

A Further Investigation of the Mercury Photosensitized Polymerization of Propylene

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law in the other two cases is in the opposite direction, as has been observed for the anhydrous sulfate of Pr.²⁴

The disagreements of our data on the sulfate with those obtained by Sucksmith⁹ should be pointed out.

²⁴ See reference 19, pp. 306-309.

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A Further Investigation of the Mercury Photosensitized Polymerization of Propylene

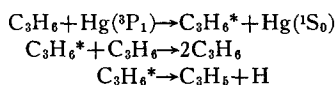
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(Received June 10, 1948)

A reinvestigation has been made of the authors' earlier work on the reaction of propylene with mercury ($^3\text{P}_1$) atoms at 30°C in a static system, with special concentration on the products of the reaction.

The mechanism

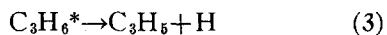
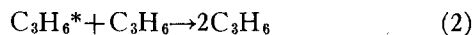
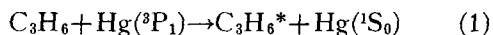


which was proposed in the earlier work has been confirmed. Some twenty-two different products were identified at low pressures, all of which, with the exception of acetylene, can be explained as the result of interactions of the free radicals present.

The quantum yield of the reaction reaches a maximum of 0.18 at 6.5 mm, and falls to 0.04 at 72 mm.

INTRODUCTION

IN an earlier publication,¹ the authors came to the conclusion that propylene reacted with mercury ($^3\text{P}_1$) atoms at 30°C by an activated molecule mechanism according to the sequence:



followed by polymerization reactions of the type



In the investigation reported below, the previous work has been repeated, and a much more detailed analysis of the products of the reaction has been made.

EXPERIMENTAL

A general description of the apparatus and experimental technique has already been given in a previous publication.²

The measurements were made in a static system at $30.00 \pm 0.01^\circ\text{C}$. The cylindrical quartz cell had a volume of 240 cc. The total volume of the system was 1050 cc.

The analyses of the condensible products of the reaction were made on a mass spectrometer through arrangement with the National Bureau of Standards. The sampling technique employed, as well as the method of analysis of the products, non-condensable in liquid air, have been previously described.³

The propylene used was obtained from the Ohio Chemical and Manufacturing Company.

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¹ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 57 (1946).

² H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **12**, 484 (1944).

³ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 544 (1946).

TABLE I. Composition of original propylene.

Component	Mole percent
Propylene	99.6
Propane	0.1
Butenes	0.15
Methyl pentenes	0.02
Dimethyl butanes	0.08
Trimethyl butanes	0.03

After several trap-to-trap distillations, the middle fraction was collected and stored in a two-liter flask provided with a Warrick-Fugassi valve.⁴ The composition of the propylene used, as determined on the mass spectrometer is shown in Table I.

RESULTS

In the present investigation the linearity of the pressure *vs.* time curves, which we had found previously,¹ was confirmed. The pressure rates are given in Table II and Fig. 1 together with the actual rates of consumption of propylene. By referring to Fig. 1, it can be seen that, at higher pressures, polymerization is practically the only reaction occurring. The rapid decrease in the rate of propylene consumption with increasing pressure in the complete quenching region is compelling evidence in favor of collisional deactivation. The maximum rate of consumption of propylene seems to occur at an initial pressure of 6.5 mm. In our previous publication¹ this maximum occurred at about 9 mm and since the same source and electrical characteristics were used in both series of measurements, the difference must be attributed to experimental error.

The products of the reaction are shown in Table III. It is interesting, first of all, to note that the rate of formation of hydrogen is five times greater than that of methane, in the complete quenching region. This is in complete agreement with our earlier work.¹ The enormous number of products formed at low initial pressures serves to show very pointedly the tremendous complexity of free radical reactions in hydrocarbons. The over-all reaction becomes considerably simpler at higher pressures, where the interactions of free radicals with each other become less important than the disappearance of

TABLE II.

P_0 mm	$-\Delta P/\Delta t$ mm/min. $\times 10^2$	$-d(C_3H_6)/dt$ mm/min. $\times 10^2$	moles/min. $\times 10^6$	ϕ (Propylene)
1.70	1.62	1.93	1.08	0.10 ₈
3.83	2.18	2.90	1.61	0.16 ₁
6.32	2.40	3.23	1.80	0.18 ₀
9.67	2.18	2.82	1.57	0.15 ₇
20.4 ₉	1.87	2.18	1.22	0.12 ₂
33.4 ₉	1.70	1.90	1.06	0.10 ₆
39.7 ₁	1.67			
53.2 ₆	1.33			
59.8 ₇	1.07	1.03	0.58	0.05 ₈
72.2 ₆	0.68	0.70	0.39	0.03 ₆

these radicals in the propagation of polymer chains. The data presented in Table III are to be regarded only as rough semi-quantitative indications of the minor products of the reaction.

