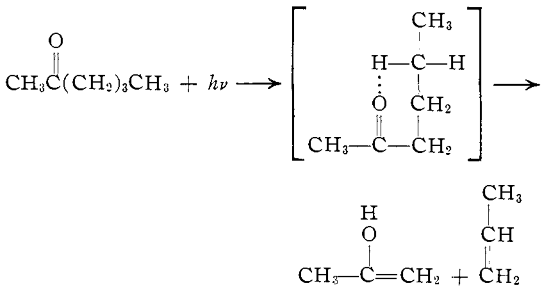
The results suggest that the type II process may lead primarily to C_3H_5D and acetone-d_1 and that secondary reactions may cause the latter to exchange the deuterium atom for a hydrogen atom. Such an exchange cannot have taken place *after* the light source had been extinguished as the time taken for conducting the analysis has no effect on the isotopic composition of the acetone. The exchanging species cannot be some impurity in the parent ketone, as a relatively large and hence easily detectable amount of it would have to be present in the starting material to explain the present results. Thus it can be estimated that if the impurity had one exchangeable hydrogen, then in the set of experiments in which the over-all decomposition was 16% and the yield of CH_3COCH_3 was 10 mole %, the impurity would have to be at least 10 mole % of the starting material. Such an amount would have been detected by gas chromatography. The exchange reaction cannot be with the parent ketone, as its mass spectrum after photolysis shows no significant increase in the ratio of mass 103 to mass 102 which would be the case if all the unaccounted deuterium atoms had been picked up by it.

The possibility that the 6.1% of 2-hexanone-d_1 in the starting material underwent preferential photolysis to give C_3H_5D and CH_3COCH_3 is ruled out by the observation that the ratio of mass 101 to mass 102 was unchanged on photolysis.

It seems most likely that the deuterium atoms not accounted for were mostly on the wall of the cell and that the exchange reaction between the acetone-d_1 formed in the type II process and sorbate on the wall, which is believed to be water, took place during the time of the photolysis. The role of the walls of the cell can be explained on the basis of the recent work of Benesi and Jones[15] and of Young[16] on the water–silica system. The difference between the surfaces of the vitreous silica of the photolysis cell and the extremely finely divided amorphous silica used by these workers is probably one of degree rather than kind.

The prolonged evacuation of the cell prior to photolysis may have removed practically all the adsorbed water, but certainly none of the bound water, since the cell was heated to only about 120°. Young[16] has shown that bound water, which is most probably present as SiOH groups on the surface of the silica, does not begin to be pumped off until 180° and may not be removed completely even at 400°. Hence, the cell that was used in this study probably was never free from bound water. Benesi and Jones[15] have demonstrated that the SiOH groups on the surface of the silica readily exchange hydrogen atoms with D_2O vapor. While the "conditioning" given to the cell with D_2O is similar to the treatment indicated by them, the exchange may not have been as complete if the diffusion of D_2O vapor inside the capillaries on the surface of the cell had been rate determining. Nevertheless, at least the more accessible sites may have exchanged and become SiOD groups.

Two mechanisms have been proposed for the type II process. In the case of 2-hexanone these would be



(1)

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[12] The experiments on 2-hexanone did not immediately follow those on 2-hexanone-d_2. In between, the cell was exposed to water vapor.

[13] D. Biquard, *Bull. soc. chim.* (*France*), **8**, 66 (1941).

[14] The production of CH_3COCH_3 by the free radical reaction $CH_3CO\cdot + CH_3\cdot \rightarrow CH_3COCH_3$ was probably no more than 2% of the total acetone produced.

[15] H. A. Benesi and A. C. Jones, *J. Phys. Chem.*, **63**, 179 (1959).

[16] G. J. Young, *J. Coll. Sci.*, **13**, 67 (1958).

