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The Mercury Photosensitized Reactions of Propane at Low Pressures

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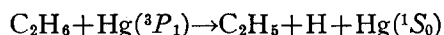
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The mercury photosensitized reactions of propane have been investigated at room temperature between 0.7 and 84.5 mm Hg. At high pressures the products consisted almost entirely of hexane and hydrogen but at low pressures methane and C₂ and C₄ hydrocarbons were produced in increasing amounts. The production of methane was much less than in the similar reactions of ethane. The effect of pressure on the nature of the reaction can be accounted for by a C—H split followed by atomic cracking and recombination reactions as proposed by Steacie and Dewar, but the difference in the products from propane and ethane make it likely that the reaction proceeds, at least in part, by the formation of an active molecule. At low pressures the rate of propane disappearance is retarded and the extent of C—C split increased by the addition of hydrogen. The effect of added hydrogen is explained by an increase in the rates of recombination of hydrogen atoms and of atomic cracking reactions.

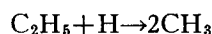
INTRODUCTION

THE reactions of the lower paraffin hydrocarbons photosensitized by Hg(³P₁) and Cd(³P₁) atoms have been investigated. Some aspects of these reactions, however, are considered to have received inadequate attention so that further investigation is desirable.

The mercury photosensitized reactions of ethane were investigated in a circulatory system^{1,2} and in single pass flow system.³ In these investigations a trap in the circulatory system was maintained at a low temperature to remove secondary products of the reaction. Steacie and Phillips found that at high trap temperatures the products consisted largely of hydrogen and butane but that with decreasing trap temperatures the production of hydrogen and butane decreased while methane and propane appeared in increasing amounts. They assumed that the initial act was a C—H split:



and accounted for the products by the occurrence of the "atomic cracking" reaction:



followed by radical recombination. The products of the similar reactions of propane,⁴ *n*-butane,⁵

and iso-butane,⁶ investigated under very similar conditions in a circulatory system, consisted almost exclusively of hydrogen and hexanes from propane and of hydrogen, octanes, and dodecanes from the butanes. The nature of the products from iso-butane was found to be independent of the working pressure of the paraffin between 6 and 60 cm whereas with ethane a marked change occurred at pressures of 15 cm and lower.

The products from propane and the butanes as well as from ethane at high pressures are certainly in accord with the assumption of a C—H split as the initial act. Since the C—H bonds in the lower paraffin hydrocarbons are known to be considerably stronger than the C—C bonds, the C—H split found indicates that the reaction is of a specific nature and it has been suggested^{7,8} that the reaction probably proceeds by virtue of the formation of HgH. This picture then leads us to believe that, in these reactions, the mercury atom does not play the part of a true sensitizer, i.e., serving only as a medium by which energy is transferred, but actually takes part in the reaction. However, the mechanism proposed to account for the C—C split with ethane at lower pressures does not appear to be adequate since Steacie and Cun-

⁴ E. W. R. Steacie and D. J. Dewar, *J. Chem. Phys.* **8**, 571 (1940).

⁵ A. W. Hay and C. A. Winkler, *Can. J. Research* **B21**, 149 (1943).

⁶ B. deB. Darwent and C. A. Winkler, *J. Phys. Chem.* **49**, 150 (1945).

⁷ E. W. R. Steacie, *Ann. N. Y. Acad. Sci.* **41**, 187 (1941).

⁸ K. J. Laidler, *J. Chem. Phys.* **10**, 43 (1942).

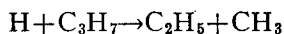
¹ S. Tolloczko, *Przemyśl Chem.* **11**, 245 (1927).

² E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.* **6**, 179 (1938); *Can. J. Research* **B16**, 303 (1938).

³ E. W. R. Steacie and R. L. Cunningham, *J. Chem. Phys.* **8**, 800 (1940).

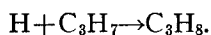
ningham³ found considerable methane in their single pass experiments, in which the H atom concentration was certainly very low. This makes it seem somewhat unlikely that the methane was produced by "atomic cracking." Hence the question arises as to whether the difference in the products from ethane indicates a reaction which differs from the similar reactions of propane and butane in type rather than in degree.

The products of the $\text{Cd}(^3P_1)$ sensitized reactions of ethane⁹ and propane¹⁰ were found to contain significant amounts of methane. The mechanisms postulated were entirely similar to those that were used to account for the products of the $\text{Hg}(^3P_1)$ sensitized reactions but, at least with propane, the products of the reactions with $\text{Hg}(^3P_1)$ and $\text{Cd}(^3P_1)$ are significantly different. It may be noted that cadmium sensitized reactions occur via CdH , while there is no evidence whether or not HgH is involved in the case of mercury. If methane is produced in both the $\text{Cd}(^3P_1)$ and $\text{Hg}(^3P_1)$ reactions of propane by atom cracking it is difficult to explain the differences in the products since the reaction:



should be independent of the initial act whereby the H and/or the C_3H_7 is produced. This point is discussed more fully at the end of this paper.

