

Short Communication

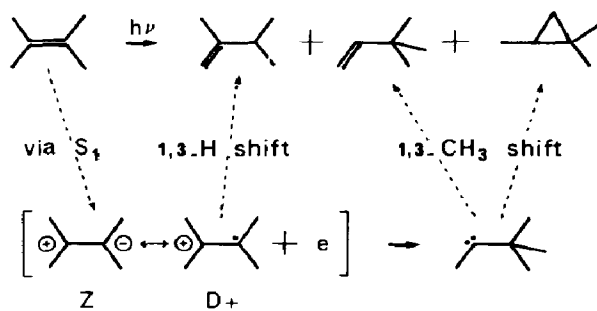
Is the vibrationally excited ground state involved in the gaseous photoisomerization of tetramethylethylene?

GUY J. COLLIN and HÉLÈNE DESLAURIERS

Département des Sciences Fondamentales, Université du Québec à Chicoutimi, Chicoutimi, Québec G7H 2B1 (Canada)

(Received June 26, 1984)

We have recently studied the photoisomerization of tetramethylethylene (TME) at 184.9 nm in the gas phase [1]. Similar isomerization has also been observed in the liquid phase [2] and it has been proposed that this isomerization is the result of an excited singlet state, or various singlet states, such as the $V(\pi, \pi^*)$ state or the Rydberg state $\pi, R(3s)$ [3, 4]:



Alternatively, the decomposition of the photoexcited molecule is an important process, at low pressure, giving rise to the formation of various light hydrocarbon compounds through $\beta(\text{C}-\text{H})$ and $\alpha(\text{C}-\text{C})$ bond ruptures [1]. These fragmentation processes are thought to be the result of the ground state with high vibrational energy content [5].

In order to throw more light on the processes involved, we have pyrolysed TME around 410 - 460 °C in a 125 cm³ Pyrex cell for a few minutes (about 1% transformation) (Table 1). Although this study demands more careful attention, it appears that isomers are also formed in a heated system. However, at least two isomers, namely 1,1,2-trimethylcyclopropane (1,1,2-TMCP) and 2-methyl-2-pentene (2-M-2-P), are not formed, contrary to what is observed in the 184.9 nm photolysis experiments. Thus, from this comparison, it can be said that the ground state with low vibrational energies is probably not involved in the photolytic mechanism. Of course, these results

TABLE 1

Formation of isomers in the pyrolysis and photolysis of tetramethylethylene^a

	<i>Relative yield of the following isomers^b</i>			
	<i>1,1,2-TMCP</i>	<i>3,3-DM-1-B</i>	<i>2,3-DM-1-B</i>	<i>2-M-2-P</i>
<i>Pyrolysis</i>				
430 °C	0.00	1.0	0.125	0.00
430 °C ^c	0.00	1.0	0.05	0.00
450 °C	0.00	1.0	0.07	0.00
<i>Photolysis^d</i>				
184.9 nm	4.0	1.0	1.0	2.0
213.8 nm	1.5	1.0	2.0	NM ^e

^a*P* ≈ 2 Torr; other light compounds are formed.^b1,1,2-TMCP, 1,1,2-trimethylcyclopropane; 3,3-DM-1-B, 3,3-dimethyl-1-butene; 2,3-DM-1-B, 2,3-dimethyl-1-butene; 2-M-2-P, 2-methyl-2-pentene.^cContains traces of oxygen.^dFrom ref. 1.^eNM, not measured.

do not preclude the possible involvement of the highly vibrationally excited ground state since it is known that at low excitation energy only a limited portion of the space phase is visited by the molecule, contrary to what is probably the case at high energy where almost all regions of the available energy phase space are explored [6].[†] IR multiphoton experiments would be pertinent in regard to this aspect.

Of course, the first suggestion, the one involving electronic excited states, is still relevant. From our previous results, at least two different states or sets of states must be involved [1]. One leads to the 1,3 hydrogen shift (a 1,2 double bond shift) [7] and the other to the formation of 3,3-dimethyl-1-butene (3,3-DM-1-B) and 1,1,2-TMCP through a carbene intermediate [3, 4]; the 1,1,2-TMCP-to-3,3-DM-1-B ratio is close to 4 in the photolysis of pure TME at any pressure between 1 and 32 Torr [1]. In the last case, the structure of the products formed also suggests that the excited 1,1,2-TMCP molecule may act as an intermediate. By using the same technique, we have pyrolysed this molecule (Table 2). The result is also evident: the low vibrationally excited ground state is not involved in the photolytic isomerization of TME, since 3,3-DM-1-B is not a product.

Finally, although triplet excited states are generally not assumed to take part in the photolytic mechanism of alkenes, it would be valuable to investigate this point. Both pyrolytic and photosensitized experiments of TME are now planned.

[†]One referee indicated that "the photochemistry could involve dynamic effects on the ground surface". If this is so, these effects lead to products different from those arising from thermal rearrangements.

TABLE 2

Formation of isomers in the pyrolysis of 1,1,2-trimethylcyclopropane^a

<i>T</i> (°C)	<i>Relative yield of the following isomers</i>			
	<i>TME</i>	<i>2,3-DM-1-B</i>	<i>3,3-DM-1-B</i>	<i>2-M-2-P</i>
400	1.0	0.32	0.00	0.43
420	1.0	1.0	0.00	1.17
468	1.0	0.23	0.00	0.38

^a*P* ≈ 2 Torr; other light compounds are formed.

Thanks are given to Professor J. Gawlowski (Warsaw University) for very helpful discussions.

- 1 G. J. Collin, H. Deslauriers and A. Więckowski, *J. Phys. Chem.*, **85** (1981) 944.
G. J. Collin and H. Deslauriers, *Can. J. Chem.*, **61** (1983) 1510.
- 2 P. J. Kropp, H. G. Fravel, Jr., and T. R. Fields, *J. Am. Chem. Soc.*, **98** (1976) 840.
- 3 P. J. Kropp, *Rep. ARO-12810-2*, 1978 (U.S. Army Research Office).
- 4 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA, 1978.
- 5 G. J. Collin and H. Deslauriers, *Int. J. Chem. Kinet.*, **12** (1980) 17.
- 6 R. Naaman, D. M. Lubman and R. N. Zare, *J. Mol. Struct.*, **59** (1980) 225.
- 7 Y. Inoue, T. Mukai and T. Hakushi, *Chem. Lett.*, (1983) 1665.