

The Mercury Photosensitized Reactions of Propylene and Isoprene

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Citation: [The Journal of Chemical Physics](#) **14**, 57 (1946); doi: 10.1063/1.1724106

View online: <http://dx.doi.org/10.1063/1.1724106>

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The Mercury Photosensitized Reactions of Propylene and Isoprene*

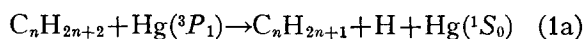
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(Received November 21, 1945)

An investigation has been made of the reactions of propylene and isoprene with mercury (3P_1) atoms, at 30°C, in a static system. The reactions are similar in that the rates of consumption of both propylene and isoprene decrease with increasing pressure in the range of complete quenching. In addition, the quantum yields of both reactions are low. The products of the propylene reaction are liquid polymer and hydrogen, together with smaller amounts of methane, ethylene, and hexene. The principal steps in the mechanism proposed for the propylene reaction are $C_3H_6 + Hg(^3P_1) \rightarrow C_3H_6^* + Hg(^1S_0)$; $C_3H_6^* + C_3H_6 \rightarrow 2C_3H_6$; $C_3H_6^* \rightarrow C_3H_5 + H$; $H + C_3H_6 \rightarrow C_3H_5 + H_2$; $H + C_3H_6 \rightarrow CH_3 + C_2H_4$; followed by polymerization reactions of the type $C_3H_5 + C_3H_6 \rightarrow C_6H_{11}$, etc.

INTRODUCTION

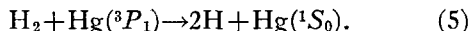
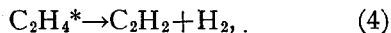
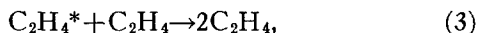
THE saturated and the unsaturated hydrocarbons exhibit striking differences in their reactions with mercury (3P_1) atoms. In the paraffins the initial step seems to be of the type¹



or



The investigations of LeRoy and Steacie on ethylene,² and of Gunning and Steacie on butadiene,³ at room temperature, suggest that the initial step in the reactions of these molecules with mercury (3P_1) atoms involves the formation of an activated molecule, or perhaps an activated hydrocarbon-mercury complex. LeRoy and Steacie,² for example, postulated the following sequence for ethylene:



Polymerization was initiated by the H atoms produced in reaction (5).

One obvious structural difference between the

paraffins, on the one hand, and ethylene and butadiene, on the other, is that in the latter all the C—H bonds are olefinic. In this connection, Taylor and his associates⁴ found a high activation energy (>10 kcal.) for the reaction of methyl radicals with ethylene, while for the corresponding reaction with propylene they found an activation energy of only 3.1 kcal. They attributed the low activation energy of methane formation with propylene to the weakness of C—H bonds in a position once removed from a double bond. Thus, in propylene, they deduce that the C—H bond strength in the methyl group must be about 5 kcal. less than in ethane; or in other words about the same value as the secondary C—H bond in propane.

With the above considerations in mind, an investigation of the reactions of mercury (3P_1) atoms with propylene and isoprene, both possessing C—H bonds once removed from a C=C bond, seemed particularly instructive. The details of these investigations are reported below.

EXPERIMENTAL

For a description of the apparatus employed, and the experimental technique, reference should be made to the paper of Gunning and Steacie on the mercury photosensitized reactions of butadiene.³ No important alterations were made in the apparatus for the present investigations.

The propylene was obtained from the Ohio Chemical and Manufacturing Company. After several trap-to-trap distillations, the middle

* Contribution No. 1345 from the National Research Laboratories, Ottawa, Canada.

¹ See D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 676, 683 (1942) for a summary.

² D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941).

³ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **12**, 484 (1944).

⁴ H. S. Taylor, *Ann. N. Y. Acad. Sci.* **41**, 231 (1941).