The quantum yields of all of the above reactions are of the order 0.1 to 0.2 which is about 5 to 10 percent of the value that would be expected on the basis of the above mechanism. This inefficiency may be caused by physical effects, such as quenching to the metastable 3P_0 state with subsequent degradation and dissipation of the energy as heat, or to recombination reactions of the type



However, Steacie, Alexander, and Phillips¹¹ and Steacie and Parlee,¹² working with deuterium

atoms and ethane and propane, respectively, found that the residual ethane and propane were entirely light, which indicates that recombination is not serious. Inefficiency of a physical type is a possibility but its extent is rather surprising.

The present series of investigations were undertaken in an attempt to elucidate some of the above inconsistencies. It seems likely that the difference in the behavior of ethane on one hand and of propane and the butanes on the other to $\text{Hg}(^3P_1)$ atoms could be caused only by the relative smallness of the ethane molecule and/or the absence of secondary or tertiary hydrogen atoms in ethane. In any case the above differences should be only in degree since all of the lower paraffin hydrocarbons are essentially similar in behavior. Hence the reaction of $\text{Hg}(^3P_1)$ atoms with propane at 30°C was investigated at low pressures with the results reported below.

EXPERIMENTAL

The reaction was investigated in a circulatory system of conventional type in which the heavy products were condensed out in one trap and propane stored as a liquid in another trap at a lower temperature.

The volume of the reaction system, about 740 cc, was made as small as was convenient as semi-micro analytical methods were used to determine whether small amounts of C_2 and C_4 hydrocarbons were produced since these were not detected in the previous investigation of the $\text{Hg}(^3P_1)$ reaction of the propane. The reactor was a quartz cell 4.9 cm in diameter and 11.5 cm long provided with plane windows. The lamp was the usual low pressure type filled with 3 mm of neon and a little mercury; it was placed near to the reaction cell from which it was separated by a shutter. The traps were kept at low temperatures, one at -80°C to prevent heavier products from reaching the second which was kept at a temperature low enough to condense propane and provide a constant vapor pressure. The circulating pump was of the type described by Puddington¹³ and circulated gas at about 400 cc per min at 760 mm. The saturator was

⁹ E. W. R. Steacie and R. Potvin, *J. Chem. Phys.* **7**, 782 (1939).

¹⁰ E. W. R. Steacie, D. J. Le Roy, and R. Potvin, *J. Chem. Phys.* **9**, 306 (1941).

¹¹ E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research* **B16**, 314 (1938).

¹² E. W. R. Steacie and N. A. D. Parlee, *Can. J. Research* **B17**, 371 (1939); *Trans. Faraday Soc.* **35**, 854 (1939).

¹³ I. E. Puddington, *Ind. Eng. Chem. Anal. Ed.* **17**, 592 (1945).

warmed to about 40°C and the mercury content of the gases was reduced to the equilibrium value at atmospheric temperature by contact with nickel pellets.

The products of the reaction were analyzed by fractionation in an apparatus of the type described by Ward.¹⁴ Tests with synthetic mixtures showed that separations could be accomplished with an accuracy of about ± 0.01 cc at 760 mm. Since the production of methane was an important part of this research, special care was taken with the analysis of the hydrogen-methane fraction. The hydrogen was removed by oxidation on copper oxide at 280°–300°C—the residue, methane, was further characterized by combustion with a measured volume of oxygen on a glowing platinum spiral; the volume of oxygen consumed as well as that of carbon dioxide produced were used in determining the composition of the residue. The products containing five or more carbon atoms per molecule were measured as gases at low pressures (up to 30 mm).

The propane used was the product of the Ohio Chemical Company. No methane or other impurities could be detected by our analytical

methods so it was subjected only to a simple bulb-to-bulb distillation, the middle $\frac{1}{3}$ being retained and stored in a 1-liter flask. Before each run the propane was condensed in liquid air and evacuated to ensure that there was no contamination with air which might have entered through leaks in the stopcocks. A suitable volume of propane was then measured accurately in the gas burette and transferred to the apparatus by condensation in a trap surrounded by liquid air. The lamp was turned on about 30 minutes before each run to ensure constancy of output and the current controlled manually and kept constant at 100 ma.

Some experiments were carried out in the presence of hydrogen. The hydrogen was taken from a cylinder of "electrolytic" hydrogen and purified by passage over heated copper followed by a trap in liquid air.