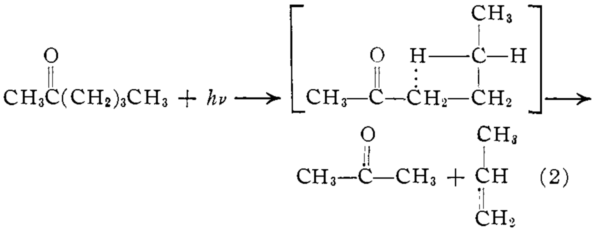
TABLE I

PHOTOLYSIS OF 2-HEXANONE-5,5-d_2 AND 2-HEXANONE AT 3130 Å.

Temperature, 27°; cell volume, 238.6 ml.; dead space, 69.6 ml.

Sample	Press., mm.	Time, min.	Filter	Pretreatment	CO + CH_4 + C_2H_6 mole/cc./sec. × 10^{-11}	Propylene, mole/cc./sec. × 10^{-11}	Acetone No. of D atoms 0	1	2	Remarks
						2-Hexanone-5,5-d_2				
C	7.0	850	Yes	None	0.11	2.28	53.1	45.9	1.0	
C	6.3	850	Yes	None	0.10	2.05	54.7	44.1	1.2	
C	7.5	20	No	None	12.0	98.2	33.8	64.0	2.2	
C	6.8	20	No	None	4.0[b]	86.9	35.6	62.7	1.7	Products left in cell for 17 hr. after photolysis
A	10.5	1015	Yes	None	0.16	2.03	89.0	10.7	0.3	Run no. 1; acetone separated by gas chromatography
B	5.2	1000	Yes	None	0.09	1.98	79.8	19.0	1.2	Run no. 2
						2-Hexanone				
	12.2	935	Yes[a]	None	0.12	3.20	100.0	0	0	
	12.2	935	Yes[a]	D_2O	.13	3.39	74.7	24.8	0.4	
	12.3	1008	Yes[a]	D_2O	.13	3.96	72.4	27.3	.3	Acetone separated by gas chromatography
	11.5	835	Yes[a]	D_2O	N.d.[c]	N.d.	75.9	23.5	.6	P_{CO_2} = 101 mm.

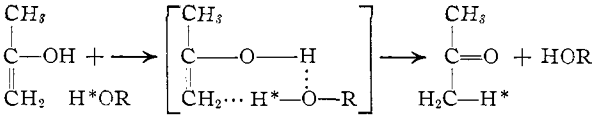
[a] Intensity different from runs on 2-hexanone-d_2. [b] Unavoidable presence of high-boiling products from previous runs may account for lower value. [c] N.d. = not determined.



$$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_3CH_3 + h\nu \longrightarrow \left[\begin{array}{c} \qquad\qquad CH_3 \\ \qquad\qquad | \\ O\quad H-C-H \\ \|\quad\ \vdots\quad\ | \\ CH_3-C-CH_2-CH_2 \end{array}\right] \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + \begin{array}{c} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array} \qquad (2)$$

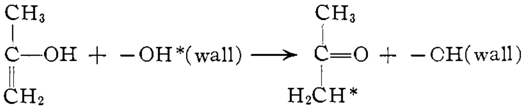
Mechanism 1, proposed by Davis and Noyes,[4] leads to the enolic form of acetone and propylene, while mechanism 2[17] would give the ketonic form of acetone and propylene. On the basis of the second mechanism, the acetone should not show any special tendency to exchange hydrogen atoms at the walls as the control experiment with pure acetone and a "conditioned" wall showed no deuterium enrichment.[18] Moreover, in experiments on 2-hexanone and a "conditioned" wall, the rate of formation of acetone-d_2 appeared to be negligible even though the ratio of acetone-d_1 to acetone-d_0 was 1 : 3 at the end of the experiment. If successive exchange reactions were dependent on the concentration of the various species in the gas phase, more acetone-d_2 would be expected.[19]

