

# PRIMARY QUANTUM EFFICIENCIES IN THE REACTION OF CYCLOPENTANE WITH MERCURY $6(^3P_1)$ ATOMS<sup>1</sup>

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## ABSTRACT

An investigation has been made of the reaction of cyclopentane with Hg  $6(^3P_1)$  atoms at a substrate pressure of 107 mm, under static conditions at 24° C. Low light intensities were used in order to minimize secondary reactions.

The products of the reaction, for small extents of decomposition, have been shown to be exclusively hydrogen, bicyclopentyl, and cyclopentene. With increasing duration of exposure, the cyclopentene-to-cyclopentane ratio achieves a steady-state value of  $5.7 \times 10^{-3}$ . Furthermore, it has been found that the same ratio is ultimately reached, upon prolonged exposure of a substrate initially containing cyclopentene at a concentration higher than the steady-state value. In the runs with added cyclopentene, a fourth product appeared in measurable quantities. Its molecular weight corresponded to the formula,  $C_{10}H_{16}$ , and it was assumed to be a cyclopentyl cyclopentene. The same compound appears in extensive decomposition of the pure substrate.

The addition of small amounts of nitric oxide was found to have a marked inhibiting effect on the reaction. Bicyclopentyl formation was completely suppressed when 0.7 mole% of nitric oxide was present; and the cyclopentene yield was reduced to one-fifth of its value for the pure substrate, by adding 0.98 mole% of nitric oxide.

In order to obtain primary quantum yields for the reaction, a series of runs were performed of 1 to 33 minutes in duration, with a cyclopentane which had been purified by gas-liquid chromatography. By a short extrapolation of the mean quantum yields of product formation to zero extent of reaction, it was found that the primary quantum yields for hydrogen, bicyclopentyl, and cyclopentene were respectively 0.8, 0.4, and 0.4.

On the basis of a simple four-step paraffinic mechanism, taken in conjunction with the primary quantum yield data, it is concluded that the reaction has a primary quantum yield of substrate decomposition of 0.8, and that cyclopentyl radicals have the same rates for disproportionation and recombination at 24° C.

## INTRODUCTION

In two previous investigations (1, 2) of the reaction of cyclopentane vapor with Hg  $6(^3P_1)$  atoms, under static conditions, at 30° C, it was shown that the primary process involves scission of the C—H bond with formation of cyclopentyl radicals and H atoms. The products of the reaction were found to be hydrogen, bicyclopentyl, and cyclopentene. In the more recent of the two studies (2), limiting quantum yield values, at high substrate pressures, were used, in conjunction with a simple paraffinic free radical mechanism, to obtain values of 0.49 for the primary quantum yield, and 5.3 for the ratio of the rates of recombination to disproportionation for cyclopentyl radicals. The results reported in this paper represent the first phase in a study of the reaction as a function of temperature. In order to obtain more direct values for the primary quantum yields, the reaction has been studied at small extents of decomposition and low light intensities. The details of the investigation follow.

## EXPERIMENTAL

The experiments were performed in cylindrical, fused, quartz reaction cells, 10 cm in length and 5 cm in diameter. For each run a breakseal, product trap, and filling tube were connected to the stem of the reaction cell. The product trap consisted of a short length of 7 mm O.D. tubing, with a constriction to facilitate removal by flame-cutting. In order to introduce the cyclopentane vapor, the cell was connected via the filling tube,

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of 3 mm I.D. capillary, to the vacuum manifold, and pumped down to at least  $10^{-3}$   $\mu$ . Mercury vapor for the reaction was supplied by placing several drops of mercury in a small depression in the connecting tube of the product trap. In all runs the cell was filled with cyclopentane vapor at a pressure of 107 mm, by placing an ice bath around the reservoir of liquid cyclopentane. After being filled, the cell was flame-cut from the manifold and placed in an oven which was maintained at  $24 \pm 0.5^\circ$  C, for the present series of runs.

The 2537- $\text{\AA}$  resonance radiation was supplied by a Hanovia, Sc-2537 source, which was wound in the form of a five-turn helix. The lamp was rigidly positioned with respect to the cell, in order to assure constant light input. The oven was provided with a filter of Vycor, 7910 glass, to prevent 1849- $\text{\AA}$  radiation from entering the cell.