RESULTS

The results of this investigation are given in the accompanying tables and illustrated graphically. The conditions under which the experiments were conducted and the amounts of the various products obtained are listed in Table I. The method of analysis used allowed accurate

¹⁴ E. C. Ward, Ind. Eng. Chem. Anal. Ed. **10**, 169 (1938).

TABLE I. Experimental conditions and results. Volume of system = 740 cc; current to lamp = 100 ma.

Run no.	Working pressure of C ₃ H ₈ mm Hg	Time of run hr.	Initial reactants		Products—cc					
			C ₃ H ₈ cc	H ₂ mm	H ₂	CH ₄	C ₂	C ₃	C ₄	C ₄ ⁺
1	5.0	2.0	24.89	—	1.74	0.65	0.16	20.29	0.25	—
2	84.5	1.0	133.3	—	6.96	0.06	0.07	119.8	0.08	6.55
3*	8.5	1.0	10.72	—	1.78	0.15	0.08	7.35	0.08	1.38
4*	7.5	1.5	7.58	—	1.66	0.25	0.10	4.49	0.07	1.19
5*	15	1.0	19.85	—	2.11	0.11	0.10	15.68	0.08	1.90
6	3	3.0	12.27	—	0.56	1.22	0.26	9.06	0.36	1.06
7	3	1.0	6.925	—	0.38	0.39	0.16	5.48	0.23	0.70
8	3	5.0	20.40	—	1.81	1.99	0.73	13.22	0.19	2.66
9	3	3.0	12.60	—	1.35	1.15	0.45	7.87	0.14	2.15
9(a)**	3.34	3.0	16.26	—	2.72	0.54	0.17	11.38	0.35	—
10	0.72	3.0	12.73	10.0	8.34	1.07	0.03	12.19	0.04	0.10
12	0.73	3.0	12.21	5.0	6.50	1.21	0.06	11.68	0.06	0.06
13	0.70	3.0	10.40	1.34	1.37	1.91	0.27	9.07	0.23	0.11
14	0.79	3.0	10.69	0.00	0.14	1.26	0.26	8.01	0.59	0.60
15	3.35	2.0	10.15	0.00	0.73	0.80	0.142	7.27	0.372	1.11
16	3.25	2.0	10.41	29.7	—	0.77	0.065	9.59	0.097	—
17	3.38	2.0	8.18	6.83	—	1.11	0.097	7.00	0.217	0.359
18	0.76	3.0	5.63	2.75	1.47	1.79	0.202	4.33	0.143	0.091
19	3.21	2.0	5.885	2.75	—	1.09	0.152	4.34	0.246	0.449
20	0.658	3.0	6.575	0.00	0.143	1.30	0.266	3.987	0.592	—
21	18.	1.0	30.09	—	2.95	0.162	0.091	24.93	0.00	2.56
22	6.5	1.0	10.30	—	1.28	0.34	0.0972	7.344	0.162	1.36

*Runs done without cold trap. The working pressure quoted is the average of the initial and final pressure of propane.

** Volume of apparatus = 4115 cc.

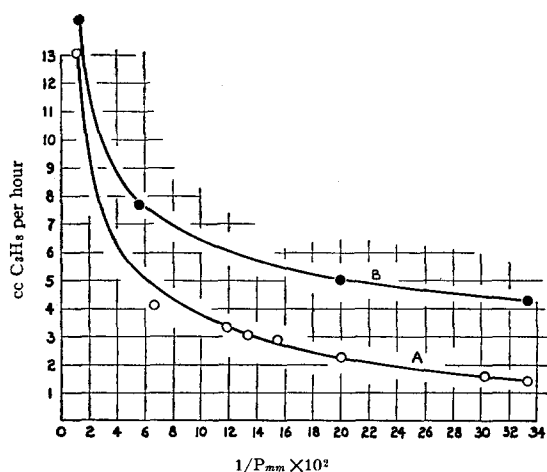


FIG. 1. Effect of working pressure of propane on rate of reaction. *A* = uncorrected rate and *B* = rate corrected for incomplete quenching.

measurement of the methane and C_2 fraction since the hydrogen and methane could be separated completely from the C_2 fraction and, by combustion of the residual hydrocarbon, after removal of the hydrogen on copper oxide, we could estimate the amount of C_2 that had been taken over with the methane. Combustion showed that the residual methane was very seldom contaminated by C_2 hydrocarbons and in no case was this contamination serious. Similarly the C_2 fraction could contain only C_3 hydrocarbons as impurities and the extent of contamination was again estimated by combustion. The purity of the C_3 , C_4 , and C_5 fractions was not estimated by combustion since the large volume of residual propane made the accurate

determination of small amounts of C_4 impurity a virtual impossibility by the method used and the C_4 fraction may have been contaminated by C_3 and C_5 hydrocarbons which could not be determined by combustion. Accordingly much more reliance can be placed in the figures quoted for the volumes of hydrogen, methane, and C_2 hydrocarbons than for the rest. In nearly all cases the combustion of the C_2 fraction indicated the likelihood that ethylene was an important constituent; the C_2 fraction from run 6 analyzed to $C_{1.96}H_{3.8}$. The gas volumes reported were corrected to 760 mm and room temperature (25° – $27^\circ C$).

