550. *The Isomerization of Cyclopropane.*

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Evidence is adduced to suggest that trimethylene is not an intermediate in the isomerization of cyclopropane to propane.

For some time the thermal isomerization of cyclopropane to propene has been believed to proceed *via* a hydrogen-atom shift followed by a rupture of a carbon–carbon bond. The evidence for this mechanism rather than for one involving formation of trimethylene comes mainly from Slater's theoretical calculations as applied to the pressure at which the first-order rate constant for the isomerization begins to decrease.[1,2] However, Seubold [3] has developed arguments which suggest that the intermediate formation of trimethylene is possible. Work by McNesby and Gordon [4] on the isomerization of cyclopropane in the presence of deuterium has ruled out the possibility of the reaction's proceeding *via* a radical

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[1] Slater, *Proc. Roy. Soc.*, 1948, *A*, **194**, 112.

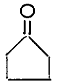
[2] Slater, *Proc. Roy. Soc.*, 1953, *A*, **218**, 224.

[3] Seubold, *J. Chem. Phys.*, 1954, **22**, 945.

[4] McNesby and Gordon, *J. Chem. Phys.*, 1956, **25**, 582.

chain. Rabinovitch and his co-workers,[5] as a result of work on the isomerization of dideuterocyclopropane, have recently revived the hypothesis of intermediate formation of trimethylene.

In order to obtain more experimental evidence three series of experiments were undertaken. In the first, cyclopentanone (2—9 mm.) was photolysed either alone or in the presence of a large excess of ethylene (700 mm.) at 25°, a Pyrex vessel and a medium-pressure mercury arc being used. The gaseous products were analysed by gas chromatography. In the absence of ethylene the products formed were mainly cyclobutane, ethylene, and carbon monoxide, in agreement with the work of Blacet and Miller.[6] Photolyses in the presence of ethylene gave also several hexene isomers and cyclohexane. Apparently, tetramethylene formed initially by the photolysis of the cyclopentanone can add to ethylene to give cyclohexane directly, or more probably to give hexamethylene which then cyclises to cyclohexane or isomerizes to a hexene.

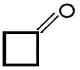


$$+ h\nu \longrightarrow CH_2\cdot[CH_2]_2\cdot CH_2 + CO \quad . . . . (1$$

$$CH_2\cdot[CH_2]_2\cdot CH_2 + C_2H_4 \longrightarrow CH_2\cdot[CH_2]_4\cdot CH_2 \quad . . . . (2)$$

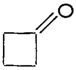
$$CH_2\cdot[CH_2]_4\cdot CH_2 \left\{ \begin{array}{ll} \longrightarrow \text{cyclohexane} & . . . . (3) \\ \longrightarrow \text{hexenes} & . . . . (4) \end{array} \right.$$

In a second series of experiments cyclobutanone (10—25 mm.) was photolysed at 100° either alone or in the presence of ethylene (500 mm.). A Pyrex reaction vessel and a medium-pressure mercury arc were again used. When photolysed alone cyclobutanone gave essentially the products reported by Blacet and Miller.[6] These authors suggested, because of the high yield of ethylene compared with the yield of carbon monoxide, that much of the cyclobutanone must decompose to ethylene and keten. In preliminary experiments to settle this point, cyclobutanone was photolysed in the presence of a large excess of n-butane. At relatively small percentage conversions (~2% of the cyclobutanone being photolysed) the presence of the n-butane did not affect the yield of products. When approximately 50% of the cyclobutanone was photolysed considerable quantities of n- and iso-pentane were produced. This is obviously due to the secondary photolysis of the keten formed from the cyclobutanone, yielding methylene, which then attacks the n-butane. The ratio of n- to iso-pentane was that expected for the attack of methylene produced from keten.[7,8] It is therefore quite certain that much of the cyclobutanone undergoes photolysis according to the reaction:



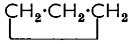
$$+ h\nu \longrightarrow CH_2{=}CH_2 + CH_2{=}CO \quad . . . . (5)$$

