THE MERCURY-PHOTOSENSITIZED DECOMPOSITIONS OF PROPANE AND ETHANE[1]

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ABSTRACT

The mercury-photosensitized decompositions of propane and ethane have been studied at pressures of 300 and 600 mm, at 24° C, at very low conversions. Hydrogen was the only product identified and measured. The hydrogen yield fell rapidly at first, with increasing time of irradiation, and finally became constant. This behavior is attributed to the accumulation in the system of propylene or ethylene formed by the disproportionation of propyl or ethyl radicals, and the constant rate of hydrogen production finally achieved is thought to correspond to a steady-state concentration of the unsaturate. Previous values of the quantum yields of these decompositions were probably measured in this steady-state region, and must be corrected upwards.

Relative values have been estimated for the various rate constants involved in this mechanism. There is some evidence that energy-rich radicals, formed by the addition of hydrogen atoms to the unsaturates, tend to disproportionate rather than dimerize.

INTRODUCTION

In a previous study of the mercury-photosensitized decomposition of *n*-pentane at very low conversion, the hydrogen production decreased rapidly at first, then more slowly, and finally became constant after about 0.5% reaction (1). This was attributed to the accumulation in the system of pentene, formed by disproportionation of pentyl radicals, and the final constant rate of hydrogen production was thought to correspond to a low, steady-state concentration of pentene. The hydrogen yield was reduced, and pentene consumed, by the addition of hydrogen atoms to pentene. Similar behavior has been observed with the cyclo-alkanes (2), and more recently with *n*-butane (3). Previous studies of the mercury-photosensitized decomposition of propane and ethane did not show this effect, as hydrogen production was independent of time (4). However, rough calculations from the relative rates of the reactions concerned suggest that even the smallest conversions achieved in these experiments were probably much too large for the initial behavior to be observed. It was decided to study these reactions at very low conversions to see whether they behaved in the same way.

EXPERIMENTAL

The apparatus, a conventional static system, and the method were essentially similar to those described previously (1). Two reaction vessels, of 38- and 180-cc volume, were used in the course of the work, the larger volume permitting measurements to be made at lower conversion. After irradiation, gases non-condensable at −210° C were removed and analyzed, and the hydrocarbon, together with any condensable products, was returned to the reaction vessel for further irradiation. In this way, the hydrogen yield could be studied as a function of total irradiation time, using a single sample of hydrocarbon. Concentrations of hydrogen and unsaturates produced in the system were always low enough so that all quenching of the excited mercury atoms was by the hydrocarbon alone. Measurements were made with propane at 300- and 600-mm pressure, and with ethane at 305-mm pressure, all at 24° C. In some experiments, unsaturates (propylene or ethylene) were added.

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Phillips Research-grade propane was used without further purification. A sample treated with $HgSO_4$–H_2SO_4 solution to remove unsaturates gave the same results as the untreated gas. Phillips Research-grade ethane was found to contain appreciable amounts of methane and ethylene. The former was removed by repeated trap-to-trap distillation and prolonged pumping at $-210°$ C. The latter was removed by condensing the ethane onto charcoal previously treated with bromine.

RESULTS

Propane

The non-condensable gas was never less than 99.5% hydrogen, measured by diffusion through a Pd thimble at 300° C. Careful analysis with a low temperature still failed to detect any C_2 hydrocarbons, so that hydrogen was the only product detected and measured. Hydrogen yield is shown as a function of total time of irradiation in Figs. 1 and 2 for propane at 600- and 300-mm pressure respectively. The effect of adding propylene to the system is shown in Fig. 3.

Ethane

When care was taken to remove all the methane present initially, the non-condensable gas produced was never less than 99% hydrogen, and this was again the only product detected and measured. The hydrogen yield is shown in Fig. 4 as a function of total time of irradiation for ethane carefully purified to remove ethylene. For comparison, the hydrogen yield from Research-grade ethane, used without purification, is shown in the same figure.