The effect of the working pressure of propane on the course of the reaction is shown in Table II and illustrated in Figs. 1 and 2. Curve *A* of Fig. 1 illustrates the effect of pressure on the rate of decomposition of propane; Curve *B* shows that the rate of disappearance of propane decreases with decreasing pressure even when corrections are applied to allow for decreased quenching. Figure 2 illustrates the linear relationships that exist between the yields of the products and the reciprocal of the working pressure of propane; the yields of hydrogen and C_3^+ hydrocarbons are decreased whereas those of CH_4 , C_2 , and C_4 hydrocarbons are increased as the propane pressure is decreased.

The effect of including a cold trap to remove the heavy products and to provide a constant working pressure of propane is demonstrated in Figs. 1 and 2 which show that in the absence of a cold trap the yield of hydrogen per cc of propane

TABLE II. Effect of pressure on the reaction. Conditions as in Table I.

Run no.	Working press. of C_3H_8 mm	Reaction rate cc C_3H_8 reacted per hr.	Production—cc/hr.					cc produced/cc C_3H_8 reacted				
			H_2	CH_4	C_2	C_4	C_5^+	H_2	CH_4	C_2	C_4	C_5^+
2	84.5	13.1	6.72	0.06	0.07	0.08	6.32	0.515	0.004	0.005	0.006	0.485
21	18.0	5.16	2.95	0.162	0.091	0.00	2.56	0.571	0.0314	0.0176	0.000	0.495
5*	15.0	4.16	2.11	0.11	0.10	0.08	1.90	0.506	0.026	0.024	0.019	0.455
3*	8.5	3.37	1.78	0.15	0.08	0.08	1.38	0.53	0.045	0.024	0.024	0.41
4*	7.5	3.09	1.11	0.17	0.07	0.05	0.79	0.536	0.081	0.032	0.023	0.384
22	6.5	2.96	1.28	0.34	0.097	0.145	1.36	0.431	0.145	0.0329	0.0545	0.46
1	5.0	2.30	0.87	0.33	0.08	0.12	—	0.377	0.142	0.035	0.055	—
9(a)*	3.3	1.63	0.91	0.18	0.06	0.12	—	0.556	0.11	0.035	0.0715	—
A**	3.0	1.40	0.35	0.40	0.12	0.15	0.56	0.250	0.285	0.086	0.107	0.40
14	0.75	0.89	0.05	0.42	0.09	0.20	0.20	0.056	0.472	0.101	0.225	0.225
20	0.658	0.863	0.048	0.43	0.089	0.197	—	0.055	0.504	0.103	0.231	—

* Runs without cold trap.

** Average of runs 6, 7, 8, 9, 15.

decomposed increases and that of C_5^+ hydrocarbon decreases with decreasing pressure of propane. This effect is the opposite to that found when a cold trap was used. The absence of a cold trap does not change either the rate of reaction (Fig. 1) nor the production of C_2 and C_4 hydrocarbons.

The effect of the duration of the run on the nature of the reaction is shown in Table III and Fig. 3. It is seen that rates of decomposition of propane and of production of hydrogen and methane are independent of the length of the run. The effect of the length of run on the production of C_4 and C_5^+ hydrocarbon is somewhat erratic but may be taken as constant within experimental error.

The effect of the addition of hydrogen is shown in Table IV and in Fig. 4. The effect of hydrogen on the reaction is quite evident from these results and will be discussed later. We find that the addition of hydrogen does affect markedly the nature of the reaction but that, in the runs at 3.2 mm, the accumulation of hydrogen in the system as the run progresses does not alter the nature of the reaction (Fig. 3); this is understandable when we realize that the amount of hydrogen produced is small compared to the

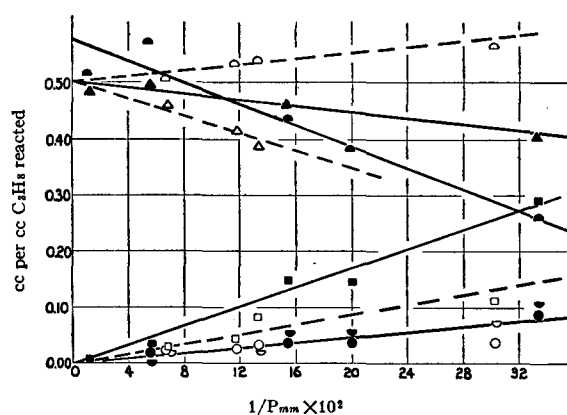


FIG. 2. Effect of working pressure of propane on the reaction. \bullet = hydrogen, \blacktriangle = C_5^+ , \blacksquare = CH_4 , \bullet = C_2 , \bullet = C_4 , and open points = runs without cold trap.

amounts added and that the effect would probably not be detectable with the methods used for analyzing and measuring the fractions.

