The Kinetics of the Thermal Isomerization of [2.1.0]Bicyclopentane

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The thermal isomerization of [2.1.0]bicyclopentane is a homogeneous unimolecular reaction and has been studied in the range 287.9 to 310.1° and pressures of 66.7 to 0.04 mm. The high-pressure rate constant at 291.2° can be expressed in the Arrhenius form $k_\infty = 10^{14.58} \exp[-(46.6 \pm 1.0)\text{kcal.}/RT]$ sec.$^{-1}$. The number of effective oscillators in the Kassel integral is estimated as 18 ± 2. Added nitrogen increases the rate in the lower pressure region with a pressure efficiency relative to the reactant molecule of 0.10 ± 0.02. Energy considerations appear to preclude a cyclic strainfree diradical as a transition state.

Introduction

Criegee and Rimmelin[1] describe the preparation and properties of [2.1.0]bicyclopentane which undergoes isomerization to cyclopentene at elevated temperatures. This reaction would seem to be analogous to the isomerization and decomposition reactions of cyclopropane and substituted cyclopropanes which have been studied[2,3] in detail. Whereas the cyclopropanes gave products corresponding to rupture of any of the cyclopropane carbon–carbon bonds with migration of a single hydrogen atom, the single product observed in the bicyclopentane reaction corresponds to rupture of only the carbon–carbon bond between the bridgehead atoms. The extremely high heat of hydrogenation of this compound[4] of 55.1 kcal. seemed to indicate high strain energies in the system. The effect of this strain in reducing the activation energy was qualitatively observable from the relatively low temperature at which reaction occurred[1] as compared to the temperatures required for the strained simple cyclopropane systems, assuming similar preëxponential factors in an Arrhenius type rate constant.

Hydrocarbon isomerization reactions yielding stable products in non free radical reactions also afford the best chances to observe energy transfer effects at low pressures if the reactant molecule is sufficiently simple. The bicyclopentane molecule has only one more atom than methylcyclopropane for which the fall of first order rate constant with pressure is readily observable and hence might show energy transfer effects at the low end of the experimentally accessible pressure region.

A kinetic study of the reaction was therefore undertaken to determine if it were a homogeneous unimolecular reaction and to evaluate the Arrhenius parameters and nature of any low pressure fall in rate.

Experimental

[2.1.0]Bicyclopentane (henceforth designated BCP) was prepared by the method of Criegee and Rimmelin.[1] Fifteen grams of endoazo-cyclopentane was heated at 150° for 48 hr. in a stainless steel bomb of 30 ml. capacity. A clear, colorless liquid was distilled out of the bomb into a trap which was cooled to Dry Ice temperature. Analysis by gas chromatography showed that this product consisted of about 90% BCP with cyclopentene as the main impurity. The BCP was purified using a gas chromatography column consisting of 2 feet of 30% by weight silver nitrate-saturated ethylene glycol on 60–80 mesh firebrick packed in 15 mm. diameter glass tubing. The trapped effluent was then dried over sodium sulfate and distilled into storage bulbs from a trap that was cooled in an ice-salt bath. A sample of this BCP, analyzed by gas chromatography using a combination column consisting of 15 inches of 30% AgNO₃-ethylene glycol on firebrick packed in $^1/_4$ inch stainless steel tubing coupled to a 4-$^1/_2$ ft. long column of 30% Dow Corning No. 703 silicone oil on firebrick, showed no detectable impurity, i.e., less than 0.5%. An infrared spectrum of this BCP, taken in the gas phase with a Perkin–Elmer Model 221 Spectrophotometer, matched the spectrum given by Criegee.[1]

In the early runs a purified sample of BCP kindly provided by Professor R. Criegee was used. Kinetic results and n.m.r. spectra obtained for this material were identical with those obtained from BCP synthesized in this Laboratory.

Aldrich Chemical Co. Research Grade cyclopentene was used for retention time determinations and detector calibrations. Matheson prepurified nitrogen was used in the inert gas runs. It was liquefied under pressure in a trap that was kept at liquid nitrogen temperature, and gas was taken from this liquid nitrogen to leave frozen any condensable impurities.

