THE Hg6($^3P_1$) PHOTOSENSITIZED REACTIONS OF 1-METHYLCYCLOPENTENE

G. R. DE MARE, N. ANTHEUNIS, J. OLBREGTS and M. TERMONIA

Service de Chimie Physique Moléculaire, Faculté des Sciences, Université Libre de Bruxelles, 50 Av F. D. Roosevelt, B 1050 Brussels (Belgium)

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Summary

The major products of the Hg6($^3P_1$) photosensitized reaction of 1-methylcyclopentene at 24 °C are 1-methyl-1-vinylcyclopropane, isopropenylcyclopropane and methylcyclopentane. Two modes of quenching of the Hg6($^3P_1$) atoms are presumed to occur: quenching into the π-bond to form vibrationally excited triplet molecules and paraffinic type quenching into the C–H bonds of the molecule. The dependence of the quantum yields of the cyclopropanes on substrate pressure can be explained either by a simple concerted mechanism or by a more complex mechanism involving allylic C–C bond cleavage to form open chain biradicals. The results are compared with those from the mercury photosensitization of other olefins.

Introduction

The triplet mercury photosensitized ring contraction of cyclopentene to vinylcyclopropane was reported by Gibbons *et al.* [1] in 1962. This isomerization, which proceeds in the opposite direction to the thermal one (vinylcyclopropane $\overset{\Delta}{\rightarrow}$ cyclopentene) [2], is pressure dependent [3] and occurs with a relatively high quantum yield (0.24 at 30 Torr and 27 °C) [1]. Similar ring contractions to the valence tautomeric vinylcycloalkanes have been subsequently observed for cyclohexenes [4, 5] and cycloheptene [4, 6]. The quantum yields decrease with increasing complexity (substitution, ring size) of the cyclic olefin to the point where no vinylcyclohexane is obtained from the mercury sensitization of cyclo-octene [7, 8].

The present study on 1-methylcyclopentene was undertaken in an attempt to determine the nature and the magnitude of the effects of a methyl group in the 1-position on the mercury photosensitization of a cyclic olefin.

Experimental

The 1-methylcyclopentene (UCB) was purified by gas chromatography

(g.c.) on a propylene carbonate column. The purity of the 1-methylcyclopentene used for the quantum yield measurements was better than 99.5%. The major impurity, 0.3%, was an isomer of the substrate.

The experiments were performed in cylindrical quartz cells, 3.7 cm in diameter and either 1.7 (A) or 4.6 (B) cm long, fitted with Vycor windows. The 253.7 nm radiation source was a UVSL-15 mineralight lamp; the intensities at 253.7 nm were determined by butene-2 (100 Torr) actinometry [9]. The absorbed light intensity was corrected for Lorentz broadening of the mercury resonance line as described previously [4, 9].

The first product peak to elute from tricresyl phosphate (30% on Chromosorb P; 14 m), silicone oil (20% on Chromosorb P; 3 m) and propylene carbonate (30% on Chromosorb P naw; 9 m) columns was shown to be methylcyclopentane by comparison of its retention times with those of an authentic sample. Mass (parent m/e = 84), i.r. and n.m.r. spectra of the unknown were also in agreement with those of the reference.

The two isomers, 1-methyl-1-vinylcyclopropane and isopropenylcyclopropane were identified by their mass, i.r. and n.m.r. spectra. They could only be resolved from the 1-methylcyclopentene on the propylene carbonate column. The quantity of each C_6 product formed was calculated using the g.c. response for 1-methylcyclopentene.

Results and Discussion

The major products of the mercury photosensitization of 1-methyl-cyclopentene vapour at 24 ± 1 °C were methylcyclopentane, 1-methyl-1-vinylcyclopropane (I) and isopropenylcyclopropane (II). Hydrogen was also formed but its relative yields were not determined.

Three series of experiments were performed at 24 ± 1 °C.

(I). The quantum yields at a substrate pressure of 80 Torr in cell A were examined as a function of reaction time and are shown in Fig. 1. The quantum yields of the cyclopropanes were independent of, or decrease very slightly with, reaction time. This clearly showed that they were primary products. The methylcyclopentane quantum yield increased with increasing percentage of reaction. This behaviour, which was confirmed in experiments at 2 and 10 Torr, does not parallel that of cyclohexane from cyclohexene [4] or of methylcyclohexane from 3-methylcyclohexene [5]. This is a clear indication that secondary photosensitization of one or more of the products occurs with a high yield of atomic hydrogen in the present study.

