The Formation of Excited Singlet Species in the Mercury 6(^{3}P$_1$) Photosensitized Decomposition of Cyclobutanone[1]

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Abstract: The photosensitized decomposition of cyclobutanone is used to evaluate the contribution of excited singlet species following Hg 6(^{3}P$_1$) photosensitization; 10.5% of the products arise from a singlet pathway. The pressure dependences of the intramolecular hydrocarbon products ethylene, cyclopropane, and propylene have been determined over the range 0.3–20 Torr. Stern–Volmer plots of quenching *vs.* cyclopentene show that the products arise almost exclusively from the mercury-sensitized pathway. An estimate of about 105 ± 2 kcal/mole is made for the average energy transferred to the cyclobutanone molecule from the excited mercury atom. The results are compared to those obtained from the mercury-photosensitized decomposition of ketene, for which an appreciable singlet contribution (13 ± 2%) has also been reported.

The photochemical decomposition of cyclobutanone, induced by direct light absorption, has been the subject of extensive study for more than 25 years. The results of these investigations have laid the foundations for an understanding of the fundamental mechanistic pathways by which the major products of the reaction, cyclopropane, propylene, ethylene, ketene, and carbon monoxide, arise.[2] In particular, use of the benzene photosensitization technique has demonstrated the involvement of both singlet and triplet species in the decomposition,[3] and more recently a study of the influence of various inert gases on the product quantum yields has defined more precisely the individual role played by each excited intermediate.[4,5] It is now believed that following the initial photon absorption process causing excitation to the first excited singlet state, S_1^*, either intersystem crossing to the triplet state, T_1^*, or internal conversion to a highly vibrationally excited ground state, S_0^*, occurs. The C_2 products arise from the latter species, whereas the sole primary hydrocarbon product from the excited triplet T_1^* is vibrationally excited cyclopropane. The "hot" cyclopropane can then either isomerize to propylene or be collisionally deactivated. Thus decomposition of cyclobutanone induced by energy transfer from triplet sensitizers might be anticipated to yield only C_3 compounds as products. This is indeed the case for sensitization by benzene in the ($^3B_{1u}$) state.[3]

Our recent experiments on the Hg 6(^{3}P$_1$) photosensitized decomposition of ketene have indicated that the methylene formed is not solely triplet in nature, but contains 13 ± 2% of singlet component.[6] We have now

used the cyclobutanone system as a clean monitoring reaction for another determination of the triplet–singlet contribution from Hg 6(^{3}P$_1$) photosensitization. The results of our experiments, carried out over a pressure range from 0.3 to 20 Torr, have again shown an appreciable (10.5%) singlet component.

Experimental Section

Cyclobutanone, manufactured by Chemical Procurement Laboratories Inc., was kindly supplied by Dr. E. K. C. Lee of this department. It was used without purification other than thoroughly degassing *in vacuo.* Cyclopentene, obtained from the Aldrich Chemical Co., showed no detectable impurities by gas chromatographic analysis.

Samples were made up in Pyrex ampoules on a mercury and grease-free metal vacuum line fitted with both brass and Monel bellows valves utilizing Kel-F seals. Gas pressures were measured on a Model FA-141 Wallace-Tiernan Inc. mechanical dial manometer. The sealed ampoules were then attached to a second vacuum system (Pyrex, greaseless Springham Viton A diaphragm valves), and broken open while being cooled at −196°; the contents were subsequently transferred to the cylindrical photolysis cell. The cell, constructed of quartz throughout with an optically flat 45-mm o.d. end window, had a volume of 285 ml and an optical path length of approximately 19.5 cm. It was closed by a Springham greaseless valve fitted with a Viton A diaphragm. No problems were encountered with absorption of reactant materials into the diaphragm, and a few runs carried out in a quartz cell of almost identical dimensions, but equipped with a Teflon needle valve, gave results that were identical within experimental error. Mercury vapor was supplied by a small mercury droplet contained within the cell.