The vacuum system and general procedures used have previously been described in detail.[3] Precision of temperature measurements should be ±0.1°, and absolute temperatures should certainly be accurate to ±0.4°. Reaction was started by expansion of the BCP from a storage flask into the 1800 ml. reaction vessel and was quenched by expansion of the vessel contents into a previously cooled trap at liquid nitrogen temperature.

In order to follow the course of the reaction during some high-pressure runs, the reaction vessel was modified by addition of a 2 mm. i.d. capillary which permitted removal of small portions of reaction mixture from the center of the vessel at any convenient time during the course of the reaction. The capillary was flushed each time before a sample was taken for analysis, and no more than 10% of the total reaction mixture was removed by this sampling method.

A packed vessel was prepared by filling a 500 ml. Pyrex flask with 4 mm. diameter soft glass beads. This increased the surface to volume ratio by a factor of about 70 relative to the unpacked vessel.

For the runs with added nitrogen, mixtures were prepared using a vessel fitted with a magnetically driven paddle stirrer. Reaction products were pumped through a three-turn loop of 6 mm. i.d. tubing, immersed in liquid nitrogen at one end, to assure complete freezout of products and rapid removal of the nitrogen mixture from the vessel.

Analyses were done by vapor-phase chromatography using the silver nitrate–silicone oil combination column with helium carrier gas. Quantitative analyses by measurement of peak areas were obtained directly from the trace of a mechanical integrator coupled to the recorder. Analysis of calibration mixtures showed the calibration factor relating area ratios to mole ratios to be unity within the precision of the analysis, ±2%. Duplicate or triplicate analyses were made whenever the reactant pressure was high enough to provide enough material.

Results

Typical data are tabulated in the Appendix. The products of the reaction were identified by comparison of relative retention times on the com-

(1) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1954).

(2) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (London), **217A**, 563 (1953).

(3) J. P. Chesick, *J. Am. Chem. Soc.*, **82**, 3277 (1960).

(4) R. B. Turner, "Kekulé Symposium on Theoretical Organic Chemistry," Butterworths, London, 1959, p. 67.

bination AgNO₃–silicone oil column with the retention times for the authentic materials. For large product samples a small peak having the same retention time as authentic methylene cyclobutane was observed. This peak amounted to about 0.5% of the cyclopentene peak and therefore was not measured in routine analyses with smaller samples.

Infrared spectra of the product peaks that were identified by retention times as BCP and cyclopentene were identical to those of the authentic materials. Trapping of the individual peaks as they were eluted and passing them through a 6 meter dimethyl formamide on firebrick column established that any other substances present amounted to less than 1%.

During a typical run in which the pressure was 27.0 mm., more than 99.5% of the reaction-vessel contents were trapped within 30 seconds so that essentially no non-condensables such as hydrogen or methane were formed during the reaction. The absence of observable pressure drops during the course of reaction indicated the absence of polymerization reactions.
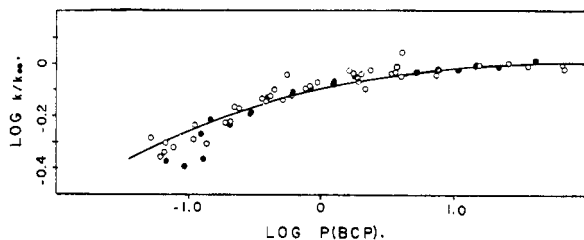

Fig. 1.—Pressure dependence of first-order k: O, 564.4°K; ●, 584.2°K. Solid curve is calculated from the Kassel integral with $s = 18.3$, $T = 564.4$°K.

Single analysis runs at varying conversions as well as runs in which samples were withdrawn at varying times demonstrated the first order nature of the reaction at constant pressure or near the high pressure limit. For example, during the course of one run at an initial pressure of 66.7 mm., samples were taken and analyzed at 18, 31, 43, 52 and 61 per cent reaction. A plot of log P_{BCP} vs. time gave a straight line with deviations of less than 2%.