(II). The effect of substrate pressure on the quantum yields of the C_6 products was investigated over the range 2 - 106 Torr in cell A (Fig. 2, open points; $I_0 = 1.14 ± 0.05 \times 10^{14}$ quanta/s). Because of the small size of cell A, i.e. the small amount of substrate, an excellent separation of the cyclopropanes from the substrate was obtained at all pressures.

(III). Experiments over the range 6 - 100 Torr were also performed in cell B (Fig. 2, solid points; $I_0 = 1.41 ± 0.05 \times 10^{14}$ quanta/s). The larger quantity of substrate may be expected to reduce the importance of second-
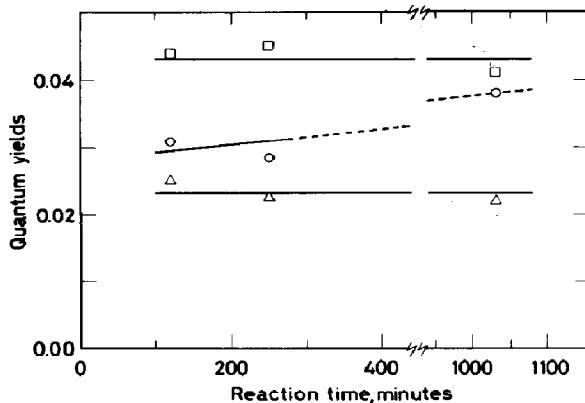
Fig. 1. Quantum yields of 1-methyl-1-vinylcyclopropane (□), isopropenylcyclopropane (△) and methylcyclopentane (○) as a function of reaction time for a substrate pressure of 80 Torr at 24 ± 1 °C. Cell A; I_0 = 1.14 ± 0.05 × 10^{14} quanta/s.
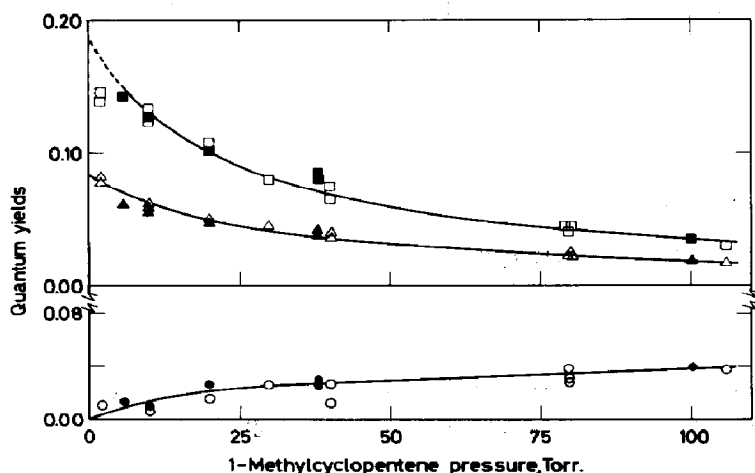

Fig. 2. Quantum yields of 1-methyl-1-vinylcyclopropane (□, ■), isopropenylcyclopropane (△, ▲) and methylcyclopentane (○, ●) as a function of substrate pressure at 24 ± 1 °C. □, △ and ○, cell A, I_0 = 1.14 ± 0.05 × 10^{14} quanta/s. ■, ▲ and ●, cell B, I_0 = 1.41 ± 0.05 × 10^{14} quanta/s. The curves for the cyclopropanes were calculated from eqns. (ii) and (iii).

ary reactions for equivalent percentages of reaction, providing that diffusion is rapid enough. Also, the longer pathlength reduces the adjustment necessary to correct the absorbed light intensity for Lorentz broadening. The results are within experimental error of those from series II.

Plots of the reciprocal of the quantum yields of the cyclopropanes *versus* substrate pressure, P, corresponding to the empirical equation:

$$\Phi^{-1} = A + BP \tag{i}$$

are shown in Fig. 3. Least squares of the points yield:

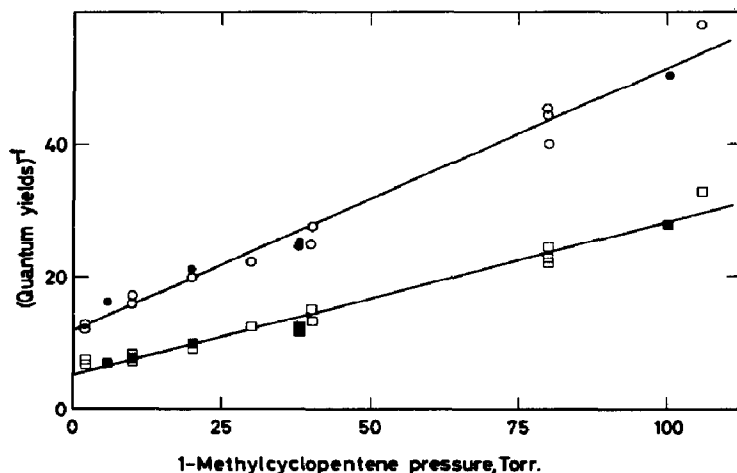$$(\Phi(\mathrm{I}))^{-1} = 5.30 + 0.2302P \tag{ii}$$

