The equilibrium constants of the first reaction (the K_2-values) all exceed unity, whereas all the K_3-values are less than one. It can be shown that, under such conditions, high concentrations of mixed disulfide are present in equilibrium mixtures.[2b] The findings emphasize the significance in general of mixed disulfides in thiol–disulfide equilibria,[2b,10] and they support the mechanism previously suggested for the mode of action of these X-ray protective agents.[11,12] A discussion of the relationship between the equilibrium constants and the X-ray protective ability of sulfur containing compounds will be the subject of a forthcoming paper.

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(10) L. Eldjarn and A. Pihl, *Acta Chem. Scand.*, **10**, 1054 (1956).

(11) L. Eldjarn, A. Pihl and B. Shapiro, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," Geneva, Vol. 11, 1956, p. 335; L. Eldjarn and A. Pihl, in J. S. Mitchell, *et al.*, "Proc. Fourth Internat. Conf. on Radiobiol.," Oliver and Boyd, London (1956), p. 249.

(12) A. Pihl and L. Eljdarn, in Proc. Fifth Internat. Conf. on Radiobiol., Oliver and Boyd, London, in press.

OSLO, NORWAY

[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE TEST STATION]

Thermal Decomposition of Cyclopentane-d_2 and Cyclopentane–Acetone-d_6 Mixtures. Reactions of the Allyl Radical

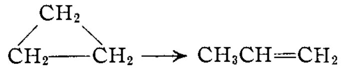
BY JAMES R. MCNESBY AND ALVIN S. GORDON

RECEIVED MARCH 15, 1957

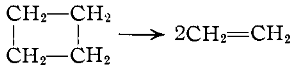
The pyrolysis of cyclopentane is shown to be at least partly free radical. The inhibition of acetone pyrolysis by cyclopentane and the reactions of the allyl radical are discussed. It is shown that allyl radicals abstract H and D very poorly at temperatures below 400°, but that they abstract quite well at temperatures around 500°. The implications for inhibition by propylene are discussed.

Introduction

The thermal isomerization of cyclopropane[1] to propylene has been shown to be intramolecular. Also, the thermal pyrolysis of cyclobutene[2] has been shown to be intramolecular.



(1)



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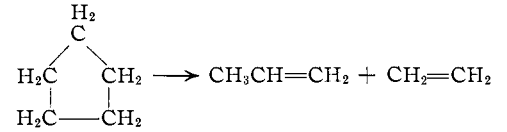
The pyrolysis of cyclopentane has been previously studied[3,4] and shown to consist of two reactions, (1) a dehydrogenation reaction to form cyclopentadiene, and (2) a ring cleavage reaction to form propylene and ethylene.

There are two possible mechanisms whereby cyclopentane can pyrolyze to ethylene and propylene: intramolecularly or *via* free radicals.



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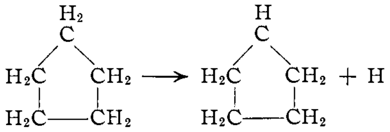

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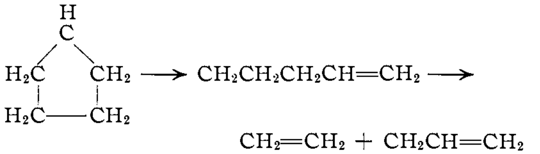

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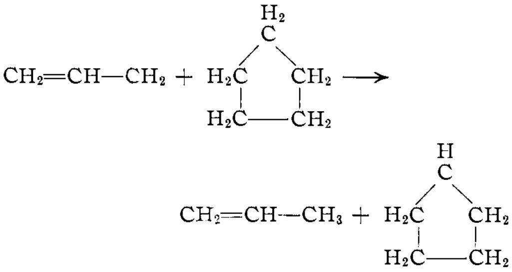

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With the object of finding out which of these mechanisms is correct, the pyrolysis was carried out in the presence of D_2 and of acetone-d_6. Photolysis of the latter system also was studied over a temperature range.