All photolyses were carried out at room temperature (24 ± 1°) using a low-pressure mercury resonance grid lamp (Mineralight R-51, UV Products, Inc.). The 2537-Å region of the arc was isolated by a Corning CS-7-54 filter and a 1.0-cm thick aqueous filter solution of 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate.[7] Care was taken to ensure that photolytic runs were only carried out under conditions of constant light intensity, and to this end an RCA 935 phototube was frequently used to monitor the lamp emission intensity.

Analysis of the photolysis mixtures was carried out on a 50 ft × 0.25 in. column containing 35% w/w dimethylsulfolane on Chromosorb P-HMDS, fitted to a conventional gas chromatograph equipped with a thermistor detector. The thermal conductivity response constants of this detector for the three hydrocarbon products ethylene, propylene, and cyclopropane were 1.0, 1.278, and 1.254, respectively. At room temperature and with a helium carrier gas flow rate of 0.5 ml/sec, the retention times of these compounds were 18.5 (C_2H_4), 35 (C_3H_6), and 62 min (c-C_3H_6). The analysis of cyclobutanone, ketene, and carbon monoxide was not necessary for the present work and was therefore not attempted.

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Results and Discussion

Pressure Effects. The room-temperature Hg $6(^3P_1)$ sensitized decomposition of cyclobutanone was studied in the pressure range 0.3–20.0 Torr. The relative yields of the hydrocarbon products, expressed as a percentage of the total intramolecular hydrocarbon product yield, are shown in Table I. The percentage

Table I. Pressure Dependence of Product Yields[a]

Pressure, Torr	% C_2H_4 (±0.5)	% C_3H_6 (±0.4)	% c-C_3H_6 (±0.4)
0.316	11.4	62.7	25.9
0.631	10.5	60.7	28.9
1.26	11.0	56.5	32.5
2.50	10.8	51.1	38.1
5.00	10.7	43.1	46.2
9.99	10.3	33.5	56.2
10.1	10.9	33.0	56.1
11.7[b]	11.5	30.0	58.5
20.0	10.9	23.5	65.6

[a] Expressed as a percentage of the total intramolecular hydrocarbon yield. [b] Oxygen scavenged; cyclobutanone, 10.1 Torr; oxygen, 1.6 Torr.

yields of ethylene (10.8 ± 0.5%) and the C_3 products, ΣC_3 (89.2 ± 0.5%), remain constant throughout the entire pressure range of the study. However, the relative yield of cyclopropane to propylene shows a marked pressure dependence. Experiments were also performed in which 1–2 Torr of oxygen was added as a monoradical scavenger. As shown in Table I the percentage yields of the products were the same within experimental error as those obtained by interpolation for nonoxygen-scavenged photolyses at the same pressure, thereby indicating the intramolecular nature of the pathways leading to the initial formation and subsequent isomerization of one of these products.

Cyclobutanone–Cyclopentene Competition Experiments. In order to elucidate further the mechanism by which ethylene is formed in these photolyses, experiments were carried out in which cyclopentene competes with the cyclobutanone as a quencher of excited mercury atoms. Under our reaction conditions none of the ketone reaction products is formed from the Hg $6(^3P_1)$ sensitized decomposition of this olefin. In these photolyses the pressure of cyclobutanone was constant at 10.1 Torr, and the cyclopentene to cyclobutanone ratio varied from zero to 1.50. Lee, et al., have shown that pressure quenching by olefins of excited cyclobutanone molecules in the S_0^* state only becomes important at pressures of several hundred Torr.[4,5] Furthermore no quenching of either the S_1^* or T_1^* states was observed. Thus even at the highest pressure used in our experiments (25.2 Torr), essentially no collisional deactivation of excited cyclobutanone occurs.