Under conditions of high pressure, low light intensity, and low temperature, and consequent absence of hydrogen atom "cracking" reactions and other complicating processes, the simple mechanism suggested previously (1) seems to account adequately for the observed behavior of both compounds.

$$h\nu + \mathrm{Hg} \longrightarrow \mathrm{Hg}^* \qquad [1]$$

$$\mathrm{Hg}^* + \mathrm{RH} \xrightarrow{\text{rate} = K} \dot{\mathrm{R}} + \mathrm{H} + \mathrm{Hg} \qquad [2]$$

$$\mathrm{H} + \mathrm{RH} \xrightarrow{k_3} \mathrm{H}_2 + \dot{\mathrm{R}} \qquad [3]$$

$$\dot{\mathrm{R}} + \dot{\mathrm{R}} \xrightarrow{k_4} \mathrm{R}_2 \qquad [4]$$

$$\dot{\mathrm{R}} + \dot{\mathrm{R}} \xrightarrow{k_5} \mathrm{RH} + \mathrm{R}' \qquad [5]$$

RH is an alkane, $\dot{R}$ is an alkyl radical, and R' is an olefin. As the olefin accumulates in or is added to the system, the following additional reactions may become important.

$$\mathrm{H} + \mathrm{R}' \xrightarrow{k_6} \dot{\mathrm{R}} \qquad [6]$$

$$\mathrm{H} + \mathrm{R}' \xrightarrow{k_7} \mathrm{H}_2 + \dot{\mathrm{R}}' \qquad [7]$$

$$\dot{\mathrm{R}} + \mathrm{R}' \xrightarrow{k_8} \dot{\mathrm{R}}_2 \qquad [8]$$

$$\dot{\mathrm{R}} + \dot{\mathrm{R}}' \xrightarrow{k_9} \mathrm{R}'_2 \qquad [9]$$

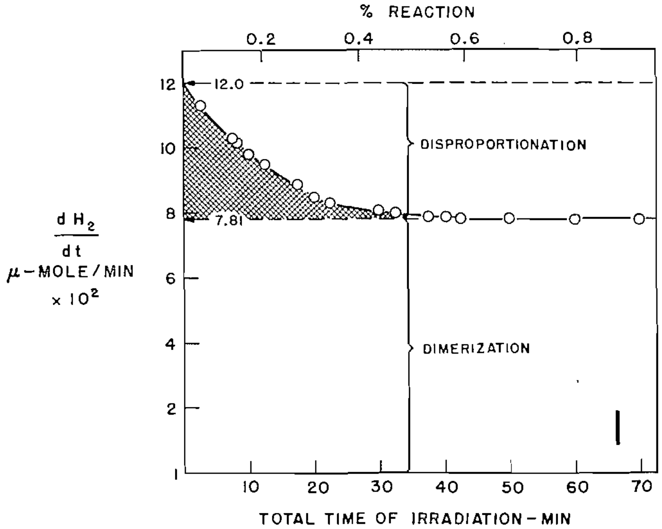
where $\dot{R}'$ is an unsaturated radical, $\dot{R}_2$ is a dimer radical, and $\dot{R}'_2$ is an unsaturated dimer. From the mechanism, it may be shown that

$$[1] \qquad d\mathrm{H}_2/dt = K(k_3[\mathrm{RH}]+k_7[\mathrm{R}'])/(k_3[\mathrm{RH}]+(k_6+k_7)[\mathrm{R}']).$$

Thus dH_2/dt is equal to K initially, decreases as R' accumulates, and becomes constant if R' attains a steady-state concentration before depletion of RH becomes appreciable.

This behavior was shown by propane and ethane, Figs. 1, 2, and 4, and the reduction of the hydrogen yield in the steady state may be taken as a measure of the extent of reaction 6. Furthermore, if loss of R′ via reaction 8 is neglected, the reduction of the hydrogen yield is also a measure of the rate of disappearance of R′, and since it is a steady state, of the rate of formation of R′ by reaction 5. Thus we may obtain the relative rates of reactions 4 and 5 directly from Figs. 1, 2, and 4, as shown.

Interesting confirmation that the plateaux do represent steady-state concentrations of