The C_2 hydrocarbon which we found in our earlier work¹ to correspond by combustion analysis to C_2H_4 , was apparently, from Table III, a roughly equimolar mixture of acetylene and ethane. It is also evident from Table III that the liquid which we isolated in our earlier runs must be a complex mixture of saturated and unsaturated hydrocarbons in the C_5 to C_8 range.

The polymer formed in the reaction has already been adequately described.¹

QUANTUM YIELD

The incident light intensity was determined indirectly by filling the cell with ethylene, at an initial pressure of 13 mm, and determining the initial rate of formation of hydrogen. The hydrogen was determined by oxidation over copper oxide at 250°C. The average of eight runs gave $dH_2/dt = 2.5 \pm 0.1 \times 10^{-6}$ moles/min. Allen and

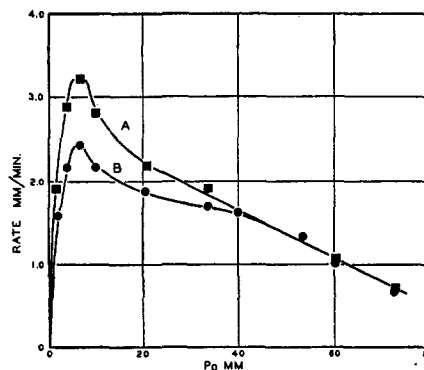


FIG. 1. Squares: rate of consumption of propylene *vs.* initial pressure. Circles: rate of pressure decrease *vs.* initial pressure.

⁴ E. Warrick and P. Fugassi, Ind. Eng. Chem. (Anal. Ed.) 15, 13 (1943).

TABLE III. The products of the reaction.

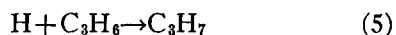
Initial pressure mm	1.70	3.83	6.32	9.67	20.4 ₉	33.4 ₉	53.2 ₈	59.8 ₇	72.2 ₆
Product	All rates are in moles per minute $\times 10^6$.								
Hydrogen	0.015	0.056	0.066	0.060	0.044	0.031	0.027	0.021	0.020
Methane	0.056	0.040	0.031	0.019	0.011	0.006	0.005	0.004	0.004
Acetylene	0.005	0.022	0.041	0.031					
Ethane	0.016	0.013	0.009	0.015					
Propane	0.044	0.091	0.076	0.052	0.018				
Butenes		0.020	0.041	0.040	0.043	0.043	0.020	0.018	0.033
Butanes	0.010	0.047	0.050	0.031					
Pentadienes		0.005	0.014						
Pentenenes	0.005	0.025	0.050	0.015					
Pentanenes	0.011								
Benzene		0.001							
Cyclohexadienes			0.003						
Hexadienes		0.006	0.040	0.022	0.018				
Methyl Pentadienes				0.005					
Methyl Pentenes	0.003	0.024	0.067	0.029	0.010	0.020			
Dimethyl Butanes	0.004	0.022	0.059	0.031	0.001				
Heptynes	0.001			0.007					
Trimethyl Butanes	0.006			0.013	0.006	0.008			
Dimethyl Pentanes		0.022	0.035						
Ethyl Cyclohexenes		0.001	0.003						
Ethyl Cyclohexanes		0.002	0.004						
Trimethyl Pentenes	0.001			0.004					

Gunning⁵ have recently shown that the initial quantum yield of hydrogen formation in the ethylene reaction is 0.25. And therefore, $I_{abs} = 1.0 \times 10^{-5}$ einsteins/min. The quantum yields of propylene disappearance for each run are shown in the last column of Table II. In our previous work¹ we found that $\phi_{C_3H_6} = 0.15 \pm 0.05$ at 14 mm. On the basis of our present data $\phi_{C_3H_6} = 0.14$ at 14 mm, in agreement, within experimental error, with our earlier value. The effect of collisional deactivation is strikingly evident in the fact that the quantum yield decreases from its maximum value of 0.18 at 6.5 mm to 0.04 at 72 mm.

DISCUSSION

The results of the present investigation seem to show fairly conclusively that the activated molecule mechanism, proposed in our previous publication,¹ describes very adequately the kinetics of the decomposition of propylene by mercury (³P₁) atoms. This mechanism is summarized in reactions (1) to (4).

In some recent work on the mercury photosensitized hydrogenation of propylene, Moore⁶ has shown very convincingly that in the reaction

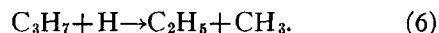


⁵ G. A. Allen and H. E. Gunning, J. Chem. Phys., in press.