Several runs were made in the packed vessel in which the surface to volume ratio was a factor of 70 greater than in the unpacked vessel. The rate constant was found to be only 4% higher than in the unpacked vessel. The isomerization therefore appears to be a homogeneous unimolecular reaction.

A plot of log k/k_∞ vs. log P is shown for $T = 564.4$°K. and $T = 584.2$°K. in Fig. 1. As predicted in the theories of unimolecular reactions, the curve at the higher temperature is shifted to lower pressures. Values of k_∞ were obtained by extrapolation of a plot of k^{-1} versus $P^{-1/2}$ to $P^{-1/2} = 0$.[5] At the highest pressures of the experiments, k had reached at least 99% of its high-pressure limit. The region of drop-off begins at about 3 mm. pres-

(5) B. S. Rabinovitch and K. W. Michel, J. Am. Chem. Soc., 81, 5065 (1959).

sure, and k falls to approximately one-half of its high-pressure value at $P = 0.07$ mm. In the runs with added nitrogen, it was found that the added gas served towards restoring the high-pressure behaviour at low pressures of BCP. From the shift of the log k/k_∞ vs. log P_{BCP} curve in the presence of added nitrogen, the relative pressure efficiency of N_2 to BCP in energy transfer is found to be 0.10 ± 0.02. This assumes the efficiency to be constant in the pressure range studied. This may be compared to the values of 0.06 for cyclopropane,[2] 0.20 for methylcyclopropane[3] and 0.18 for cyclobutane.[6] An Arrhenius plot in the range 287.9–310.1° is presented in Fig. 2. Fitting the points
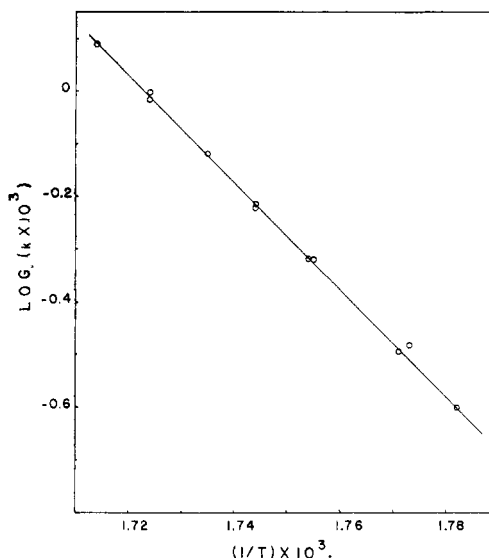

Fig. 2.—Arrhenius plot for BCP isomerization in the high-pressure range.

to a straight line by the least squares method gives a value for the activation energy of 46.6 ± 1.0 kcal. From this value and the rate constants at 287.9°C., k_∞ can be expressed in the Arrhenius form: $k_\infty = 10^{14.58} \exp [-(46.6 \pm 1.0 \text{ kcal.})/RT]$ sec.$^{-1}$.

Discussion

Schlag, Rabinovitch and Schneider[7] have evaluated the Kassel integral for a range of values of s

$$\frac{k}{k_\infty} = I_s(\theta') = [\Gamma(s)]^{-1} \int_0^\infty \frac{x^{s-1} e^{-x} dx}{1 + [x/(b + x)]^{s-1} \theta'^{-1}}$$

and b, including $s = 15, 21, 26$ and $b = E/RT = 36, 40, 44$. In the equation $\theta' = W/A$, where $W =$ collision frequency per molecule, and A is taken as the Arrhenius preëxponential factor; s is the effective number of oscillators contributing to dissociation in the Kassel theory. A linear interpolation was made on curves that were drawn from the tabulated values between the values of $s = 15$ and 21, and $b = 40$ and 44. Over small ranges, log P is a suf-

(6) H. Pritchard, R. Sowden and A. F. Trotman-Dickenson, Proc. Roy. Soc. (London), A218, 416 (1953).