Experimental

Pyrolyses were carried out by immersion of Pyrex reaction flasks in a molten salt-bath at about 500°. The pressure was 110 mm. of cyclopentane measured at room temperature. In addition, equimolar mixtures of cyclopentane and D_2 were made up to a total pressure of 110 mm. measured at room temperature. Photolyses and analyses were carried out as described previously.[5] A medium pressure mercury arc was the light source. In all cases 5% or less of the reactants were consumed.

Results and Discussion

It was found that in the presence or absence of D_2, the important pyrolysis products are ethylene and propylene in roughly equal amounts. The rough equivalence of the amounts of ethylene and propylene was demonstrated by comparing the gas chromatogram of a 1:1 mixture of ethylene and propylene with that obtained in the pyrolysis of cyclopentane. H_2 is one of the products. One of the ways to generate hydrogen is *via* hydrogen atoms. If reaction 4 is important, it could be followed by

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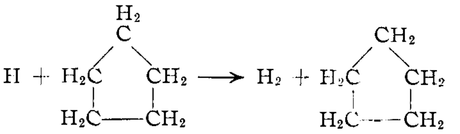
(1) J. R. McNesby and Alvin S. Gordon, *J. Chem. Phys.*, **25**, 582 (1956).

(2) C. T. Genaux, F. Kern and W. D. Walters, THIS JOURNAL, **75**, 6196 (1953).

(3) D. Vanas, N. Lodge and W. Walters, *ibid.*, **74**, 451 (1952).

(4) L. Kuchler, *Z. physik. Chem.*, **B53**, 307 (1943).

(5) J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 4196 (1954).


(7)

However, results of experiments with cyclopropane–acetone-d_6 reported later in this section, clearly show that the hydrogen is generated almost entirely by an intramolecular process.

The 515° pyrolysis products of a 1:1 mixture of cyclopentane and D_2 were separated by gas chromatography; the ethylene and propylene fractions were trapped and analyzed for D content on the mass spectrometer. The results are shown in Table I. Examination of the propylene fraction reveals the following mass peaks: based on 100 divisions for mass 43, there are 976 divisions at mass 42, and 1328 divisions at mass 41. In order to estimate the ratio propylene-d_1/propylene, it is necessary to know the mass spectrum of propylene-d_1. Since this has not been measured, one can get a fairly good estimate by assuming that the mass 42–43 ratio in $CH_2DCH{=}CH_2$ is 2/3 of the mass 41/42 ratio in propylene. Using this estimate, propylene-d_1/propylene $\approx 100/875 = 0.11$. An explanation of the fact that the ethylene is entirely C_2H_4 while a fairly large amount of propylene-d_1 is formed, lies in the free radical mechanism represented in part by reactions 4, 5 and 6. According to this reaction scheme ethylene should be entirely C_2H_4. Propylene, which is formed by the allyl radical abstracting hydrogen by reaction 6, and abstracting D by

TABLE I

ISOTOPIC MARKING IN ETHYLENE AND PROPYLENE FROM THE DECOMPOSITION OF CYCLOPENTANE

Reaction	T, °C.	C_2H_4	C_2H_3D	Propylene	Propylene-d_1
 + D_2	515	99.6	0.4	89.8	10.2
 + CD_3COCD_3	500	99.7	.3	82.7	17.3

$$CH_2CH{=}CH_2 + D_2 \longrightarrow CDH_2{=}CH_2 + D \quad (8)$$

should be a mixture of propylene and propylene-d_1. The ratio of the rates of attack of CH_3 on equimolar mixtures of D_2 and cyclopentane is

$$\frac{R_{D_2}}{R_{CP}} = 1.76 \exp \frac{2600}{1580} = 0.33$$

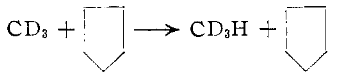
The pre-exponential factor and the energy of activation difference are calculated from the attack of CH_3 on D_2,[6] and CD_3 on cyclopentane,[7] assuming no difference between CH_3 and CD_3. If the allyl radical were to discriminate in exactly the same way as CH_3, the ratio of propylene-d_1/propylene should be 0.33. It must be concluded that either some of the propylene is being formed intramolecularly, or that the allyl radical discriminates between H and D differently than the CH_3 radical.