On the other hand, mechanism 1 offers a suitable explanation for the present observations. The enolic form of acetone formed in the primary process may have a considerable lifetime in the gas phase. In water solution, it is known that the reaction from enol to keto form is a rapid reaction which proceeds with the involvement of a hydrogen donor and a hydrogen acceptor, both of which may be present in the same molecule.[20] Denoting the second molecule as ROH* and using the asterisk to label the hydrogen the reaction may be written as



$$\begin{array}{l} CH_3 \\ | \\ C-OH \\ \| \\ CH_2 \end{array} + H^*OR \longrightarrow \left[\begin{array}{l} CH_3 \\ | \\ C-\!\!-O-\!\!-H \\ \vdots\qquad\quad\ \vdots \\ CH_2\cdots H^*-O-R \end{array}\right] \longrightarrow \begin{array}{l} CH_3 \\ | \\ C=O \\ | \\ H_2C-H^* \end{array} + HOR$$

It is seen that the reaction is accompanied by an exchange of one and only one hydrogen atom between the two molecules and that in the case of the enol it is the hydrogen attached to the oxygen that is involved. The results of the present study can be explained if reaction 1 is followed by



$$\begin{array}{l} CH_3 \\ | \\ C-OH \\ \| \\ CH_2 \end{array} + -OH^*(\text{wall}) \longrightarrow \begin{array}{l} CH_3 \\ | \\ C=O \\ | \\ H_2CH^* \end{array} + -CH(\text{wall}) \qquad (3)$$

The suggestion that the transformation from enol to keto form in the type II process occurs at the wall already has been made by Gruver and Calvert[21] on the basis of the results of McNesby and Gordon[7] on the photolysis of 2-pentanone-1,1,1,3,3-d_5.

In the experiments with 2-hexanone-d_2, the bound water on the walls was very likely in the form of SiOH groups so that these experiments are

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[17] For a discussion, see J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

[18] That CH_3COCH_3 may exchange a hydrogen atom on the wall *under the influence of light* is not excluded by the present set of experiments. Since 2-hexanone did not appear to exchange at the walls under the action of light, the possibility that acetone may do so seems small. It may also be pointed out that at low conversions, the absorption of light and subsequent reactions of the acetone product can be disregarded.

[19] It is interesting to note that no analog of the type II process has been reported in a cyclic ketone such as cyclohexanone, which possesses two γ-hydrogen atoms. If the mechanism of the type II process were as in reaction 2, it would be expected to take place even in cyclic ketones which are known to undergo hydrogen shifts involving three carbon atoms and a hydrogen atom, under the influence of light (R. Srinivasan, THIS JOURNAL, **81**, 1546, 2601 (1959)). A mechanism such as 1 would be excluded in cyclic ketones by steric considerations. The author is indebted to Professor S. Winstein of the University of California at Los Angeles for pointing out the above.

[20] C. G. Swain, *ibid.*, **72**, 4578 (1950).

[21] J. T. Gruver and J. G. Calvert, *ibid.*, **80**, 3524 (1958).

equivalent to the photolysis of 2-hexanone in a D_2O "conditioned" cell. Since H_2O and hydroxylic compounds are more or less ubiquitous in comparison to –OD groups, the number of SiOH groups available for exchange in the experiments on 2-hexanone-d_2 probably greatly exceeded the number of SiOD groups available in the experiments on 2-hexanone. Hence reaction 3 may be expected to lead more often to the replacement of a deuterium by a hydrogen in the product in the photolysis of 2-hexanone-d_2 than the replacement of a hydrogen by a deuterium in the photolysis of 2-hexanone.

The term "intramolecular" as applied to the type II process may not be exact if the enolic form of the ketone produced frequently exchanges a hydrogen with some other molecule, in rearranging to the stable ketonic form. As a result, studies on the type II process with partially deuterated ketones are bound to give varied results according to (a) the nature of the walls of the cell and (b) the nature of trace impurities in the starting material. Since simple aliphatic ketones retain traces of water very tenaciously,[22] the presence of such contaminants may very well alter the nature of even a preconditioned cell, when the ketone vapor is introduced.[23] Conflicting results such as those on the photolysis of 2-pentanone-1,1,1,-3,3-d_5[7,8] may be explained in this way.