(7) E. W. Schlag, B. S. Rabinovitch and F. W. Schneider, J. Chem. Phys., 32, 1599 (1960).

ficiently linear function of s, for a given log k/k_∞ that a linear interpolation may be used for intermediate values of s. The solid curve in Fig. 2 is derived by this method and corresponds to $b = 41$ and $s = 18.3$. A collision diameter of 5 Å. was assumed for BCP. We can therefore assign a value of $s = 18 \pm 2$. The scatter of the data and experimental limitations on the minimum pressure and hence on the minimum observable k/k_∞ prevent a more precise evaluation of s. This value for BCP with thirty-three vibrational degrees of freedom is close to, although a bit lower than, the value of the Kassel parameter observed for reactions of twelve atom molecules with thirty degrees of freedom such as methylcyclopropane and cyclobutane. Thus the lower pressure behavior and hence the inter- and intramolecular energy transfer properties of the BCP reaction correspond roughly to those predicted from the pressure dependence of isomerization and decomposition rates of other ring systems with similar molecular complexity. Increasing importance of vibrational energy quantization at the lower energies and temperatures of this study may account for the slightly lower than expected value of s found using the Kassel integral based on classical vibrations. The A factor is in the "normal" range for isomerization reactions of this type.[8]

An estimate of the minimum energy required to rupture the bridgehead bond in BCP may be made as follows. The heat of hydrogenation of BCP to cyclopentane in acetic acid solution of 55.1 kcal./mole[4] probably does not differ from the value in the gas phase by more than 0.5 kcal.[9] By breaking the hydrogenation of BCP into the following steps, one can estimate the energy for step 1, the rupture of the central bond to give a system in which the bicyclic strain energy has been relieved through absence of bonding between the former bridge-head atoms.

$$\Delta H = -55.1 \text{ kcal./mole}$$
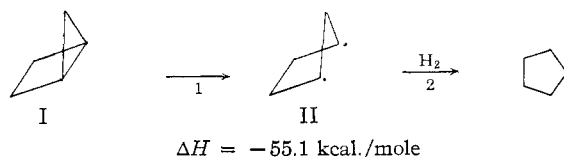
Taking 89 kcal. as the probable energy change for each of the secondary carbon hydrogen bonds formed in reaction 2,[10] ΔH is calculated to be $+19 \pm 4$ kcal./mole for reaction 1.

An upper bound of 15 kcal. may be estimated for the activation energy for intramolecular hydrogen migration necessary to get cyclopentene from II. This value may be rationalized by taking as a model the abstraction of hydrogen from methane by methyl radicals for which the activation energy is about 14.7 kcal./mole.[11] Unfavorable orientation in II is likely to be offset by the gain in formation of a double bond. The 65 kcal. activation energy for isomerization of cyclopropane to

propylene is only 1.3 kcal. greater than the activation energy for cis-trans isomerization of cyclopropane $-d_2$ and is only 11 kcal. greater than the heat of formation of the trimethylene species from cyclopropane as estimated by Benson.[12] The estimate of a maximum barrier of 15 kcal. for hydrogen atom migration with double bond formation to yield cyclopentene is therefore compatible with the 11 kcal. figure for the migration of hydrogen if the trimethylene species is an intermediate or transition state in the cyclopropane reaction. Combination of this maximum of 15 kcal. with the probable energy for formation of II of 19 kcal. gives 34 kcal. for an activation energy of BCP isomerization, considerably less than the observed figure of