A simple kinetic analysis of the reaction system shows that a familiar Stern–Volmer linear relationship should express the dependence of the relative quantum yields of the ΣC_3 product formation on the olefin/ketone ratio for photolyses carried out under identical irradiation conditions. The experimental results are displayed in Table II and show that the absolute yields decrease with increasing quencher/ketone ratio and the predicted inverse linear relationship obeyed, for both the ΣC_3 products and ethylene, indicating in each case formation by
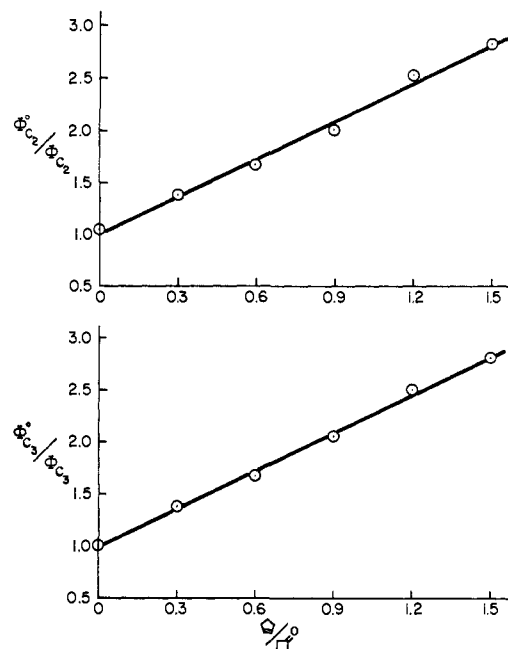

Figure 1. The mercury photosensitization relative quantum yield of ethylene vs. the ratio of cyclopentene to cyclobutanone (upper part). The mercury photosensitization relative quantum yield of the ΣC_3 products vs. the ratio of cyclopentene to cyclobutanone (lower part).

pathways involving sensitization by excited mercury atoms. The relative rates of Hg $6(^3P_1)$ quenching by cyclobutanone and by cyclopentene derived from Stern–Volmer plots are 1.0 (C_2H_4) and 0.85 (ΣC_3). We interpret the inequality of these values as being due to the minor but not negligible contribution to product formation from cyclobutanone excited by direct light absorption. The observed product yields can be corrected for this minor pathway using the data of Denschlag and Lee on the wavelength dependence of the product distribution in the direct photolysis.[3] They

Table II. Product Yield Data for the Hg $6(^3P_1)$ Sensitized Decomposition of Cyclobutanone–Cyclopentene Mixtures

Total pressure, Torr	10.09	13.12	16.14	19.19	22.20	25.22
Cyclopentane/cyclobutanone	0.00	0.30	0.60	0.90	1.20	1.50
$[\Phi_{C_2}{}^0/\Phi_{C_2}]$[a]	1.03	1.35	1.60	1.89	2.31	2.55
$[\Phi_{C_3}{}^0/\Phi_{C_3}]$[a]	1.01	1.37	1.65	2.03	2.46	2.76
% C_2H_4[a] (±0.5)	10.9	11.2	11.4	11.8	11.7	11.9
% C_3H_6[a] (±0.4)	33.0	29.3	25.7	23.3	23.0	20.0
% c-C_3H_6[a] (±0.4)	56.1	59.5	62.9	64.9	65.3	68.1
$[\Phi_{C_2}{}^0/\Phi_{C_2}]$[b]	1.04	1.38	1.67	2.01	2.53	2.84
$[\Phi_{C_3}{}^0/\Phi_{C_3}]$[b]	1.02	1.38	1.67	2.05	2.50	2.81
% C_2H_4[b]	10.3	10.5	10.5	10.7	10.4	10.4

[a] Calculated from the experimentally observed product yields. [b] Calculated from the corrected product yields assuming a direct photolysis contribution of 1.2% to the observed total yield.