Fig. 3. Plots of the reciprocal of the quantum yields of 1-methyl-1-vinylcyclopropane (□, ■) and isopropenylcyclopropane (○, ●) *vs.* substrate pressure. The conditions are given in the legend of Fig. 2. Open points, cell A; solid points, cell B.
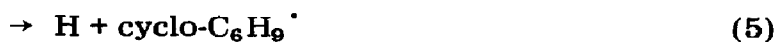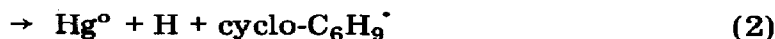
and

$$(\Phi(\text{II}))^{-1} = 11.96 + 0.3965P \qquad \text{(iii)}$$

The curves drawn in Fig. 2 for the cyclopropanes are obtained from eqns. (ii) and (iii).

Mechanism

The nature of the products and the dependence of the quantum yields on substrate pressure suggests that the mechanism could be quite simple:

$$\text{Hg}^\circ + h\nu(253.7 \text{ nm}) \rightarrow \text{Hg6}(^3\text{P}_1) \qquad I_a$$

$$\text{Hg6}(^3\text{P}_1) + \text{M} \qquad \rightarrow \text{Hg}^\circ + {}^3\text{M} \qquad (1)$$

$$\rightarrow \text{Hg}^\circ + \text{H} + \text{cyclo-C}_6\text{H}_9{}^\bullet \qquad (2)$$

$${}^3\text{M} \qquad \rightarrow \text{I}^* \rightsquigarrow \text{I} \qquad (3)$$

$$\rightarrow \text{II}^* \rightsquigarrow \text{II} \qquad (4)$$

$$\rightarrow \text{H} + \text{cyclo-C}_6\text{H}_9{}^\bullet \qquad (5)$$

$$\rightarrow \text{M}^* \qquad (6)$$

$$\text{M} + {}^3\text{M} \qquad \rightarrow 2\text{M} \qquad (7)$$

where $\text{Hg}^\circ = \text{Hg6}(^1\text{S}_0)$, M and ${}^3\text{M}$ are 1-methylcyclopentene in the ground and triplet states, respectively, and the asterisks indicate vibrational (or electronic) excitation which does not lead to reaction. Cyclo-C$_6$H$_9{}^\bullet$ represents all the radicals (α, β, etc.) which can be formed.

1-methyl-1-vinylcyclopropane and isopropenylcyclopropane

Steady state treatment of this concerted mechanism leads to the equations:

$$(\Phi(I))^{-1} = (ab/k_3) + (ak_7/k_3)[M] \qquad\qquad \text{(iv)}$$

and

$$(\Phi(II))^{-1} = (ab/k_4) + (ak_7/k_4)[M] \qquad\qquad \text{(v)}$$

where $a^{-1} = k_1/(k_1 + k_2)$ = the quantum yield of triplet 1-methylcyclopentene formation and $b = k_3 + k_4 + k_5 + k_6$, *i.e.* the sum of the rate constants of the monomolecular steps involving triplet 1-methylcyclopentene. Equations (iv) and (v) are of the same form as the empirical eqn. (i). Equations of exactly the same form can be obtained from a mechanism in which steps (3) and (4) are the formations of the allylic biradicals III and IV:

These steps are then followed by ring closure to the vibrationally excited cyclopropanes (which could be formed in their triplet states).

The ratios of the ordinate intersections and of the slopes of eqns. (ii) and (iii) are 0.443 and 0.580, respectively. From eqns. (iv) and (v) these ratios should both be equal to k_4/k_3, the ratio at which triplet 1-methylcyclopentene isomerizes to II compared to I (concerted) or to IV compared to III (biradical mechanism). The non-equivalence of the two ratios may be due to the necessity of collisional stabilization of the "hot" cyclopropanes (either concerted or biradical mechanism; the ratio of the slopes is the better approximation of k_4/k_3). In the case of a biradical mechanism, collisional deactivation of the biradicals III and IV to the substrate:

$$\text{III or IV} + M \rightarrow 2M \qquad\qquad \text{(vii)}$$

could also lead to a difference in the ratios and ratio of the ordinate intersections would be a better approximation of k_4/k_3. The data do not permit us to choose between the above possibilities.

