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Activated Cyclopropane from the Photolysis of Carbon Suboxide with Trimethylene Oxide

By R. T. K. BAKER, J. A. KERR, and A. F. TROTMAN-DICKENSON (Edward Davies Chemical Laboratory, Aberystwyth, Cards.)

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:

(Propene + Cyclopropane)/Cyclopropane = 1.47 + 25.0/Pressure (torr).

The following mechanism accounts for the products:

 $C_{3}O_{2} + h\nu = CCO + CO \qquad (1)$

 $\mathrm{CCO} + \mathrm{C_3H_6O} \quad = \mathrm{C_2H_2} + \mathrm{CH_3}\text{-}\mathrm{CHO} + \mathrm{CO} \quad (2)$

 $CCO + C_3H_6O = C_2H_4 + CH_2 \cdot CO + CO \quad (3)$

$$CCO + C_3H_6O = (CH_2)_3^* + 2CO$$
 (4)

$$(CH_2)_3^* = CH_3 \cdot CH : CH_2$$
(5)

 $(CH_2)_3^* = cyclo-C_3H_6^*$ (6)

 $cyclo-C_{3}H_{6}^{*} + M = cyclo-C_{3}H_{6} + M$ (7)

$$cyclo-C_3H_6^* = CH_3 \cdot CH: CH_2$$
(8)

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 $k_7 = 1.6 \times 10^7$ torr⁻¹sec.⁻¹, hence $k_8 = 2.7 \times 10^8$ sec.⁻¹ This value is close to that found by Roquitte¹ 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 Roquitte. The $(CH_2)_3^*$ 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 $k_8 = 10^{15 \cdot 17} (1 - 65 \cdot 0/E)^{(13-1)}$ is 89 kcal.mole⁻¹ in our case and 86 in that of Roquitte. Within experimental error, this is the energy that is released by the combination of two

	IADLE			
Intermediate	$\left(\frac{\text{Propylene}}{\text{Cyclopropane}}\right)_{\infty}$	<i>E</i> (kcal. mole-1)	$\log k_8 (\sec^{-1})$	Ref.
Distorted molecule	0.04	82	6.90	2
Distorted molecule	0.03	103	10.05	2
·CH ₂ ·CH ₂ ·CH ₂ ·	0.48	89	8.43	This work
·CH, CH, CH,	0.40	86	7.78	1
·CH ₂ ·CH ₂ ·CH ₂ ·	0.35	93	8.96	3
·C ₈ H ₆ ĊO	0.027	89	8.34	3
	Intermediate Distorted molecule $CH_2 CH_2 CH_2$ $CH_2 CH_2 CH_2$ $CH_2 CH_2 CH_2$ $CH_2 CH_2 CH_2$ $CH_2 CH_2 CH_2$ $CH_2 CH_2 CH_2$	Intermediate $\left(\begin{array}{c} Propylene\\ \hline Cyclopropane \end{array} \right)_{\infty}$ Distorted molecule0.04Distorted molecule0.03·CH_2·CH_2·CH_2·0.48·CH_2·CH_2·CH_2·0.40·CH_2·CH_2·CH_2·0.35·CA_3H_6\dot{C}O0.027	Intermediate $\left(\begin{array}{c} Propylene\\ \hline Cyclopropane \end{array} \right)_{00}$ $E\\ (kcal. mole^{-1}) \end{array}$ Distorted molecule0.0482Distorted molecule0.03103.CH_2.CH_2.CH_2.0.4889.CH_2.CH_2.CH_2.0.4086.CH_2.CH_2.CH_2.0.3593.CA_3H_6CO0.02789	Intermediate $\left(\begin{array}{c} Propylene \\ \hline Cyclopropane \end{array} \right)_{\infty}$ E $\log h_3$ Distorted molecule0.04826.90Distorted molecule0.0310310.05·CH_2·CH_2·CH_2·0.48898.43·CH_2·CH_2·CH_2·0.40867.78·CH_2·CH_2·CH_2·0.35938.96·C_3H_6CO0.027898.34

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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 $(CH_2)_3^*$ 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 formed directly, mostprobably from is ·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. Roquitte, 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.