TABLE II

ISOTOPIC MARKING IN H_2 IN PHOTOLYSIS AND PYROLYSIS OF 1:1 MIXTURES OF CYCLOPROPANE AND ACETONE-d_6

T, °C.	HD/H_2	Time of reactions (min.)
250	0.04	2
250	.03	4
306	.03	2
306	.02	4
357	.03	2
357	.03	1
402	.04	2
402	.04	1
505 (pyrolysis)	.07	3
505 (pyrolysis)	.07	3

In Table II the HD/H_2 ratios resulting from photolysis and pyrolysis of a 1:1 mixture of acetone-d_6 and cyclopentane are shown. The rate of H_2 production is quite low at 250° and increases with temperature. The ratios at higher temperature are therefore more reproducible. There is no effect of time of reaction on these higher temperature ratios, so that the ratios are not generated from any reaction products. These ratios indicate that almost all of the hydrogen is formed intramolecularly. Since pure cyclopentane is stable in the temperature range of the photolysis experiments, the cyclopentyl radical must be the source of hydrogen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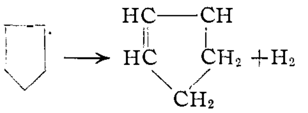
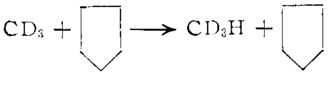

(10)

The cyclopentyl radical is resonance stabilized, making the energy of activation low enough so that there is an appreciable reaction rate at even 250°.

Reactions of the Allyl Radical.—It has been shown that methyl radicals will attack both cyclopropane and cyclopentane,[7] leading in the first instance to allyl radicals and in the second to allyl radicals and ethylene. The attack on cyclopentane is much easier than that on cyclopropane. Also, cyclopentane is thermally more stable than cyclopropane so that the attack by methyl radicals can be studied over a longer temperature range than cyclopropane.

When acetone-d_6 is photolyzed in the presence of cyclopentane at 381°, ethylene is formed in large amounts, while propylene is very small. Butene-1 has been identified as a major product in the above reaction. The analysis for diallyl was unsuccessful, perhaps due to the fact that it is obscured by the acetone parent in the chromatogram. All the products, including their deuterium marking, agree with the mechanism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$$CD_3 + AD_6 \longrightarrow CD_4 + AD_5 \quad (11)$$

$$C_5H_9 \longrightarrow CH_2{=}CH_2 + CH_2CH{=}CH_2 \quad (12)$$

$$CH_2CH{=}CH_2 + CD_3 \longrightarrow CD_3CH_2CH{=}CH_2 \quad (13)$$

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(6) J. R. McNesby, A. S. Gordon and S. R. Smith, THIS JOURNAL, **78**, 1287 (1956).

(7) J. R. McNesby and A. S. Gordon, *ibid.*, **79**, 825 (1957).

$$2CH_2CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \quad (14)$$

$$CH_2CH{=}CH_2 + C_5H_{10} \longrightarrow CH_3CH{=}CH_2 + C_5H_9 \quad (15)$$

$$CH_2CH{=}CH_2 + Ad_6 \longrightarrow CH_2DCH{=}CH_2 + Ad_5 \quad (16)$$

At a temperature of 453°, butane-1 is still present, but propylene/ethylene ratio has increased considerably.