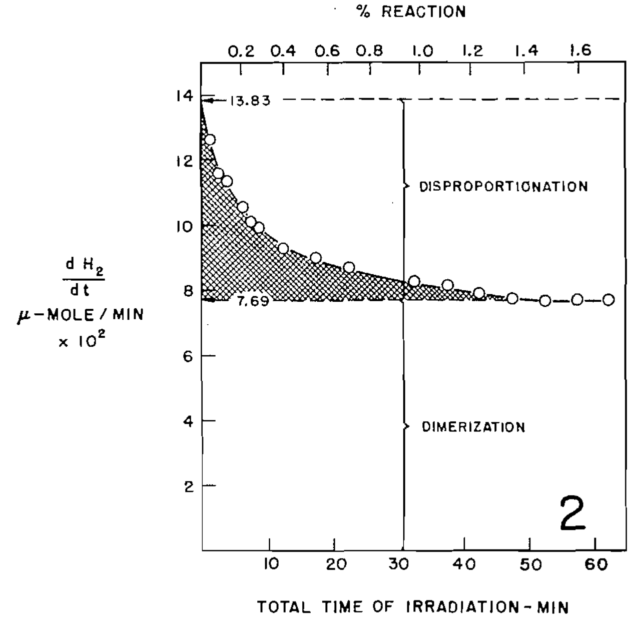


FIG. 1. Rate of production of hydrogen vs. total time of irradiation for the mercury-photosensitized decomposition of propane at 600-mm pressure.

FIG. 2. Rate of production of hydrogen vs. total time of irradiation for the mercury-photosensitized decomposition of propane at 300-mm pressure.

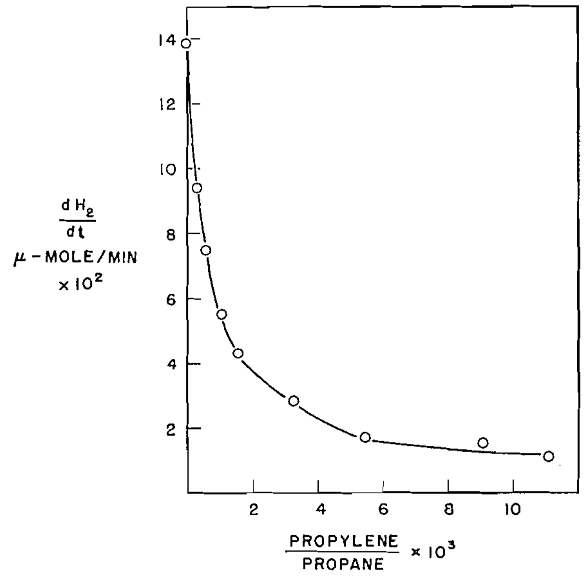


FIG. 3. The effect of added propylene on the rate of hydrogen production from the mercury-photosensitized decomposition of propane at 300-mm pressure.

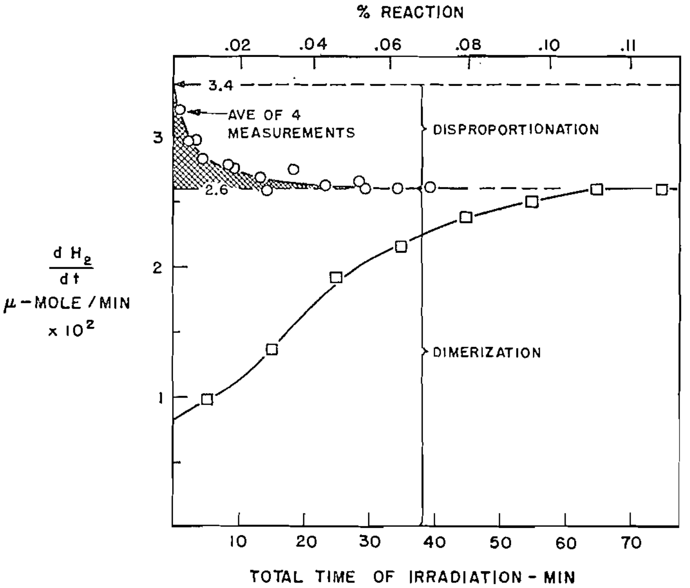


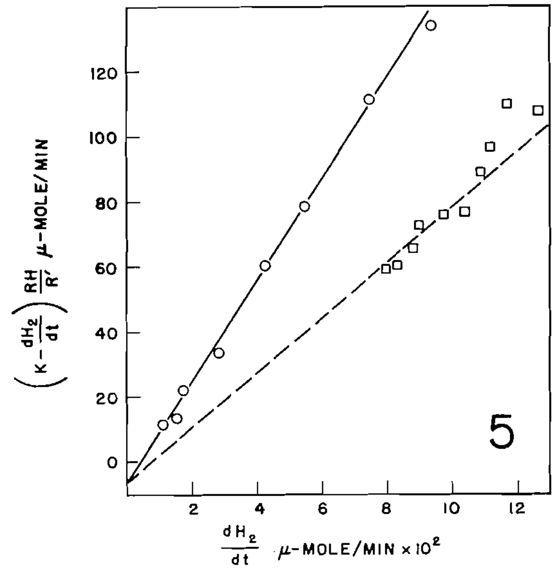
FIG. 4. Rate of production of hydrogen vs. total time of irradiation for the mercury-photosensitized decomposition of ethane at 305-mm pressure; ○ pure ethane, □ Research-grade ethane.