find that at 2537 Å the value of the ratio $[C_3H_6 + c$-$C_3H_6]/[C_2H_4]$ is 0.785. Using this figure the experimental product yields have been corrected for various arbitrary fractions of direct photolysis and further Stern–Volmer plots constructed. The slopes of the ΣC_3 and C_2H_4 plots become identical for an assumed direct photolysis contribution of 1.2% as shown in Figure 1. The value of 0.83 thus obtained for the ratio

of the quenching efficiencies of Hg 6(^{3}P$_1$) atoms by cyclobutanone and cyclopentene is of a magnitude consistent with that expected from a consideration of the quenching efficiencies for various other olefins and ketones.[8] Furthermore correction of the data in this manner for 1.2% direct photolysis results in a constant value of 10.5 ± 0.2% for the corrected percentage of ethylene in each run.

Triplet Mechanism. In accord with the generally accepted mechanism for cyclobutanone photolysis, we interpret the pressure dependence of the C$_3$ products as resulting from the competitive collisional stabilization and decomposition of vibrationally excited cyclopropane formed from the T$_1$* state. A crude RRKM calculation using the semiclassical statistical approximation method of Rabinovitch, et al.,[9] shows that the experimental decomposition/stabilization ratio (D/S) for excited cyclopropane can be explained if the internal excitation energy, E, of the cyclopropane is approximately 75 ± 5 kcal/mole. A more exact treatment is precluded, however, by the broad internal energy distribution of the cyclopropane, resulting not only from the energy partitioning in the initial decomposition of cyclobutanone,[2g] but also from the probable spread in energies transferred in the sensitization process. The variation of the product ratio of propylene to cyclopropane at a pressure of 9.5–11.0 Torr with the initial excitation energy of the cyclobutanone molecule, measured by Denschlag and Lee,[3] enables an estimate of the average energy transferred from the excited mercury atom in the triplet sensitization process to be made. Our propylene/cyclopropane ratio of 0.58 at 10.5 Torr leads to a value of approximately 105 ± 2 kcal/mole. The D/S ratio for excited cyclopropane is relatively sensitive to changes in the excitation energy at this pressure. Thus if the entire Hg 6(^{3}P$_1$) electronic excitation energy

of 112.7 kcal/mole were to have been transferred, the resulting D/S ratio would have been 1.08.

Singlet Mechanism. Singlet Species from Hg 6(^{3}P$_1$). The quenching data indicate unambiguously that ethylene (and presumably ketene) are products of a sensitization process. In view of the fact that there is no evidence to suggest that the excited triplet of cyclobutanone can decompose to products other than vibrationally excited cyclopropane at all direct photolysis excitation energies (89.9–115.3 kcal/mole) and also at the lower energy of the triplet benzene photosensitized decomposition, it would appear unlikely that such a triplet species would be the precursor of ethylene in this system. By analogy with the previously studied systems we propose that the intermediate involved is the highly vibrationally excited ground-state singlet, S$_0$*. The mechanistic pathways leading to its formation are, however, open to speculation. One possible mode for its production is via intersystem crossing from the T$_1$* state either directly or through the intermediacy of the S$_1$*. While such processes do not occur in benzene photosensitization, they could conceivably become important at the higher energies of mercury photosensitization. An alternative postulate is that an excited singlet state of cyclobutanone is produced via exciplex[10] formation in the sensitization process.

The formation of products in this system, characteristic of excited singlet-state precursors to the extent of 10.5%, is analogous to the similar behavior observed in the Hg 6(^{3}P$_1$) photosensitized decomposition of ketene, in which it is believed that 13 ± 2% of the methylene is produced in the singlet state.[6] The production of ^{1}CH$_2$ in this latter system, primarily via a sensitization pathway, strongly supports the postulate that excited singlet states are produced in the cyclobutanone system. Finally it may be concluded that the apparent formation of excited singlet species in these two mercury–carbonyl systems indicates that the participation of similar excited singlets in other systems of this type cannot necessarily be ruled out.

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