At the end of each run, products condensable in liquid nitrogen were frozen into the product trap. In order to assure that high-boiling products were quantitatively transferred to the trap, the remainder of the cell was heated to  $250^\circ$  C during the transfer process. By connecting the cell, via its breakseal, to an analytical system, the non-condensable gases could be transferred, by means of a Toepler pump, to a gas burette. The hydrogen was determined by standard procedures involving combustion over heated copper oxide at  $250^\circ$  C.

The product trap, containing the condensable products, was flame-cut from the cell, and placed in a 4-in. length of 3/8-in. copper tubing, which, in turn fitted into a special sample-insertion device. This device was provided with double-compression fittings, a thumbscrew for shattering the product trap, and a preheater.

The sample-insertion device was placed in series with the hydrogen gas stream to a special gas-liquid chromatographic (G.L.C.) unit. The katharometer was of the Gow-Mac, T/C type, with temperature regulation. Ten-foot chromatographic columns were used, containing 30-60 mesh, silica gel. The analyses were made with the katharometer at  $106^\circ$  C.

The cyclopentane and cyclopentene used were Phillips, Research Grade (P.R.G.). G.L.C. analysis of the cyclopentane showed that the only impurity was 0.051 mole% of cyclopentene. For one series of runs at low conversion, the cyclopentane was further purified by isolating the G.L.C. fraction. This sample showed no detectable impurities. It is estimated that the purity was at least 99.999 mole%. The nitric oxide used was Matheson, C.P. grade, of 99 mole% purity. The gas was further purified by trap-to-trap distillation.

## RESULTS

In order to minimize complexities associated with the localized build-up of products in the reaction zone, the runs were carried out at a low absorbed light intensity. By using propane as an actinometer (3), the absorbed light intensity was found to be  $3.75 \pm 0.05 \times 10^{-7}$  einstein/minute. All quantum yields reported here are based on this light intensity.

In Fig. 1, the relations are shown between product yield and duration of exposure, for a series of runs with P.R.G. cyclopentane. The cyclopentene yields were corrected for the small amount of cyclopentene present initially in the substrate. From the graph, it is apparent that the rate of bicyclopentyl production is constant throughout the range of duration of exposure studied. For hydrogen production, there is a slight indication of a decreased rate in the runs of long duration. The fact that cyclopentene achieves a steady-state concentration after approximately 120 minutes of exposure is shown clearly in

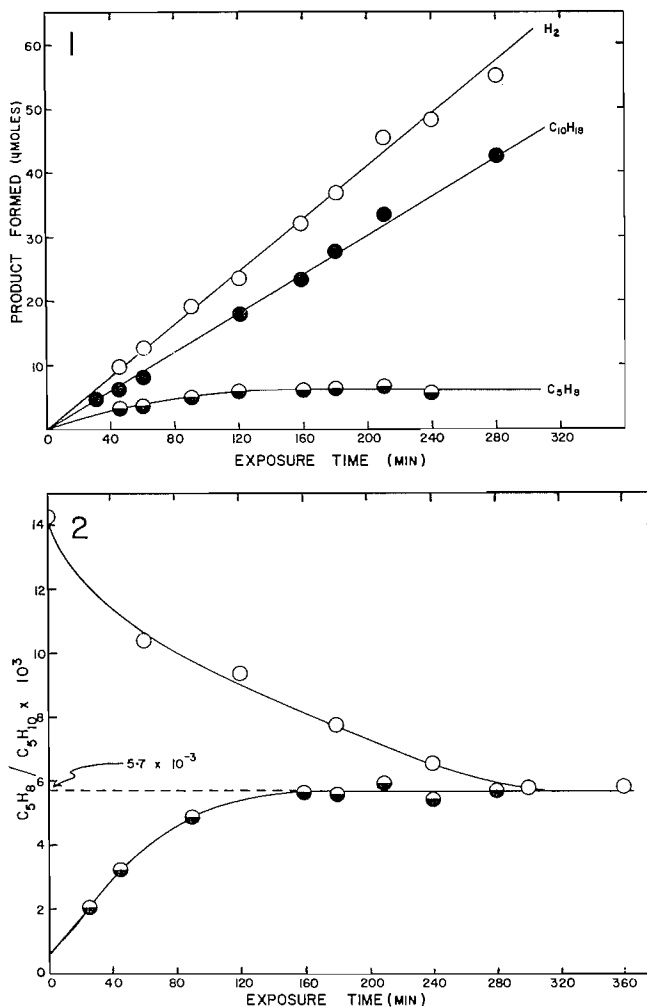


FIG. 1. Yields, in micromoles, for hydrogen, bicyclopentyl, and cyclopentene vs. exposure time in the mercury-photosensitized decomposition of Phillips, Research Grade (P.R.G.) cyclopentane.