The other products of the photolysis of pure cyclobutanone (taken to small percentage decomposition) were those reported by Blacet and Miller,[6] namely carbon monoxide, cyclopropane, and propene. These products presumably arise from the reactions:



$$+ h\nu \longrightarrow CH_2\cdot CH_2\cdot CH_2\cdot CO \quad . . . . (6)$$

$$CH_2\cdot CH_2\cdot CH_2\cdot CO \longrightarrow CH_2\cdot CH_2\cdot CH_2 + CO \quad . . . . (7)$$



$$CH_2\cdot CH_2\cdot CH_2 \left\{ \begin{array}{ll} \longrightarrow CH_3\cdot CH{=}CH_2 & . . . . (8) \\ \longrightarrow \underbrace{CH_2\cdot CH_2\cdot CH_2} & . . . . (9) \end{array} \right.$$

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[5] Rabinovitch, Schlag, and Wiberg, *J. Chem. Phys.*, 1958, **28**, 504.
[6] Blacet and Miller, *J. Amer. Chem. Soc.*, 1957, **79**, 4327.
[7] Knox and Trotman-Dickenson, *Chem. and Ind.*, 1957, 731.
[8] Frey and Kistiakowsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6373.

Photolyses in the presence of a large excess of ethylene yielded, in addition to the products found in the absence of ethylene, the various five-carbon olefins. Pent-1-ene and 2-methylbut-1-ene were the major constituents of this group with smaller quantities of 2-methylbut-2-ene and *cis*- and *trans*-pent-2-ene. The total quantity of the five-carbon olefins indicated that approximately 8% of the trimethylene adds to the ethylene before it undergoes reactions (8) and (9). No cyclopentane was detected. Thus reactions (10)

$$CH_2{\cdot}CH_2{\cdot}CH_2 + C_2H_4 \longrightarrow CH_2{\cdot}[CH_2]_3{\cdot}CH_2 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (10)$$

$$CH_2{\cdot}[CH_2]_3{\cdot}CH_2 \longrightarrow C_5 \text{ olefins} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (11)$$

and (11) occur. It is rather surprising that the pentamethylene yields no cyclopentane, since it is clear from the experiments with cyclopentanone that hexamethylene gives some cyclohexane.

Besides the five-carbon olefins, the only gaseous products were small quantities of propane and n-hexane. The presence of both of these compounds suggests that some hydrogen abstraction by the trimethylene occurs to yield propyl radicals. Combination and disproportionation would then account for the hexane and propane.

In the third series of experiments, cyclopropane (a few mm.) was allowed to isomerize in the presence of a large excess of ethylene (1 atm.) at 475°. From the reactions of trimethylene formed in the photolysis of cyclobutanone, it was to be expected that if cyclopropane isomerized *via* trimethylene, then some pentenes would be formed. Blank experiments were performed with ethylene alone at 1 atm. pressure and at 475°. No compounds were formed from the cyclopropane–ethylene mixture that were not formed when ethylene alone was used. Further, although when ethylene was used alone small quantities of four-carbon and five-carbon olefins were produced, the relative amounts of these compounds did not increase when cyclopropane–ethylene mixtures were used; in particular the quantity of pent-1-ene did not increase. If trimethylene radicals were involved in the isomerization of cyclopropane then the results of the photolysis of cyclobutanone indicate that considerable quantities of pent-1-ene should have been formed.

While the temperatures in the photochemical and thermal decompositions differ considerably this should not invalidate the argument for the formation of five-carbon olefins in the thermal experiments. The cyclization or isomerization of trimethylene probably requires a very small energy of activation. In any case it will certainly be no greater than the energy of activation for its addition to ethylene, and is probably appreciably less than this. In these circumstances, if trimethylene were formed in the thermal isomerization, its rate of addition to ethylene at 475° compared with its rate of isomerization, would be greater than at 100°. It does not seem probable that the photochemically produced trimethylene is a " hot " radical, and in any case since radical additions to olefins have rather low " steric " factors this is not likely to have any appreciable effect.

The experiments described strongly suggest therefore that trimethylene is not an intermediate in the isomerization of cyclopropane to propene.

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