The increased yield of CH_3COCH_2D relative to CH_3COCH_3 in the photolysis of 2-hexanone-d_2 when an unfiltered mercury arc was used suggests that a reaction similar to (3) may occur in the gas phase at high intensities. This opens up interesting possibilities for further investigation.

Acknowledgments.—The author wishes to thank Professor W. Albert Noyes, Jr., for advice and encouragement during the course of this work, and Dr. William H. Saunders, Jr., for many stimulating discussions.

[22] K. S. Howard and F. P. Pike, *J. Chem. Phys.*, **63**, 311 (1959), discuss the difficulties in drying acetone.

[23] The contaminant may have –OH groups as in 2-hexanone-d_2 in the preparation of which no compound with an –OD group was used, or –OD groups as when D_2O is used to deuterate the α-carbon atoms of a ketone.

ROCHESTER, NEW YORK

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

The Thermal Unimolecular *cis–trans* Isomerization of *cis*-Butene-2[1]

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The unimolecular *cis–trans* isomerization of *cis*-butene-2 has been studied at 469° as a function of pressure, down to 3×10^{-3} mm. and up to 2000 mm. N_2. The fall-off region lies essentially below 2 mm butene-2. Activation energies were measured at four pressures between 5×10^{-3} and 100 mm. butene-2. $k_\infty = 6.1 \times 10^{13}\, e^{-62{,}800/RT}$ sec.$^{-1}$. Side reactions occur which strongly affect the observed kinetics above 10 mm. butene-2 pressure, but which are believed negligible below 5 mm. The observed unimolecular behavior is considered with respect to the Slater theory and is discussed in the light of other experimental findings on unimolecular reactions from the literature.

The first quantitative study of the *cis–trans* isomerization of *cis*-butene-2 by Kistiakowsky and Smith[3] gave the high pressure Arrhenius parameters $A = 2$ sec.$^{-1}$, $E = 18$ kcal./mole. Both internal evidence recognized by the authors, and external evidence, have suggested possible errors in this work. While the present study was in progress, Anderson, *et al.*,[4] reported a re-examination of this reaction and found $A = 10^{11}$ sec.$^{-1}$, $E = 52$ kcal./mole. The latter value approaches that for the singlet isomerization of ethylene-d_2 ($E = 65$ kcal./mole).[5] However the marked dependence of rate on pressure found by Anderson, *et al.*, just below one atmosphere led them to an anomalously low value for the lifetime of energized butene molecules.

The present study of this elementary reaction offers further clarification both of earlier work and of the status of this reaction as an illustration of a unimolecular process.

Experimental

Materials.—*cis*-Butene-2 was Phillips research grade. After purification it contained 0.026% *trans*-butene-2, 0.014% butene-1, 0.02% CO_2, 0.015% butane, 0.01% propane, 0.007% propylene. Propylene of the same grade contained only traces of CO_2 after treatment. Nitrogen, Linde's oil pumped grade, was passed through silica gel at −183° and then through a heated copper column.

Apparatus and Procedure.—A conventional vacuum apparatus was employed; a 175-cc. quartz bulb and a 4250-cc. Pyrex vessel served as reactors. Packed vessel runs were made in a 175-cc. Pyrex vessel, filled with glass wool. Reactors were heated in aluminum core furnaces. Temperature was read with chromel–alumel thermocouples calibrated against a standard. During a run, temperature was constant to 0.5° while the variation over the reactor was 0.5° in the small vessel and roughly 1° for the large reactor.

Rate studies were made as described. The reactor and lines were evacuated to 10^{-5} mm. or better. Hg vapor has no effect on reaction and was not excluded from the reactor. The desired pressure of butene (and addend if any) was admitted to the reactor. A sample for analysis was obtained after a given reaction time through a capillary sampling tube which first had been quickly swept out. At most pressures, five or six samples could be taken during one run with a pressure drop of not more than 10% (470°). At very low pressures, all material was frozen out of the reactor to provide sufficient sample. Runs were not carried beyond 15% *trans* isomer formation. The whole reactor was emptied at the end of a run for analysis of side products.

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