FIG. 2. The change in the cyclopentene-to-cyclopentane ratio with increasing exposure time in the mercury-photosensitized decomposition of cyclopentane: ● P.R.G. cyclopentane, ○ cyclopentane containing 1.43 mole% of cyclopentene.

Fig. 1. In the runs exceeding about 200 minutes in duration, small amounts of a fourth product were detected in the G.L.C. analyses. This product is discussed in more detail below.

The lower curve in Fig. 2 shows the behavior of the cyclopentene-to-cyclopentane ratio, as a function of exposure time, for P.R.G. cyclopentane. The steady-state value for the  $(C_5H_8)/(C_5H_{10})$  ratio was found to be  $5.7 \pm 0.1 \times 10^{-3}$ . In order to determine whether the same steady-state would be achieved with added cyclopentene, a series of runs were done with a sample of cyclopentane for which the  $(C_5H_8)/(C_5H_{10})$  ratio was initially  $14.3 \times 10^{-3}$ . It can be seen from the upper curve in Fig. 2 that the same steady-state value is ultimately reached, as with the P.R.G. cyclopentane.

In the runs with added cyclopentene, it was noted that a fourth product appeared in

measurable quantities. In the G.L.C. analysis, the retention time for this product was identical with that of the minor peak obtained in runs of long duration with the P.R.G. substrate. The product was isolated, and a parent-peak determination was made on a mass spectrometer. The molecular weight corresponded to the formula  $C_{10}H_{16}$ . It was concluded that the product was likely a cyclopentyl cyclopentene. On the assumption that the  $C_{10}H_{16}$  product had the same sensitivity as bicyclopentyl (4), the  $(C_{10}H_{16})/(C_5H_{10})$  ratio could be estimated. These values, together with the  $(C_5H_8)/(C_5H_{10})$  ratios, are given in Table I, for the runs with added cyclopentene. It can be seen from the table that the  $(C_{10}H_{16})/(C_5H_{10})$  ratio reaches a steady-state value of  $1.6 \pm 0.1 \times 10^{-3}$ . It should further be noted that the  $C_{10}H_{16}$  product and cyclopentene reach their respective steady-state concentrations in essentially the same period of time.

TABLE I  
Quantum yields and steady-state concentrations for runs with added cyclopentene\*

| Exp. time,<br>minutes | Quantum yields |                |                | $(C_5H_8)/(C_5H_{10})$<br>$\times 10^3$ | $(C_{10}H_{16})/(C_5H_{10})$<br>$\times 10^3$ |
|-----------------------|----------------|----------------|----------------|---|---|
|                       | $C_5H_8$       | $C_{10}H_{16}$ | $C_{10}H_{16}$ |   |   |
| 0                     |                |                |                | 14.3                                    |   |
| 60                    | -0.173         | 0.37           | 0.016          | 10.4                                    | 0.28  |
| 120                   | -0.116         | 0.40           | —              | 9.4                                     | —   |
| 180                   | -0.124         | 0.46           | —              | 7.7                                     | —   |
| 240                   | -0.114         | 0.35           | —              | 6.5                                     | —   |
| 300                   | -0.090         | 0.43           | 0.015          | 5.8                                     | 1.3   |
| 360                   | -0.076         | 0.40           | 0.014          | 5.8                                     | 1.6   |
| 420                   | -0.065         | 0.36           | 0.013          | 5.8                                     | 1.6   |
| 420                   | —              | 0.38           | 0.011          | —                                       | 1.6   |

\*Initial cyclopentane pressure = 107 mm. Absorbed light intensity =  $3.75 \times 10^{-7}$  einstein/minute.

The data in Table I also show clearly that the quantum yield of bicyclopentyl formation is invariant in exposure time at  $0.39 \pm 0.03$ .

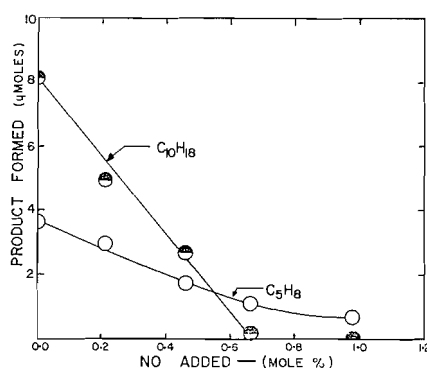


FIG. 3. The effect of added nitric oxide on the yields, in micromoles, of bicyclopentyl, and cyclopentene for 1-hour runs in the mercury-photosensitized decomposition of P.R.G. cyclopentane.