Appendix

A. Data for runs without added nitrogen

Reactant P, mm.	Conversion %	$k \times 10^4$, sec.$^{-1}$	T, °K.	Reactant P, mm.	Conversion %	$k \times 10^4$, sec.$^{-1}$	T, °K.
68.4	28.8	3.18	564.4	25.4[a]	32.3	3.56	
36.4	64.1	3.27		29.3[a]	32.4	3.53	
26.0	24.9	3.37		33.2[a]	31.7	3.36	
15.8	23.2	3.35		42.1	67.4	14.17	584.2
7.8	22.4	3.18		18.7	55.8	13.66	
7.7	22.3	3.18		22.1	41.2	13.33	
7.3	22.3	3.04		10.8	37.6	13.11	
4.10	22.4	3.77		5.23	39.7	12.86	
4.04	17.1	2.99		3.71	49.2	13.40	
3.64	22.6	3.12		1.78	44.4	12.41	
3.38	22.3	3.08		1.22	34.4	11.61	
2.34	25.6	3.18		1.22	32.4	11.77	
2.00	24.5	3.08		0.84	42.0	11.30	
1.89	17.8	2.86		.608	30.0	10.66	
1.88	18.8	2.96		.603	31.5	10.52	
1.80	38.4	3.07		.397	39.8	10.41	
1.73	21.9	3.07		.293	33.5	9.07	
1.60	21.9	3.16		.288	29.7	9.03	
1.08	16.6	2.69		.205	27.8	8.15	
0.935	21.0	2.85		.145	32.2	8.52	
.89	19.6	2.85		.131	22.6	5.99	
.81	19.7	2.76		.123	28.8	7.52	
.75	18.8	2.70		.094	19.0	5.62	
.51	16.0	2.43		.076	10.4	2.18	
.440	22.0	2.66		.067	18.0	5.90	
.411	18.7	2.53		.058	22.1	3.62	
.379	17.3	2.41		.043	15.0	2.60	
.351	17.8	2.46		17.34	22.5	2.52	561.1
.238	15.6	2.26		68.4	23.8	3.21	564.5
.217	19.9	2.30		26.0	24.9	3.30	564.1
.206	15.1	2.02		10.4	25.0	4.83	570.0
.188	14.3	1.99		5.00	22.1	4.79	569.8
.136	9.4	1.65		12.6	26.4	6.02	573.4
.109	14.7	1.95		5.9	26.4	6.10	573.4
.108	15.7	1.72		17.4	27.6	7.60	576.3
.108	16.5	1.95		8.27	27.6	7.60	576.4
.076	9.8	1.60		23.2	30.0	9.63	579.9
.066	14.9	1.67		11.17	29.5	9.92	579.9
.065	12.3	1.53		21.0	36.9	12.29	583.3
.060	15.4	1.48					
.051	4.8	1.75					

[a] Packed vessel.

B. Data for runs with added nitrogen; $T = 564.4°$ K.

Nitrogen/BCP	Reactant P, mm.	Conversion %	$k \times 10^4$, sec.$^{-1}$	Nitrogen/BCP	Reactant P, mm.	Conversion %	$k \times 10^4$, sec.$^{-1}$
21.19	1.36	22.3	2.98	17.83	3.98	25.7	3.50
	0.451	21.5	2.85		1.33	21.8	3.34
	.150	19.9	2.67		0.436	21.4	2.98
	.047	16.1	2.06		.143	16.8	2.30
	.017	6.1	0.66		.045	17.0	1.94

(8) B. G. Gowenlock, Quart. Revs., 14, 133 (1960).

(9) R. B. Turner, W. R. Meador and R. E. Winkler, J. Am. Chem. Soc., 79, 4116 (1957).

(10) M. Szwarc, Chem. Revs., 47, 75 (1950).

(11) F. S. Dainton, K. Ivin and F. Wilkinson, Trans. Faraday Soc., 55, 929 (1959).

(12) S. W. Benson, J. Chem. Phys., 34, 521 (1961).

47 kcal. Hence it becomes likely that the actual transition state does not go through an intermediate such as II in which the bond is completely broken and that the rearrangement is a concerted process.

Corroborative evidence is that the reversible *cis–trans* isomerization reaction of 2-methyl[2.1.0]-bicyclopentane appears to have an activation energy of 39 kcal./mole,[13] which is also much larger than the maximum figure of 24 kcal. for complete release of bicyclic strain in the transition state. Hence, strainfree II is also not the transition state

(13) J. P. Chesick, unpublished work.

for this geometrical isomerization. This reaction will be discussed more thoroughly in another paper.