unsaturates is seen in the behavior of the impure Research-grade ethane (Fig. 4). Upon repeated irradiation, the ethylene in excess of the steady-state value was slowly used up, until finally the hydrogen yield rose to the same steady-state value as before. In another experiment, a sample of pure ethane was irradiated until the hydrogen yield had attained the plateau value. At this point, a small amount (0.02%) of ethylene was added, whereupon the hydrogen yield was reduced to 0.0042 micromoles/minute. Upon repeated irradiation, the hydrogen yield slowly increased, following the same curve as the sample of impure ethane, and again attained the same limiting value. Thus the same steady state, which is a function only of the ratio k_4/k_5, was approached in three different ways.

Equation 1 may be rewritten as

$$[2] \qquad (K - dH_2/dt)\,[RH]/[R'] = A(dH_2/dt) - BK$$

where $A = (k_6+k_7)/k_3$ and $B = k_7/k_3$. Plots of this equation for the experiments with propane–propylene mixtures are shown in Figs. 5 and 6. Ratios of rate constants calculated from the slopes and intercepts of these plots are shown in Table I, together with values of k_5/k_4.



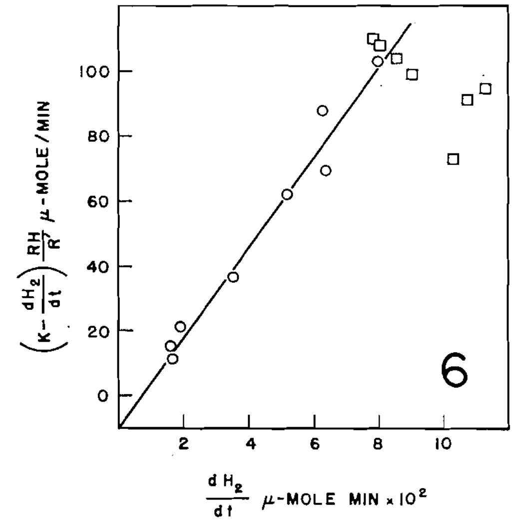


FIG. 5. A plot of equation 2 for propane at 300-mm pressure; □ pure propane, ○ added propylene.
FIG. 6. A plot of equation 2 for propane at 600-mm pressure; □ pure propane, ○ added propylene.

The same ratios of rate constants may be calculated in a different way from the experiments with pure propane and ethane. If one assumes a constant rate of formation of R′ by reaction 5, and a loss of R′ equal at any time to the net decrease in hydrogen production (thus neglecting reaction 8), it may be shown that the net rate of production of R′ is given by

[3] $$dR'/dt = d_2H/dt-(dH_2/dt)_S$$

where $(dH_2/dt)_S$ is the rate of production of hydrogen in the steady state. R′ may then be evaluated as a function of time by a graphical integration of this equation, represented by the shaded areas in Figs. 1, 2, and 4. Using values of R′ obtained in this way, the data were plotted according to equation 2 and are shown in Figs. 5 and 6, for propane, and Fig. 7 for ethane. A similar graphical integration of the data for the impure ethane, integrating backwards from the steady state, permitted calculation of ethylene concentrations in this system. These data are also plotted in Fig. 7, together with a single point obtained in the experiment, mentioned previously, when ethylene was added to ethane already irradiated until the steady state had been reached. From the pure ethane data, a rough value of $k_6/k_3 = 25{,}000$ was estimated from a straight line drawn through the origin (since k_7 is zero for ethylene). All ratios of rate constants are summarized in Table I.

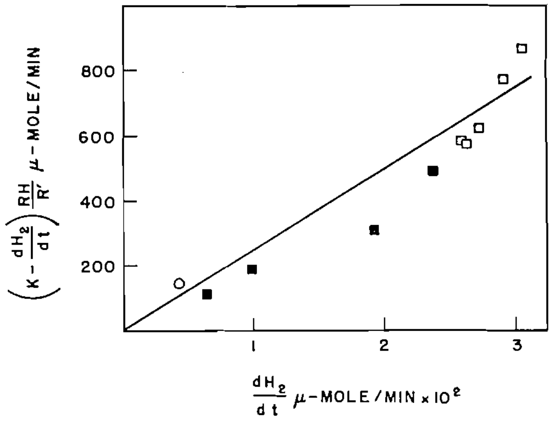


FIG. 7. A plot of equation 2 for ethane at 305-mm pressure; □ pure ethane, ■ Research-grade ethane, ○ added ethylene.