In Fig. 3 the effect is shown of the addition of small amounts of nitric oxide on the yields of cyclopentene and bicyclopentyl. The data are for 1-hour runs. The results demonstrate rather strikingly the free radical nature of the reaction. With 0.7% nitric oxide present, no bicyclopentyl is formed. With 0.98% added nitric oxide, the cyclopentene yield is reduced to 18% of its value for the pure substrate. In the 1-hour run,

with 0.98% nitric oxide, the total yield of cyclopentene was only 0.66  $\mu$ mole. This small value is liable to considerable error, since correction must be made for the cyclopentene present in the P.R.G. substrate, apart from the inherent error in the determination. It can be concluded that the presence of approximately 1% nitric oxide completely inhibits bicyclopentyl formation, and reduces the cyclopentene yield to a very low value.

In Fig. 4, the mean quantum yields for the formation of hydrogen, bicyclopentyl, and cyclopentene are shown as a function of the exposure time, for P.R.G. cyclopentane. It should first be noted that the quantum yield of bicyclopentyl formation does not change with duration of exposure, maintaining throughout a constant value of  $0.40 \pm 0.01$ . Reference to Table I shows that the value is the same as that obtained in the runs with added cyclopentene, within the experimental error. Extrapolation of the mean quantum yields of cyclopentene formation to  $t = 0$  suggests a value of 0.4 for  $\phi_{C_5H_8}$ . From the stoichiometry  $\phi_{H_2}^0$  must be 0.8.

In order to obtain more accurate data on the primary quantum yields of the reaction, a special batch of P.R.G. cyclopentane was purified by G.L.C. This ultrapure material showed no detectable impurities, and it was estimated that total impurities could not exceed 0.001 mole%. Runs were made with exposure times from 1.4 to 33 minutes. The

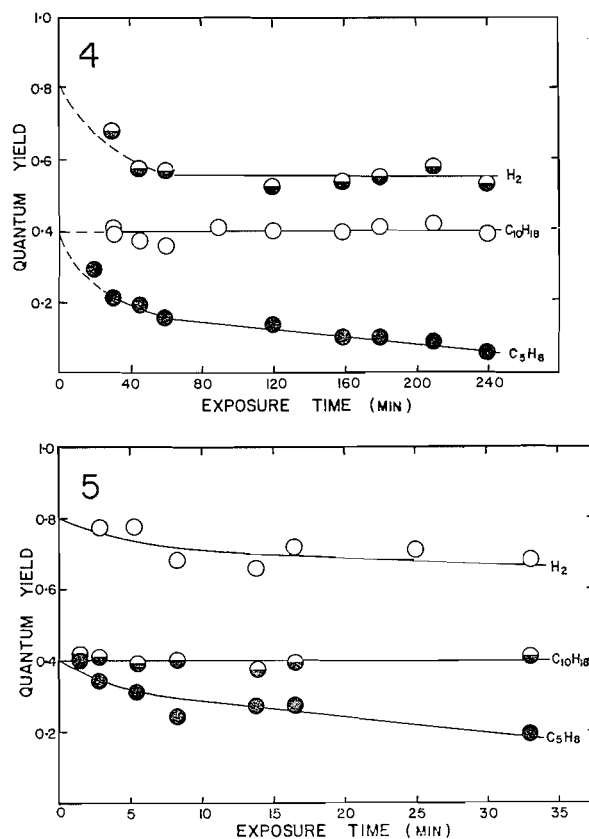


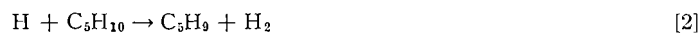
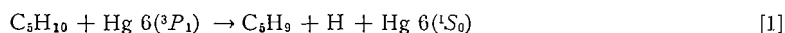
FIG. 4. The mean quantum yields of formation for hydrogen, bicyclopentyl, and cyclopentene vs. exposure time in the mercury-photosensitized decomposition of P.R.G. cyclopentane.