Methylcyclopentane

The hydrogen atoms and the cyclo-$C_6H_9{}^\bullet$ radicals formed in steps (2) and (6) will ultimately lead to the formation of hydrogen, C_{12} products, methylcyclopentadiene and methylcyclopentane. Considering the increase in Φ(methylcyclopentane) with pressure, it is probable that paraffinic quenching (step 2) occurs with a quantum yield of about 0.1. This is roughly a factor of 3 to 10 times higher than the estimations for paraffinic quenching in cyclopentene, cyclohexene or 3-methylcyclohexene. Indeed, the quantum yield of cyclopentane from cyclopentene, which is 0.01 to 0.02 at 20 Torr, *decreases* with increasing pressure [3]. Thus the enhanced occurrence of paraffinic type quenching in the present study must be a consequence of the presence of the methyl group in the 1-position (see Table 1).

TABLE 1

Comparison of the quantum yields of various processes in the Hg6($^3P_1$) photosensitization of olefins

Olefin	Quantum yields[a]				Intersystem crossing[b]	References
	Paraffinic quenching	Retro Diels–Alder	Ring contraction to vinylcycloalkanes	Other products		
Ethylene	—	—	—	~1.0 [c]	0.0	10
Cyclopentene	~0.02	—	0.35	—	0.6	3
1-Methylcyclopentene	~0.12	—	0.3	—	0.6	This work
Cyclohexene	~0.03	~0.2	0.06	—	0.7	4
3-Methylcyclohexene	~0.04	~0.04	0.05	—	0.8$_5$	5
Cycloheptene	—	—	>0.05$_4$	>0.11 [d]	<0.83	5†
Cyclo-octene	—	—	~0	—	—	7, 8
Methylenecyclopropane[e]	—	—	—	~0.1	~0.9	11
Methylenecyclobutane[e]	—	—	—	~1.0	~0 [f]	11, 12
Methylenecyclopentane[e]	—	—	—	<0.1	>0.9	11

[a] Obtained by extrapolation of the data to zero or infinite pressure (excited molecule or paraffinic type quenching, resp.). Φ(paraffinic quenching) = 4 × Φ(cycloalkane, same ring size) at high pressure.

[b] This is equal to the photons unaccounted for and is an upper limit for non-collisionally induced intersystem crossing (except for methylenecyclopentane).

[c] The yields of C_{10} compounds [3] seem to be abnormally high.

[d] Numerous products.

[e] These exocyclic olefins are included to demonstrate the effect of the absence or presence of a facile decomposition to molecular products on the apparent intersystem crossing yield.

[f] One could argue that the decomposition to ethylene and allene occurs from the vibrationally excited ground state after intersystem crossing.

† The quantum yields for the ring contraction to vinylcyclopentane (0.054) and for the other products (0.11) are from ref. [6]. The pressure at which these apply was not specified. These yields are considerably higher than those determined by De Maré (unpublished work) for cycloheptene pressures of 20 to 30 Torr. In De Maré's experiments the quantum yield of cycloheptene dimerization (or polymerization) was quite high (~0.15).

Intersystem crossing

Extrapolation of the quantum yields of the cyclopropanes to zero pressure should give the maximum yield of the biradicals formed (or of the triplet 1-methylcyclopentene which isomerize to the cyclopropanes in a concerted mechanism). This gives Φ_{max} (I or III) = 0.19 and Φ_{max} (II or IV) = 0.08. Combining these values with the estimated quantum yield of step (2), one calculates that two-thirds of the triplet 1-methylcyclopentene molecules always return to the ground state without requiring collisional stabilization (step 7). The occurrence of such intersystem crossing to the ground state is a general phenomenon in mercury photosensitization of cyclic olefins (see Table 1).

Conclusions

The formation of 1-methyl-1-vinyl- and isopropenyl-cyclopropane in the mercury photosensitization of 1-methylcyclopentene can be accounted for either by direct isomerization of the triplet 1-methylcyclopentene or by the intermediate of allylic biradicals. Paraffinic type quenching is more important, ($\Phi \sim 0.1$), than in other cyclic olefin sensitizations, presumably because of the methyl group in the 1-position. Intersystem crossing to the ground state, not induced by collisions, occurs for every two out of three triplet 1-methylcyclopentene molecules.

Acknowledgements

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