

Activated Cyclopropane from the Photolysis of Carbon Suboxide with Trimethylene Oxide

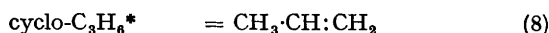
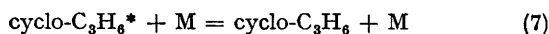
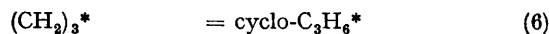
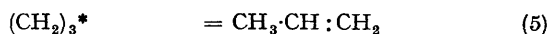
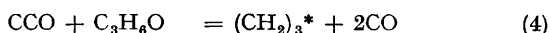
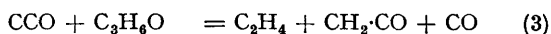
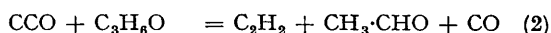
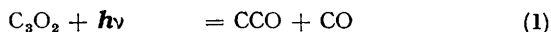
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A 10 : 1 MIXTURE of trimethylene oxide and carbon suboxide has been photolysed at 0°, in a quartz vessel with light from a medium pressure mercury arc with a filter to remove light of less than 2200 Å wavelength. From 20 to 134 torr the products of a novel series of reactions were ethylene, acetylene, propene, cyclopropane, and carbon monoxide. The yields of cyclopropane and propene were given by:

$$\frac{(\text{Propene} + \text{Cyclopropane})/\text{Cyclopropane}}{1.47 + 25.0/\text{Pressure (torr)}}$$

The following mechanism accounts for the products:



where the asterisk denotes a chemically activated molecule. The keten and acetaldehyde could not have been detected on our analysis system. If the collisions in (7) are strong we can write $k_7 = 1.6 \times 10^7 \text{ torr}^{-1}\text{sec.}^{-1}$, hence $k_8 = 2.7 \times 10^8 \text{ sec.}^{-1}$. This value is close to that found by Roquette¹ for the activated cyclopropane formed in the photolysis of tetrahydrofuran. Furthermore the proportion (68%) of cyclopropane in our products at infinite pressure is close to that (72%) found by Roquette. The $(\text{CH}_2)_3^*$ formed in reaction (4) and in the tetrahydrofuran photolysis is probably the trimethylene biradical. The energy content of the activated cyclopropanes calculated from the classical formula $k_8 = 10^{15.17} (1 - 65.0/E)^{(13-1)}$ is 89 kcal.mole⁻¹ in our case and 86 in that of Roquette. Within experimental error, this is the energy that is released by the combination of two

TABLE

| Source | Intermediate | $\left(\frac{\text{Propylene}}{\text{Cyclopropane}}\right)_{\infty}$ | E (kcal. mole ⁻¹) | $\log k_3$ (sec. ⁻¹) | Ref. |
|---|--|--|------------------------------------|-------------------------------------|-----------|
| Thermal reaction | Distorted molecule | 0.04 | 82 | 6.90 | 2 |
| CH ₃ + C ₂ H ₄ | Distorted molecule | 0.03 | 103 | 10.05 | 2 |
| CCO + C ₃ H ₆ O | ·CH ₂ -CH ₂ -CH ₂ · | 0.48 | 89 | 8.43 | This work |
| C ₄ H ₈ O + $h\nu$ | ·CH ₂ -CH ₂ -CH ₂ · | 0.40 | 86 | 7.78 | 1 |
| C ₄ H ₈ O + $h\nu$ (2600 Å) | ·CH ₂ -CH ₂ -CH ₂ · | 0.35 | 93 | 8.96 | 3 |
| C ₄ H ₈ O + $h\nu$ (3100 Å) | ·C ₃ H ₆ CO | 0.027 | 89 | 8.34 | 3 |

primary alkyl radicals. It is therefore the energy from the cyclization of trimethylene (though because of strain energy it is not the dissociation energy of the C-C bond in cyclopropane).

The (CH₂)₃* is different from any intermediate in the isomerisation of cyclopropane. Rabinovitch and co-workers² have argued that the activated complex is a strained and distorted cyclopropane. The difference is shown by studies of the isomerisation of 1,2-dideuterocyclopropane² in which the complex yields geometrical (to cyclopropane) and structural (to propene) isomers in the ratio of 12 : 1 for thermal reactions at 445° and 16 : 1 for activated reactions from methylene + ethylene.

The products of the photolysis of cyclobutanone

vary considerably with wavelength. We calculate that at 2600 Å the propene : cyclopropane ratio is 1 : 2.9 at infinite pressure indicating that the trimethylene biradical is an intermediate. The slightly higher energy content shown in the Table could have been inherited from the initial photolytic act. At 3100 Å the propene : cyclopropane ratio is 1 : 37. The ratio indicates that cyclopropane is formed directly, most probably from ·CH₂-CH₂-CH₂·CO, which could be comparatively long-lived when formed at the longer wavelength. The position is summarised in the Table.

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¹ B. C. Roquette, *J. Phys. Chem.*, 1966, **70**, 1334.

² B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *J. Amer. Chem. Soc.*, 1959, **81**, 1081; E. W. Schlag and B. S. Rabinovitch, *ibid.*, 1960, **82**, 5996.

³ Calculated by us from R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Canad. J. Chem.*, 1965, **43**, 1934.