The thermal decomposition of acetone-d_6 occurs rapidly at 500° at which temperature cyclopentane is relatively quite stable. It was therefore possible to investigate the reactions of the allyl radical at about 500° by pyrolyzing acetone-d_6 in the presence of cyclopentane. The propylene/ethylene ratio at 500° has increased still more until it roughly approaches unity. A small amount of butene-1 is formed at the same time.

We see from the foregoing that allyl radicals can abstract hydrogen with some facility at higher temperatures, although the specific rate is lower than the analogous process with methyl radicals.

Propylene Inhibition of Free Radical Chain Processes.—Propylene is an excellent inhibitor of many organic chain reactions. The propylene functions by virtue of a more labile hydrogen atom than the parent. When this hydrogen is abstracted by a free radical, an allyl radical results

$$R + CH_3CH{=}CH_2 \longrightarrow RH + CH_2CH{=}CH_2 \quad (17)$$

The allyl radical is resonance stabilized and is much less reactive than the free radical it replaces. But, as shown above, the allyl radical is quite capable of efficiently abstracting hydrogen in the temperature range of hydrocarbon and ketone pyrolysis. Radical-radical reaction products usually are not seen in our pyrolysis and photolysis experiments at 500° because the radical concentrations are so low. However, in this work, butene-1, a product of methyl and allyl radicals is seen in the products of a system of acetone-d_6 and cyclopentane which has reacted only a few per cent. at 500°. No detectable ethane is in the products. This shows allyl radicals to be in relatively high concentration. Since free radical reaction chains are terminated by radical-radical reactions, the allyl radicals stop chains more effectively than, say, methyl radicals. Thus, propylene, which generates allyl radicals, is an inhibitor but not a complete arrestor of free radical chain reactions.

As the propylene-reactant ratio is increased, the reaction is further inhibited, but less efficiently, until at a critical value there is no further effect of continued propylene addition. At maximum inhibition, all the stable free radicals generated react with propylene and the allyl radical concentration is maximized. Some of these allyl radicals attack the parent compound and are thus chain continuing steps.

There is one other mechanism for propylene action. Using marked compounds, free radicals have been shown[8] to add efficiently to double bonds even at elevated temperatures; the lifetime of the resulting saturated free radical is short. It has two main fates: either it decomposes to the original materials, or it abstracts hydrogen from propylene. If it suffers the latter fate, an allyl radical results; over-all the above reactions are then the same as the abstraction of hydrogen from propylene by the thermally stable free radical.

To summarize, propylene inhibition is due to the replacement of the usual free radicals which propagate the reaction by allyl radicals. These are much less reactive, but still can abstract H and carry the reaction. Without a complete understanding of the reaction system, one cannot interpret the quantitative meaning of maximum propylene inhibition.

The Inhibition of the Pyrolysis of Acetone-d_6 by Cyclopentane.—The pyrolysis of 1:1 cyclopentane-acetone-d_6 mixtures at about 500° is most interesting since acetone pyrolysis is severely repressed by the cyclopentane. The methane/CO ratio is about two, showing that the acetone chain length is cut back to about unity. The rate of methyl attack on cyclopentane at 500° is about six times the rate of attack on acetone-d_6. At this temperature the cyclopentyl radical easily decomposes to ethylene and an allyl radical. The allyl radical, as discussed above, will attack cyclopentane and acetone-d_6, but more sluggishly than the methyl radical. As a result, the steady-state concentration of allyl radicals increases and radical-radical reactions (which quench the chain) become important. The acetonyl radical concentration is much reduced over its normal concentration in uninhibited acetone-d_6 pyrolysis because of the above effects. The acetonyl radical concentration is further reduced since this radical can stabilize itself readily by abstracting H from cyclopentane. For all of these reasons, the acetonyl steady-state concentration is reduced to a very low value. Thus the reaction

$$CD_2COCD_3 \longrightarrow CD_3 + CD_2CO \quad (18)$$

which accounts for the acetone chain is effectively suppressed.

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[8] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **79**, to be published.

CHINA LAKE, CAL.