FIG. 5. The mean quantum yields of formation of hydrogen, bicyclopentyl, and cyclopentene vs. exposure time in the mercury-photosensitized decomposition of cyclopentane containing less than 0.001 mole% of impurities.

mean quantum yields vs. exposure time are shown in Fig. 5. Again the invariance of the quantum yield of bicyclopentyl formation at 0.40 is to be noted. The extrapolation of  $\phi_{\text{C}_5\text{H}_8}^0$  to  $t = 0$  can now fairly confidently be said to lead to a value of 0.4 for  $\phi_{\text{C}_5\text{H}_8}^0$ . Under such conditions,  $\phi_{\text{H}_2}^0$  must be 0.8, and an inspection of Fig. 5 shows that 0.8 is a reasonable extrapolation of the actual data on the mean quantum yield of hydrogen formation to  $t = 0$ .

#### DISCUSSION

As in the previous two studies (1, 2) on the cyclopentane reaction, the mechanism under initial conditions will be represented by the following paraffinic sequence:



The above four-step sequence should apply only in the limiting case of zero extent of reaction. A steady-state treatment leads to the following expressions for the primary quantum yields:  $\phi_{\text{H}_2}^0 = K$ ,  $\phi_{\text{C}_5\text{H}_8}^0 = K[1/(1+r)]$ ,  $\phi_{\text{C}_{10}\text{H}_{18}}^0 = K[r/(1+r)]$ , and  $\phi_{\text{C}_5\text{H}_{10}}^0 = K[(1+2r)/(1+r)]$ . The constant  $K$  represents the fraction of the primary quenching collisions which lead to reaction, and  $r$  is the ratio  $k_4/k_3$ , or the relative rate of recombination to disproportionation for cyclopentyl radicals. Both  $K$  and  $r$  can now be obtained from the primary quantum yields of formation of hydrogen, cyclopentene, and bicyclopentyl, which, in turn, were derived by short extrapolations of the mean quantum yields of product formation for ultrapure cyclopentane, as shown in Fig. 5. Thus taking  $\phi_{\text{H}_2}^0 = 0.8$ , and  $\phi_{\text{C}_{10}\text{H}_{18}}^0 = \phi_{\text{C}_5\text{H}_8}^0 = 0.4$ , we find that  $K = 0.8$  and  $r = k_4/k_3 = 1.0$ . The data would therefore indicate that the primary chemical efficiency of the reaction is 80%, and that cyclopentyl radicals have the same rates for disproportionation and recombination.

In the earlier study of the cyclopentane reaction at 30° C by Beck, Kniebes, and Gunning (2), the primary quantum yields, and the efficiency constant,  $K$ , were calculated from the limiting high-pressure values for the mean quantum yields. Their data were obtained for runs of 60-minute duration, at an absorbed light intensity of  $2.5 \times 10^{-6}$  einstein/minute. It was further assumed that the cyclopentene achieved a steady-state concentration by the reaction



In this study we have measured directly the change in cyclopentene concentration with increasing duration of exposure, at an absorbed light intensity of  $3.75 \times 10^{-7}$  einstein/minute. The data, represented in Fig. 2, as a plot of the ratio  $(\text{C}_5\text{H}_8)/(\text{C}_5\text{H}_{10})$  vs. the duration of exposure, show unequivocally that a steady-state concentration is indeed achieved, after approximately 160 minutes of irradiation. The steady-state value of  $(\text{C}_5\text{H}_8)/(\text{C}_5\text{H}_{10})$  was found to be  $5.7 \times 10^{-3}$ . At an absorbed light intensity of  $2.5 \times 10^{-6}$  einstein/minute, with all other reaction parameters remaining constant, we would expect the steady-state to be reached in ca.  $160(3.75 \times 10^{-7})/(2.5 \times 10^{-6}) = 24$  minutes. If reaction [5] is assumed to be the only method whereby cyclopentene is consumed, then the conditions in the previous study (2) should indeed represent a steady-state situation for cyclopentene. However, in the present investigation, we have found that

prolonged irradiation leads to the formation of an additional product, C<sub>10</sub>H<sub>16</sub>, which is assumed to be a cyclopentyl cyclopentene.

This product can be accounted for by the reactions

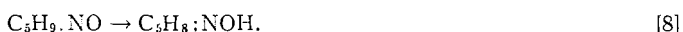


where C<sub>5</sub>H<sub>7</sub> represents a cyclopentenyl radical. Now, if hydrogen, cyclopentene, and bicyclopentyl are the only products of the reaction, the stoichiometry would demand that the mean quantum yields for hydrogen and bicyclopentyl formation approach each other with increasing exposure. From Fig. 4, it can be seen that the mean quantum yield of hydrogen formation is slightly larger than that calculated from the quantum yields of cyclopentene and bicyclopentyl. The discrepancy, furthermore, becomes greater with increasing duration of exposure. It should also be emphasized that the invariance of the quantum yield of bicyclopentyl formation strongly suggests that the secondary product, C<sub>10</sub>H<sub>16</sub>, arises by the decomposition of cyclopentene, rather than from bicyclopentyl. The most compelling evidence, however, for ascribing C<sub>10</sub>H<sub>16</sub> formation to the secondary decomposition of cyclopentene is presented in Table I, and also in the upper curve of Fig. 2. For the series of runs in which cyclopentene was initially added, the C<sub>10</sub>H<sub>16</sub> product becomes considerably more important than in the runs with the P.R.G. cyclopentane.