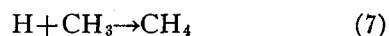
⁶ W. J. Moore, paper presented at the Chicago meeting of the American Chemical Society, April, 1948.

the radical formed is isopropyl, since he found that di-isopropyl was the only important hexane formed. Our results tend to confirm Moore's findings, in view of the fact that dimethyl butane is the only hexane found in our products. Of course, in our case dimethyl butane is only an important product at low pressures where radical recombination would assume a significant role in the reaction.

It would seem unwise, without more extensive data, to attempt to write reactions to account for the large number of products found at lower pressures. It is important to note, however, that, with the exception of acetylene, all the significant products found at lower pressures could quite naturally arise by the interaction of the free radicals already postulated in reactions (3) to (5), together with methyl and ethyl radicals formed by an "atomic cracking" reaction of the type



The marked rise in the rate of formation of methane at very low pressures, as recorded in Table III suggests that the reaction

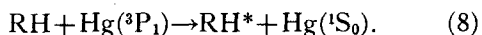


might be occurring to a major extent under these conditions at the wall. As a matter of fact it is quite possible that the wall plays a very important part as a third body for radical recombination.

nation in the formation of many of the products found at low pressures.

CONCLUSIONS

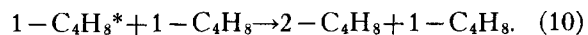
The investigations which the authors have made on the alkyl-substituted alkenes and alkadienes^{1,3,7} offer fairly unequivocal evidence for the initial formation of an activated molecule by the reaction



The low quantum yields of the reaction, together with the decreasing rate with increasing pressure follow from the collisional deactivation of the activated molecule formed in (8) by



Reaction (9) is somewhat different in the case of butene-1,⁷ owing to its ease of isomerization to butene-2, with the result that in butene-1, collisional deactivation seems to proceed in the main by



On the basis of the authors' work³ isobutene seems to be excluded from this generalization, since the evidence for activated molecule formation with isobutene was by no means compelling. However, recently the isobutene reaction has been reinvestigated by Allen and Gunning⁵ up to initial pressures of 250 mm. The results of this investigation definitely bring isobutene into line with the other alkyl-substituted olefins, which react with mercury (³P₁) atoms by reactions (8) and (9).

The actual chemical reaction in these compounds results from the unimolecular decomposition of the activated hydrocarbon molecule formed in (8), by the reaction



as we pointed out in our previous paper on propylene,¹ this bond split would likely occur at one of the C—H bonds in a position once-removed from the double bond. Polymerization would then proceed by the successive addition of olefin molecules to the radicals generated in (11).

Laidler⁸ has recently discussed the electronic

configuration of activated molecules of the type postulated in reaction (8). He has suggested that the Wigner Spin Conservation Principle may apply to collisions between photo-excited atoms and molecules. And since the mercury atom in reaction (8) undergoes a triplet-to-singlet transition in reverting to the ground state, the hydrocarbon, which is normally in a singlet state, must be in a triplet state after collision with the mercury (³P₁) atom, in order that spin angular momentum be conserved in the over-all process. Laidler's explanation of the large quenching cross sections of the unsaturated hydrocarbons in comparison with the alkanes, and of the tendency in the former to form activated molecules, derives its strength from its plausibility, rather than from any direct evidence for the existence of such triplet states in hydrocarbons. However, Lewis and Kasha,⁹ on the basis of their phosphorescence studies, have concluded that there is a triplet state in ethylene at 72–74 kcal. above the ground (singlet) state. Theoretical calculations of the singlet-triplet separation in ethylene were made by Hartmann¹⁰ who obtained the rather low value of 70 kcal. Craig¹¹ has recently repeated Hartmann's calculation and obtained a value of 95 kcal. or greater. Now the transition $\text{Hg}(^6\text{P}_1) \rightarrow \text{Hg}(^6\text{S}_0)$ in reaction (8) corresponds to a transfer of 112 kcal. per mole to the hydrocarbon molecule, and if Craig's calculation is correct, it is quite possible that the resonance for the energy exchange in reaction (8) might be very satisfactory, leaving only a small amount of residual energy to be imparted to the vibrational degrees of freedom of the hydrocarbon molecule.

ACKNOWLEDGMENT

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Our thanks are also due to Mr. Yves Lupien for assistance in performing some of the measurements.

⁷ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 581 (1946).

⁸ K. J. Laidler, *J. Chem. Phys.* **15**, 712 (1947).

⁹ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).

¹⁰ H. Hartmann, *Zeits. f. physik. Chemie* **B53**, 96 (1943).

¹¹ D. P. Craig, *J. Chem. Phys.* **16**, 158 (1948).