DISCUSSION

The results of this investigation indicate that the following points are of significance in establishing the mechanism of the reactions of the lower paraffin hydrocarbons with active mercury atoms: (a) At high propane pressures the products consist almost entirely of hydrogen and

TABLE III. Effect of time of run on the reaction at 3-mm propane pressure. Conditions as in Table I.

Run no.	Time hr.	Rate cc/hr.	H_2	Production—cc/hr.				H_2	Production—cc/cc C_3H_8 reacted			
				CH_4	C_2	C_4	C_5^+		CH_4	C_2	C_4	C_5^+
7	1	1.45	0.38	0.39	0.16	0.23	0.70	0.26	0.27	0.11	0.16	0.48
15	2	1.44	0.36 ₅	0.40	0.07	0.18 ₆	0.55 ₅	0.25 ₄	0.277	0.05	0.13	0.36
6	3	1.07	0.19	0.41	0.09	0.12	0.35	0.17	0.38	0.08	0.11	0.33
9	3	1.58	0.44	0.38	0.15	0.05	0.72	0.27 ₅	0.24 ₃	0.09 ₆	0.03	0.45
8	5	1.36	0.36	0.40	0.15	0.04	0.53	0.27	0.29	0.11	0.03	0.39

TABLE IV. Effect of hydrogen on the reaction. Conditions as in Table I.

Run No.	H ₂ added mm	Reaction rate	Production—CC/hr.				cc product/cc C ₃ H ₈ reacted			
			CH ₄	C ₂	C ₄	C ₅ ⁺	CH ₄	C ₂	C ₄	C ₅ ⁺
(a) Working pressure of propane = 3.2 to 3.4 mm										
15	0.00	1.44	0.40	0.071	0.186	0.55	0.277	0.049	0.129	0.358
19	2.75	0.772	0.54 ₅	0.076	0.123	0.224	0.71	0.097	0.16	0.29
17	6.83	0.59	0.56	0.049	0.109	0.179	0.94	0.082	0.184	0.304
16	29.7	0.41	0.39	0.032	0.049	—	0.94	0.039	0.18	—
(b) Working pressure of propane = 0.70 to 0.80 mm										
14	0.00	0.893	0.42	0.09	0.19	0.20	0.47	0.097	0.22	0.22
13	1.34	0.44	0.64	0.09	0.08	0.04	1.43	0.20	0.17	0.08
18	2.75	0.43	0.59 ₇	0.06 ₇	0.04 ₈	0.03	1.38	0.15 ₆	0.11	0.07
12	5.0	0.18	0.40	0.02	0.02	0.02	2.28	0.13	0.13	0.13
11	10.0	0.14	0.36	0.01	0.01	0.03	2.55	0.071	0.095	0.237

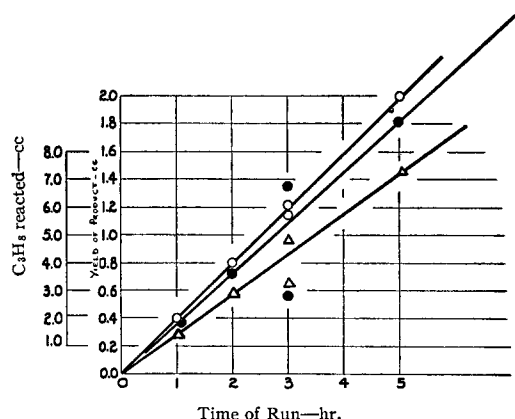
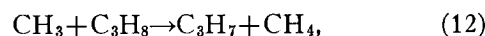
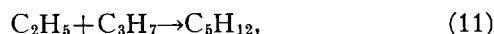
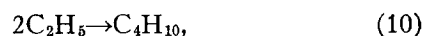
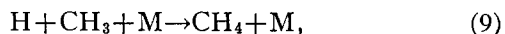
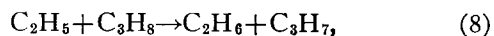
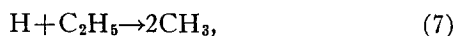
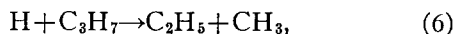
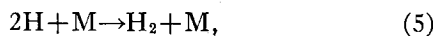
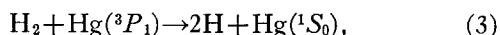
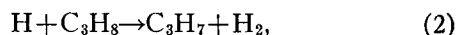
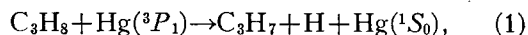