In comparing the results obtained in the previous investigation (2) with those in the present study, there is another factor which should be considered. In mercury photosensitization, the zone of reaction is concentrated near the window through which the radiation enters the cell. With increasing light intensity, there will be a localized build-up of reaction products near this incident window. Secondary reactions should therefore assume greater importance at higher light intensities. In the previous study (2), the light intensity was 6.7 times higher than in the present work.

Probably the most interesting result of this study is the fact that cyclopentyl radicals, at 24° C, have equal rate constants for recombination and disproportionation. There seems little doubt that the ratio  $k_3/k_4$  is at least 1.0, and by inspection of Fig. 5, it can be seen that the initial rate of cyclopentene formation could conceivably be slightly greater than that for bicyclopentyl. That these rates are essentially identical might suggest that both recombination and disproportionation proceed through the same reaction intermediate.

The results of the runs with added nitric oxide demonstrate rather strikingly the free radical nature of the reaction. From Fig. 3, it can be seen that bicyclopentyl formation is completely suppressed by the addition of 0.7% of nitric oxide. With 1% nitric oxide present in the cyclopentane, there is no bicyclopentyl present after a 1-hour run, and the cyclopentene yield is reduced to about 18% of its value for the pure substrate. Such behavior would indicate that there is a fairly stable compound formed when cyclopentyl radicals interact with nitric oxide. A possible explanation would be that the C<sub>5</sub>H<sub>9</sub>.NO intermediate rearranges to the stable cyclopentanone oxime,



The fact that cyclopentene formation is not completely suppressed would suggest that the intermediate has an alternate mode of decomposition,



From the data represented in Fig. 2, for the change in the  $(C_5H_8)/(C_5H_{10})$  ratio with duration of exposure, it is apparent that the same steady-state concentration of cyclopentene is ultimately achieved, regardless of the initial cyclopentene concentration. If we assume that the over-all reaction in the steady-state region can be described by steps [1] through [7], we find that the steady-state value,  $(C_5H_8)/(C_5H_{10})_{SS}$ , is related to the rate constants by the equation

$$(C_5H_8)/(C_5H_{10})_{SS} = k_2/(2k_6+k_5).$$

Now  $k_6$ , the rate constant for the abstraction reaction, should be considerably smaller than that for the addition reaction,  $k_5$ . To a first approximation, therefore,

$$(C_5H_8)/(C_5H_{10})_{SS} = k_2/k_5 = 5.7 \times 10^{-3}.$$

In other words, our results would indicate that reaction [5] is about 175 times faster than reaction [2].

#### CONCLUSIONS

As a result of this study, it has been shown that the reaction of cyclopentane vapor with Hg  $6^3P_1$  atoms leads to the formation of cyclopentyl radicals and H atoms with a primary quantum efficiency of at least 80%. The complete free radical nature of the reaction has been demonstrated by showing that as little as 0.7 mole% of added nitric oxide leads to a complete inhibition of bicyclopentyl formation. From the fact that cyclopentene and bicyclopentyl have the same primary quantum yields, it is concluded that cyclopentyl radicals have identical rates for disproportionation and recombination at 24° C. The results of the investigation would further suggest that meaningful values for the ratio of the rates of disproportionation to recombination for free radicals can only be obtained when the reaction in question is studied at low light intensities and at very short durations of exposure.

#### REFERENCES

1. G. A. ALLEN, D. L. KANTRO, and H. E. GUNNING. *J. Am. Chem. Soc.* **72**, 3588 (1950).
2. P. W. BECK, D. V. KNIEBES, and H. E. GUNNING. *J. Chem. Phys.* **22**, 678 (1954).
3. S. BYWATER and E. W. R. STEACIE. *J. Chem. Phys.* **19**, 319 (1951).
4. A. E. MESSNER, D. M. ROSIE, and P. A. ARGABRIGHT. *Anal. Chem.* **31**, 230 (1959).