

Thermal Unimolecular Decomposition of isoPropenylcyclobutane

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The thermal decomposition of isopropenylcyclobutane has been investigated in the temperature range 304–348°C; the decomposition was homogeneous and first order. Two parallel reactions took place, an isomerization to yield 1-methylcyclohexene and a decomposition to yield ethylene and isoprene. The ratio of products from each reaction path was essentially independent of temperature. The Arrhenius equations for these two reactions were found to be:

$$k(\text{isoprene}) = 10^{14.64} \exp(-51,030/RT) \text{ sec}^{-1},$$

$$k(1\text{-methylcyclohexene}) = 10^{14.53} \exp(-51,030/RT) \text{ sec}^{-1}.$$

Both reactions are probably unimolecular.

Cyclopropane ¹ and alkylcyclopropanes ² undergo thermal unimolecular structural isomerization reactions to yield olefines. Cyclobutanes similarly decompose to yield two molecules of an olefine (or olefines) for each molecule of the cyclobutane. The discovery ⁴ that 1,2-dideuterocyclopropane undergoes a unimolecular cis-trans isomerization (in addition to the structural isomerization to propylene) led to a re-examination of probable transition states for the cyclopropane reactions. The cis-trans isomerization of cyclopropanes is not confined to the dideutero-derivative but also occurs in 1,2-dimethylcyclopropane,⁵ 1,2,3-trimethylcyclopropane ⁶ and 1-methyl-2-ethylcyclopropane.⁷ Thus, the 3 membered cyclopropane ring either breaks (or expands sufficiently) to allow free (or slightly hindered) rotation, and then reforms. This reaction is faster than the structural isomerization reaction. An investigation of the thermal reactions of 1,2-dimethylcyclobutane has shown ⁸ that as well as the unimolecular decomposition to yield propylene, ethylene and butene-2, a cis-trans isomerization reaction also occurs. Unlike the cyclopropane reactions, the geometric isomerization is slower in the cyclobutanes than is the corresponding decomposition to olefines.

With some unsaturated cyclopropanes, a further type of unimolecular isomerization has been shown to occur. Thus, vinyl cyclopropane isomerizes to cyclopentene ^{9, 10} and isopropenylcyclopropane to 1-methylcyclopentene.¹¹ These reactions are even faster than the cis-trans isomerization reactions and throw some light on the transition state involved in all types of cyclopropane rearrangements.^{11, 12} It is therefore of interest to determine whether the corresponding cyclobutanes undergo similar reactions (to yield cyclohexenes) and determine the relative values of the various rate constants. It was intended to study initially the reactions of vinyl cyclobutane. Considerable difficulties were, however, encountered in trying to prepare a reasonable quantity of the pure compound. Since isopropenylcyclopropane had been shown to behave in essentially the same manner as vinyl cyclopropane it was decided, therefore, to study the more readily obtainable isopropenylcyclobutane.

EXPERIMENTAL

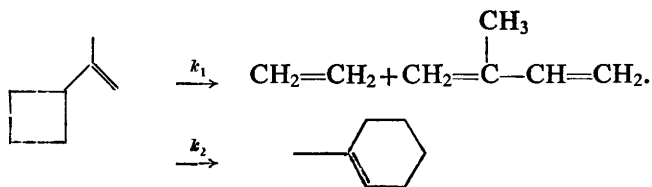
Cyclobutane carboxylic acid was converted into the acid chloride by treatment with excess thionyl chloride.¹³ Treatment of the latter with methylmagnesium iodide gave a good yield of dimethylcyclobutyl carbinol. Isopropenylcyclobutane was obtained from the carbinol by dehydration using one drop of concentrated sulphuric acid in 10 ml of the carbinol, and removing the hydrocarbon by distillation.¹⁴ It was purified by low-temperature distillation through a Podbielniak column operated at a reflux ratio of approximately 60 : 1.

APPARATUS.—The apparatus and method of analysis employed were essentially identical with that used earlier in the study of the isomerization of bicyclo[3,1,0]hexane.¹⁵

PROCEDURE.—isoPropenylcyclobutane was admitted to the reaction vessel from a gas pipette. After each run the reaction mixture was removed by opening the reaction vessel to an evacuated bulb cooled in liquid oxygen. Between runs the reaction vessel was pumped down to 10^{-3} mm. Before any runs were carried out the vessel was aged by leaving the cyclobutane in the vessel for 48 h at 380°C.

RESULTS

Between 304 and 348°C isopropenylcyclobutane decomposes in an aged reaction vessel to yield ethylene, isoprene and 1-methylcyclohexene. The yields of ethylene and isoprene were always equal, within experimental error, and the average ratio of ethylene to methylcyclohexene was 1.3 : 1.



Both reactions were first order, and the rate constants were independent of the pressure in the range 1-40 mm. Use of a packed reaction vessel showed that the rate of production of these compounds was independent of the surface to volume ratio of the reaction vessels. Since 1-methylcyclohexene is an inhibitor of radical reactions, the fact that the rate constant was independent of percentage decomposition indicates the absence of a chain component of the reaction. It is therefore probable that both reaction paths are true unimolecular transformations.