FIG. 3. Effect of length of run on reaction.
 $\bigcirc = \text{CH}_4$, $\bullet = \text{H}_2$, $\triangle = \text{C}_3\text{H}_8$.

hydrocarbons with more than four carbon atoms per molecule. The previous work of Steacie and Dewar⁴ has shown that these hydrocarbons consist principally of hexanes. (b) Decrease in pressure causes a marked decrease in the rate of disappearance of propane; this effect holds even when the rate is corrected for decreased quenching at low pressures. (c) The production of methane and hydrocarbons containing two and four carbon atoms per molecule increases with decreasing propane pressure. (d) The addition of hydrogen markedly alters the nature and the rate of the reaction. This effect becomes increasingly important with decreasing propane pressure. (e) The production of methane is much less prevalent with propane than with ethane at similar pressures.

Steacie and Dewar⁴ proposed the following series of reactions to explain the products of the reaction of propane with $\text{Hg}(^3P_1)$ atoms:



which certainly accounts adequately for the products obtained at high pressures where the "atomic cracking" reactions (6) and (7) were of minor importance. It is of interest to examine the above series more closely and to find out how well it fits the results obtained in the present investigation at low pressures.

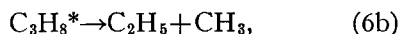
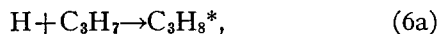
On the basis of the above mechanism we can account for the pressure dependence of the rate corrected for quenching only by an increase in the rates of reactions (5) and (6) with decreasing pressure; this presupposes that hydrogen atoms recombine more readily on the wall than with another molecule as third body.

It has been found that the volume of methane produced per volume of propane reacted varies inversely as the working pressure of propane. This result is in reasonable agreement with the kinetics as outlined in the above mechanism scheme, since decreasing the working pressure of propane will lead to an increase in the rate of reaction (6) relative to that of (2).

The fact that the rate of production of methane is independent of the duration of the run within the limits covered may be taken as evidence that the stationary concentrations of C_3H_7 and H atoms are established instantaneously and that the initial $[\text{H}]$ is not greatly affected by the accumulation of hydrogen in the system although eventually increased quenching by the accumulated hydrogen would increase the rate of production of H atoms, especially in runs at low propane pressures.

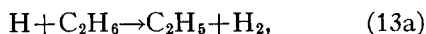
The question now arises as to the relation between the concentrations of propyl radicals, hydrogen atoms, and propane that are necessary to account for the increased rate of production of methane per volume of propane decomposed, bearing in mind the activation energies of reactions (2) and (6). The activation energy of reaction (2) has been estimated¹² to be 10 ± 2 kcal., and the assumptions¹² are that reaction (6) has an activation energy of ≤ 5 kcal. For the rates of (2) and (6) to be equal at room temperature it would be necessary that the concentration of

propyl radicals be 3.35×10^{-4} times that of propane, or that the partial pressure of propyl radicals be 10^{-3} mm in the run at 3.0 mm. Since it is probable that propyl radicals recombine with about zero activation energy it is likely that the actual concentration of propyl radicals would be much lower than this figure. However, if "atom cracking" reactions be regarded as proceeding through the following steps:

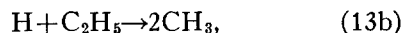


it would seem likely that they would proceed without real activation energy since (6a) is of the same type as the radical recombination reactions which probably do not require real activation energy.¹⁵ If we then assume that $E_6 = 0$, we find that the rates of reactions (2) and (6) will be equal at room temperature when the concentration of propyl radicals is $10^{-8} \times [\text{C}_3\text{H}_8]$, a figure which seems much more likely.

Hence the above mechanism does offer an adequate explanation for the results obtained and indicates that the reactions of propane and ethane with $\text{Hg}(^3P_1)$ atoms are of the same type. The difference in the extent of atomic cracking with ethane and propane is, however, surprisingly large and, if we accept the value of 7 kcal. for the activation energy of the reaction



and assign zero activation energy to the reaction



we find that the above type of mechanism would indicate that atomic cracking, and hence methane production, would be much more serious with propane than with ethane, which is contrary to experimental fact. This discrepancy could be eliminated if either the activation energy of reaction (13a) were greater than 10 kcal. or if reaction (6), although occurring with zero activation energy, had a much smaller steric factor than (13b)—either because of spatial considerations or of more efficient deactivation of C_3H_8^* than of C_2H_6^* . There has been considerable discussion about the activation energy of reaction