DISCUSSION

The mercury-photosensitized decompositions of propane and ethane both show the same initial behavior that has been observed with *n*-pentane (1), *n*-butane (3), and some cyclo-alkanes (2). Because of the larger values of k_6/k_3, this was observed only at very low conversions (shown as upper abscissae in Figs. 1, 2, and 4). This was especially true for ethane, with which the steady state was attained after about 0.05% reaction, with an estimated steady-state concentration of ethylene of one part in 80,000. All previous studies of these reactions, in which hydrogen production was observed to be linear with time, were undoubtedly made in the steady-state region, and the measured quantum yields must be corrected upwards by the factor $(k_4+k_5)/k_4$, as indeed the authors anticipated. Bywater and Steacie reported a pressure-independent quantum yield of 0.50

for hydrogen production from propane at high pressures and room temperature (4), from which values of the initial quantum yield of 0.90 and 0.77 at 300 and 600 mm, respectively, may now be estimated. It may be noted that while the steady-state hydrogen yields at the two pressures are almost identical, confirming the pressure independence observed by Bywater and Steacie, the initial quantum yield appears to decrease with increasing pressure, suggesting, perhaps, the intermediate formation of an excited propane molecule of appreciable lifetime in the primary process. The quantum yields for the ethane decomposition reported by Darwent and Steacie (4), which tended towards unity at high pressure, should be revised upward in a similar way, although the correction here is smaller than for propane.

Values of k_5/k_4 for both ethyl and propyl radicals appear to be rather higher than those observed for thermally equilibrated radicals (5, 6, 7, 8). Some of this discrepancy may be attributed to inaccuracy in the extrapolation to zero time. However, it should be noted that in the steady-state region, where this ratio is estimated, a fraction $k_5/2(k_6+k_4)$ of the radicals in the system were formed via reaction 6, and would be vibrationally excited until stabilized by collisions. It has clearly been shown by several authors that such "hot" radicals tend to disproportionate rather than dimerize, and that these effects can persist to quite high pressures (9, 10, 11). The decrease in k_5/k_4 for propane in going from 300- to 600-mm pressure lends support to such an explanation. It might be noted, incidentally, that the "propyl" radicals in the present study are very probably isopropyl radicals (9).

Values of k_6/k_3 obtained from the experiments with propane–propylene mixtures (Table I) are in fair agreement with a value of about 3000 which may be estimated from separate measurements of the two rate constants by Schiff and Steacie (12), and Bradley, Melville, and Robb (13). The values of $k_7/(k_6+k_7)$, the fraction of hydrogen atoms reacting with propylene which abstract hydrogen (Table I), are rather lower than previous estimates of this ratio (14). The variation with pressure is probably not significant, considering the relatively long extrapolation which is involved.

TABLE I

Ratios of rate constants

Hydrocarbon	k_6/k_3	$k_7/(k_6+k_7)$	k_5/k_4
Propane, 300 mm	1515	0.032	0.08
Propane, 600 mm	1304	0.061	0.54
Ethane, 305 mm	25000	—	0.31

The data from the experiments with pure propane at 300 mm, plotted in Fig. 5, using calculated values of the propylene concentration, lie considerably below the data from the experiments with added propylene, and, taking the same intercept, would lead to values of k_6/k_3 about half as large. A similar behavior was previously observed with *n*-pentane at 300 mm, which was tentatively attributed to the formation of 2-pentene in the disproportionation reaction (1). Such an explanation is impossible with propylene, and another cause must be sought. The values of the propylene concentration were calculated assuming, first, disappearance of propylene by reaction 6 only, and secondly, a constant rate of formation of propylene equal to that in the steady state. If propylene disappeared by other reactions, such as 8, or by direct photosensitized decomposition, the calculated values of propylene concentration would be too high, and k_6/k_3 would be low, as observed. It is doubtful, however, that reaction 8 would occur to such an extent, and the very low concentrations of propylene eliminate the possibility of direct decomposition. It may be noted that the reaction sequence, 7+9, would merely substitute hexene for propylene, which would not have a large effect.