Detailed studies were carried out at ten temperatures and at a pressure of 3.5 mm. At each temperature, between 8 and 12 runs were performed with decompositions varying from 5 to 50 %. The plots of the logarithm of unchanged isopropenylcyclobutane against time were linear over the range of decompositions studied.

TABLE 1.—RATE CONSTANTS FOR THE OVERALL DECOMPOSITION OF ISOPROPENYL-CYCLOBUTANE

temp., °C	348.4	343.2	339.5	334.6	330.3
$10^4 k$ (sec ⁻¹)	8.63	5.94	4.73	3.54	2.55
°C	326.5	323.3	315.5	310.2	304.3
$10^4 k$ (sec ⁻¹)	1.84	1.53	0.820	0.592	0.385

At each temperature the rate constant (table 1) was calculated by the method of least squares. The value of the rate constant determined from runs in the packed reaction vessel was 4.60×10^{-4} sec⁻¹ at 338.9°C (calculated value for the unpacked vessel 4.68×10^{-4} sec⁻¹).

An Arrhenius plot of these results gave a good straight line. The frequency factor and energy of activation for the overall decomposition were calculated by the method of least squares giving

$$k = 10^{14.89} \exp(-51,030/RT) \text{ sec}^{-1}.$$

Over the entire temperature range the mean value for the ratio of isoprene to 1-methylcyclohexene was 1.3:1 and, within experimental error, there was no change in the value of this ratio with either temperature or percentage decomposition. Thus, both reaction paths must have virtually the same energy of activation, and their frequency factors must be in the ratio of 1.3:1 whence

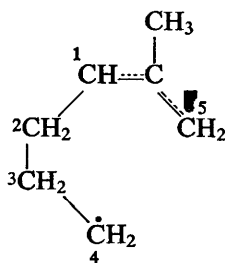
$$k(\text{isoprene}) = 10^{14.64} \exp(-51,030/RT) \text{ sec}^{-1},$$

$$k(1\text{-methylcyclohexene}) = 10^{14.53} \exp(-51,030/RT) \text{ sec}^{-1}.$$

All the results so far reported refer to aged reaction vessels. Runs carried out in clean reaction vessels gave irreproducible rate constants, which were uniformly much higher than the values obtained in aged vessels. The reaction products were different, the major one being isopropylidene cyclobutane. Two other products were tentatively identified as 3,3-dimethylcyclopentene and 1,2-dimethylcyclopentene. The reaction appeared to be entirely heterogeneous, being much faster in the packed reaction vessel than in the empty one, and faster in a silica vessel than in a Pyrex vessel. Isomerization of isopropenylcyclobutane to a mixture of dimethylcyclopentenes on a silica gel catalyst has been noted previously.¹⁶ None of these products were detected in runs carried out in the aged vessels.

DISCUSSION

The results suggest that the transition state for both types of reaction of the isopropenylcyclobutane must be virtually identical. The most obvious activated complex is the biradical



which is stabilized by allylic resonance. The formation of the methylcyclohexene would then be due to ring closure at C₄C₅. (Ring closure at C₁C₄ would regenerate the parent compound and would not have been detectable in this work.) The formation of the isoprene and ethylene would result from the secondary rupture of the C₂C₃ bond. The pre-exponential factors in the Arrhenius equations for both these reactions are about one order of magnitude smaller than for the "normal" cyclobutane decompositions and this may be attributed to more rigid steric requirements in the activated complex in order that most of the allylic resonance energy is available.

It is of interest to compare these results with those for some other cyclobutanes and cyclopropanes. The energy of activation of 50 kcal is some 12 kcal less than the value for the decomposition of ethyl cyclobutane and is a clear measure of the contribution of allylic resonance to the stabilization of the transition complex. (In the decomposition of acetylcyclobutane, resonance stabilization due to the

acetyl group lowers the energy of activation by 7.5 kcal with ethylcyclobutane.) This suggests that the transition state in the decomposition of the alkyl cyclobutanes is also the substituted tetramethylene biradical.¹⁷ Some confirmation of this point comes from the work of Gerberich and Walters⁸ on the decomposition of cis- and trans-1,2-dimethylcyclobutane.

The energy of activation for the reaction leading to ethylene is virtually the same for both compounds, again to be expected from the suggested mechanism. Finally, the occurrence of ring closure of the biradical to reform the cyclobutane can be observed in these experiments.

In this biradical, free or partially hindered rotation of the C—CH₃ groups occurs so that this ring closure results in a cis-trans isomerization reaction. The suggested mechanism leads one to expect that the energy of activation for cis→trans would be the same as for cis→propylene, and this is found to be true, experimental values being 60.1 and 60.4 kcal respectively. Similarly one expects trans→cis and trans→propylene to be the same; experimental values are 61.3 and 61.6 kcal.

The results reported in the present work taken in conjunction with related investigations on other cyclobutanes and cyclopropanes strongly support a biradical transition state for the reactions of these two classes of compounds.

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