(13a) which has been extensively investigated by the Wood-Bonhoeffer technique. However, it has been found that ethane reacts much more rapidly than does propane or butane with H atoms under those conditions, and it seems certain that the activation energy of reaction (13a) is smaller, or at least not greater than that of reaction (2). The assignment of a steric factor to reaction (6) small enough to account for the observed results would seem unwarranted on the basis of present information. The possibility of stabilization of C_3H_8^* formed in reaction (6a) must be ruled out as a possibility since Steacie and Parlee¹² found that the residual propane was entirely light in their investigation of the reaction of deuterium atoms with propane. This also eliminates the possibility that reaction (2) is

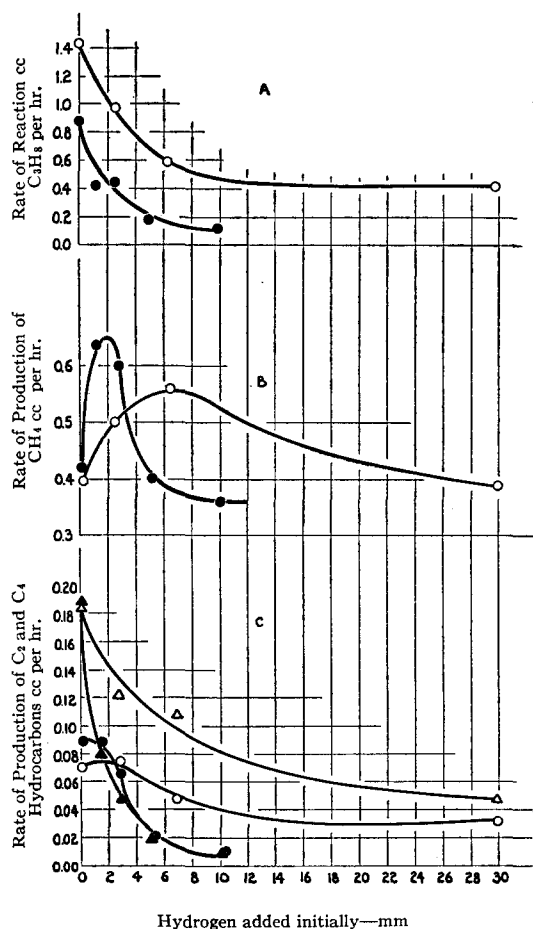
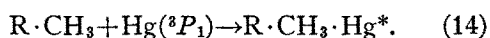


FIG. 4. Effect of added hydrogen on the reaction. Open points = runs at 3 mm; closed points = runs at 0.75 mm. In graph C, circles represent C₂ hydrocarbons and triangles C₄ hydrocarbons.

¹⁵ E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, J. Chem. Phys. 7, 633 (1939).

faster than indicated but appears to be slow because of recombination of C_3H_7 and H. Although it is generally accepted that the activation energy of reaction (13a) is less than that of (2) the relative extents of exchange with ethane and propane are still somewhat uncertain; this point is now under investigation.

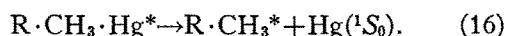
If we examine the steps leading to reaction between a paraffin hydrocarbon, $R \cdot CH_3$, and an active mercury atom more closely the first stage of the process could be represented by the formation of an "active complex" of the type:



This complex can now either react, and the most probable path would seem to be ^{7,8}



or return to the original state. If the latter occurs, in a system in which the $Hg(^3P_1)$ atoms are fully quenched, the energy of the 3P_1 atom will be transferred to the paraffin molecule:



We have omitted the possibility of quenching to the metastable 3P_0 state since $Hg(^3P_0)$ atoms are known to be efficient in causing reactions due to atomic hydrogen in mixtures containing hydrogen molecules,¹⁶ and, presumably, would also be efficient in their reaction with hydrocarbons.

The portion of the molecules that react by a C—H split (i.e., reaction (5)) could be expected to follow along the course outlined in the original mechanism. The excited molecule produced in reaction (16) may either react or be deactivated. Since it is possible that these molecules are similar to thermally activated molecules, we would expect them to decompose by a C—C split.¹⁷⁻¹⁹ Since the extent of deactivation varies as the reciprocal of the total pressure we would expect that the rate of production of methane would also be a linear function of $1/p$ —as found in the present investigation.

¹⁶ E. Meyer, *Zeits. f. Physik* **37**, 639 (1926).

¹⁷ R. N. Pease, *J. Am. Chem. Soc.* **50**, 1779 (1928).

¹⁸ F. E. Frey and D. F. Smith, *Ind. Eng. Chem.* **20**, 948 (1928).

¹⁹ E. W. R. Steacie and I. E. Puddington, *Can. J. Research* **B16**, 411 (1938).

The probable occurrence of ethylene in our products and the low quantum yield at high pressures strengthen the possibility of decomposition at low pressures and deactivation at high pressures of an active propane molecule.