The second assumption, that the rate of production of propylene is constant, is more likely at fault. The high value of k_5/k_4 noted previously was attributed to preferential disproportionation of "hot" propyl radicals formed by reaction 6. Initially, however, all the propyl radicals were formed by reactions 2 and 3, and reaction 6 only becomes important as propylene accumulates in the system. Thus if "hot" propyl radicals were the cause of the high values of k_5/k_4 in the steady state, the rate of formation of propylene may have been much lower in the earlier stages of the reaction, and the graphical integration may have thus overestimated the concentration of propylene quite considerably. In support of this explanation is the improved agreement of the two sets of data at 600-mm pressure, where a lower value of k_5/k_4 was observed, and, presumably, "hot" radical reactions were less important. It seems that a similar explanation is probably valid for *n*-pentane. With ethane, at 305 mm, only one experiment was done with added ethylene, and it again lies somewhat above the data for pure ethane using calculated concentrations of ethylene. It should be noted, finally, that all these data for low concentrations of unsaturates lie in an inherently inaccurate region for the plot of equation 2, towards the right-hand side of Figs. 5, 6, and 7.

The value of k_6/k_3 of 25,000, calculated from the data obtained with pure ethane, may also be compared with values calculated from the literature. Berlie and LeRoy measured k_3 over a range of temperature, and from their data a collision yield of 4.5×10^{-8} at 24° C may be estimated (15). Bradley, Melville, and Robb estimated a collision yield of 9.3×10^{-5} for reaction 6 (13), which, assuming similar collision numbers, gives $k_6/k_3 = 2100$, an order of magnitude lower than found in the present study. Pursuing the discrepancy further, the collision yield of 4.5×10^{-8} for reaction 3, with ethane, is almost identical with the value 4.6×10^{-8} found by Schiff and Steacie for the same reaction with propane (12). From the results of Darwent and Roberts, however, a ratio k_3(propane)/k_3(ethane) of about 19, at 24° C, may be calculated (14). Taking a value of the ratio k_6(propylene)/k_6(ethylene) of 1.5 (13), from the present results a value of k_3(propane)/k_3(ethane) of about 25 may be estimated, in fair agreement with Darwent and Roberts, but much higher than the value of about 1 indicated from the combined results of Berlie and LeRoy, and Schiff and Steacie. One would expect the reaction of hydrogen atoms with the primary hydrogen atoms of ethane to be considerably slower than with the secondary hydrogen atoms of propane, and it would appear that the values of k_3 (ethane) found by Berlie and LeRoy may be too high, as has been suggested elsewhere (16), although perhaps the discrepancies are simply an indication of the rather unsatisfactory knowledge of accurate absolute values for the rates of hydrogen atom reactions.

It may be noted that all the relative rate constants measured in the present work are dependent upon the values chosen for K, the initial rate of hydrogen production. The sharply rising nature of the curves (Figs. 1, 2, and 4) makes this extrapolation to zero time inherently inaccurate, while the presence of even minute amounts of unsaturates initially present in the hydrocarbon could seriously reduce the observed value of K. The reasonable agreement between values of k_5/k_4 observed, and those measured by other methods suggests that the initial extrapolations were not grossly in error. The value of 0.9 for the initial quantum yield estimated for propane at 300 mm puts an upper limit on the possible value of K for that particular system. The reaction

$$H + R + M \rightarrow RH + M \qquad [10]$$

may be of some importance, especially with ethane (6), and probably accounts for the decrease in quantum yield with decreasing ethane pressure observed by Bywater and Steacie (4). The occurrence of this reaction would not seriously affect the kinetics and rate constants observed in the present study, since for a given pressure and light intensity, it may be regarded, to a first approximation, simply as a constant factor reducing the extent of reaction 2.

A careful measurement of initial quantum yields of the mercury-photosensitized decompositions of the simple alkanes would be of obvious value in determining the exact nature of the primary process, and it is perhaps worth while to note briefly the conditions essential for such measurements as indicated by the present study. These are: (1) very low conversions, preferably 10 or 100 times lower than in the present work, in order to improve the accuracy of the extrapolation to zero time; (2) rigorous purification of hydrocarbons to eliminate trace amounts of unsaturates; and (3) low light intensities, sufficiently low to make reaction 10 negligible.

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