[Contribution from the Department of Chemistry, Harvard University, Cambridge 38, Mass.]

Nuclear Magnetic Resonance Studies of Keto-enol Equilibria. III. α,β-Unsaturated-β-ketoamines

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The proton resonance spectra of a number of compounds obtained from the 1:1 condensation of a β-diketone with a monoamine have been measured. Of the three tautomeric possibilities, these compounds exist predominantly in the ketamine

form $-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{\overset{\displaystyle |}{}}{C}-NHR$. Proof of this structure is obtained from the observed spin-spin splittings of N–H with the α-protons of R. The position of the tautomeric equilibrium could not be altered by large changes in the nature of the solvent nor by variation of the substituent R. The preferential existence of the ketamine form over the ketimine and enimine forms is ascribed to greater stabilization through resonance and hydrogen-bonding.

Introduction

In the first paper[1] of this series proton resonance studies were made of the 2:1 condensation products of acetylacetone and various diamines. These bases are capable of existing in any of three tautomeric forms, the Schiff base *1*, the ketamine *2* and the enimine *3*. The interchange between the last two tautomers involves a small displacement in the
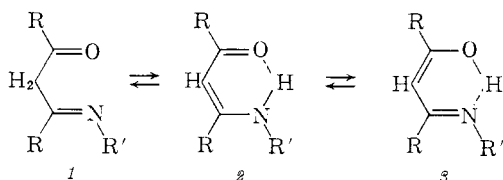
equilibrium position of the acidic proton. It was observed that in solution, with acetone as the sole exception among the solvents studied, these compounds were virtually completely tautomerized in the ketamine form *2*. Structures were inferred from the presence of spin–spin coupling of the α protons of R′ with that on the nitrogen ($J = 6$–7 c.p.s.). For example, if R′ is a tri- or tetramethylene bridging group, the spectrum of this group is that of form *2* since the α protons are split into a quartet. When the bridging group is dimethylene, a triplet of peculiar shape[2] arises, but in this case the proton is also located on the nitrogen for the

(1) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961).

(2) The nature of this triplet has been further clarified; J. D. Baldeschwieler, R. H. Holm and G. O. Dudek, to be published.

signal was found to collapse to a singlet upon deuteration. The prototype of the series, "bis-(acetylacetone)-ethylenediimine," is then properly described as the di-chelated form of N,N′-di-(1-methyl-3-oxobutylidene)-ethylenediamine. The observed composition of the solutions was found to be insensitive to solvent acidity and polarity and to substituent effects at the carbonyl carbon. This behavior is in strong contrast to that of β-dicarbonyls such as acetylacetone and ethylacetoacetate whose enolic content, as assessed by proton resonance or more classical techniques, is strongly dependent on the nature of the solvent.[3–5]

The structure of bases derived from the 1:1 condensation of β-dicarbonyls and primary monoamines has not yet been definitely established, although strong presumptive evidence, principally from infrared studies, favors the ketamine form. Cromwell[6,7] has consistently described these compounds as α,β-unsaturated-β-ketoamines and has reported them to behave chemically more like vinylogs of amides than like ketones or vinylamines.[7] The infrared data of Cromwell, *et al.*,[7] Weinstein and Wyman,[8] Holtzclaw, *et al.*,[9] and Witkop[10] strongly support structure *2* for bases

(3) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

(4) M. Geissner-Prettre, *Compt. rend.*, **250**, 2547 (1960).

(5) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., pp. 663–702.

(6) N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

(7) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, *J. Am. Chem. Soc.*, **71**, 3337 (1949).

(8) J. Weinstein and G. M. Wyman, *J. Org. Chem.*, **23**, 1618 (1958).

(9) H. F. Holtzclaw, Jr., J. P. Collman and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

(10) B. Witkop, *ibid.*, **78**, 2873 (1956).