The relative rates of reactions (15) and (16) will depend on the relative ease with which the C—H bond in question is broken to form the radical and HgH . It seems likely that the secondary C—H bonds in propane and butane, and the tertiary bond in isobutane would break more easily than would the primary bonds of ethane. Hence we would expect a relatively greater extent of C—H split with propane and the butanes than with ethane. Moreover it is likely that the active molecules formed in reaction (16) from propane and the butanes, because of the larger number of vibrational degrees of freedom in those molecules, would be longer lived than $C_2H_6^*$ and would thus have greater chances of deactivation. Therefore we would expect less C—C split to occur with propane and butane than with ethane at the same pressures. Hence the active molecule mechanism offers a reasonable explanation for the increased production of methane from ethane and propane with decreasing pressure of the hydrocarbon as well as for the difference found between ethane on one hand and propane and the butanes on the other. This mechanism would also indicate that the reaction of the paraffins with $Hg(^3P_1)$ atoms is of the same general type as the similar reactions of the olefins and diolefins since Le Roy and Steacie and Gunning and Steacie have shown that ethylene²⁰ and butadiene²¹ both react, at least partially, by an active molecule mechanism. The fact that the rate varies inversely as $1/p$ (Fig. 1) is not in accord with the occurrence of an active molecule unless deactivation of $C_3H_8^*$ or recombination of atoms is faster at the wall than in the presence of another molecule as third body.

The explanation of the difference observed in the nature of the products obtained from propane with $Hg(^3P_1)$ and $Cd(^3P_1)$ atoms is also ambiguous. It seems certain that CdH is formed in

²⁰ D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941).

²¹ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **12**, 484 (1944).

these reactions though the formation of HgH in the similar reaction is uncertain. Steacie, Le Roy, and Potvin¹⁰ have pointed out the possibility that the difference between the Cd(³P₁) and Hg(³P₁) reaction of propane lies in the longer life of CdH which may therefore enter into reactions such as:



However, if the reactions of the paraffins with Hg(³P₁) and Cd(³P₁) atoms proceed in both cases by an active molecule mechanism, then the energy distribution may be sufficiently different to account for the altered nature of the products with cadmium.

There is no clear-cut evidence available to help in deciding whether these reactions proceed entirely by a C—H split as originally proposed or by a combination of C—H split and the formation of an activated molecule as suggested in this paper. The activated molecule mechanism has the advantage that it allows explanation for the difference between the products obtained from ethane and Hg(³P₁) atoms and from the similar reactions of propane and the butanes with which the original mechanism cannot be reconciled unless drastic, and unwarranted, changes are made in the accepted value for the activation energy of the reaction between hydrogen atoms and ethane.

Experiments in the Presence of Added Hydrogen

The experiments carried out in the presence of added hydrogen establish the following: (a) The rate of propane disappearance decreases as the amount of hydrogen added initially is increased at constant propane pressure. (b) The rate of production of methane increases to a maximum and then decreases attaining a constant value when larger amounts of hydrogen are added. The yield of methane per cc of propane decomposed is increased by the addition of hydrogen; the extent of this increase is diminished by increase in the propane pressure. (c) The rate of production of C₂ and C₄ hydrocarbons is decreased by the addition of hydrogen; the extent of this decrease varies inversely as the working pressure of propane.

The experiments described were carried out

with propane at 0.75- and 3.25-mm working pressure. It was found that in all cases the effect of added hydrogen was more pronounced in the runs at low propane pressure. Since propane quenches only slightly at these pressures we would have expected that the addition of a small amount of hydrogen, which quenches strongly, would have increased the concentration of H atoms and so increase the rate of both reactions (2) and (6). We find, however, that the rate of disappearance of propane is strongly retarded; the rate of (6) is increased with small amounts of hydrogen but is repressed by the addition of larger amounts. The addition of small amounts of hydrogen increases the rate of production of H atoms since the extent of quenching is greater than with propane alone. Increasing the rate of production of H atoms must increase somewhat the rate of production of propyl radicals by reaction (2). Since we assume that propane disappears only by the production of propyl radicals and since these radicals are produced principally by reactions (1) and (2), we must assume, to account for the decreased reaction rate, that reaction (1) is repressed to a greater extent than (2) is increased by the addition of hydrogen. This appears to be a reasonable assumption since the added hydrogen competes with propane for the available Hg(³P₁) atoms and since hydrogen atoms probably disappear more rapidly by reactions (5) and (6) than by (2). The increased rate of production of methane with small amounts of hydrogen is then due to an increase in the rate of reaction (6) which more than compensates for the decreased rate of the over-all production of propyl radicals in (1) and (2). The addition of larger amounts of hydrogen, beyond the pressure required for complete quenching, does not serve to increase the rate of production of H atoms but does increase the concentration of third bodies and so lowers the stationary H atom concentration by reaction (5), thus causing a decrease in the rates of reactions (2) and (6).

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