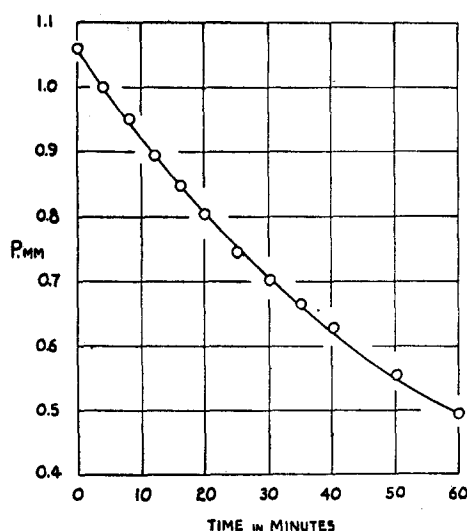


FIG. 1. Pressure vs. time for a typical static run.

fraction was collected and stored in a flask, provided with a Warrick-Fugassi valve.⁵

The isoprene was an Eastman product. It was dried over freshly fused calcium chloride, and stored in a small bulb, attached to the cell system by a Warrick-Fugassi valve.⁵

All runs were made in a static system. The cylindrical quartz cell employed had a volume of 240 cc, and was immersed in a water thermostat, maintained at $30.00 \pm 0.01^\circ\text{C}$.

RESULTS

I—Propylene

The Effect of Pressure on the Rate

Figure 1 shows a typical one-hour run at an initial pressure of about 1 mm of propylene. As soon as the lamp is turned on, the pressure begins to fall linearly with time, and at the same time the window of the cell slowly becomes covered with tiny droplets of liquid polymer. When the amount of polymer accumulated on the cell window becomes sufficient to decrease effectively the amount of $\lambda 2537$ entering the cell, the rate of pressure decrease begins to fall off. Unlike butadiene or ethylene, there is neither a period of induction nor an initial pressure rise observable. The polymer can be seen on the windows of the cell even in the early stages of the run.

⁵ E. Warrick and P. Fugassi, *Ind. Eng. Chem. Anal. Ed.* **15**, 13 (1943).

In Fig. 2, the actual rate of propylene consumption, $[-d(\text{C}_3\text{H}_6)]/dt$, in moles per minute, is plotted against the initial pressure. The rate of propylene consumption, as can be seen from the diagram, reaches a maximum at about 10 mm. Below 10 mm, the rate is less, owing undoubtedly to incomplete quenching. The decrease in rate above 10 mm strongly suggests collisional deactivation.

Products of the Reaction

The products of the reaction were particularly difficult to investigate, since over 90 percent of the propylene molecules decomposed went toward the formation of polymer. The procedure adopted was to analyze the gas, non-condensable in liquid air, and the residual propylene for each run. A complete analysis was done by collecting the gas from 10 to 15 runs at 10-mm initial pressure, and performing a careful fractionation of the products using the modified Ward method.³

The products, non-condensable in liquid air, proved to be a mixture of hydrogen and smaller quantities of methane. The results of these analyses are tabulated in Table I. Each value is the average of two separate runs.

The identity of the methane was established by combustion in excess oxygen.

Analysis of the accumulated products resulted in the isolation of a small amount of C_2 fraction, which upon combustion proved to be ethylene. At 10-mm pressure, approximately 0.01 mole of ethylene was produced per mole of propylene decomposed.

Since it was suspected that methyl acetylene might be present, a careful analysis of the C_3 fraction was made for acetylenic compounds, using the method of Ross and Trumbull, as

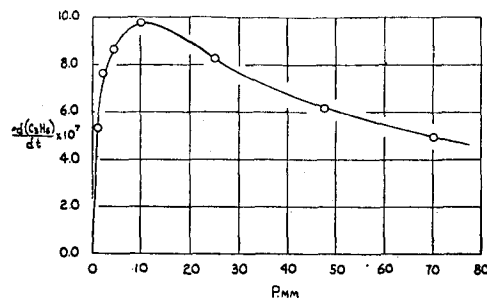


FIG. 2. The rate of propylene consumption in moles per minutes vs. the initial pressure.

modified by LeRoy and Steacie.² No trace of any such compound could be found. Allene, however, which is an isomer of methyl acetylene, might be present.

The fractionation of the products of 10 runs at 10 mm produced about 0.1 cc of a volatile liquid, whose vapor pressure corresponded roughly to hexene. A solution of this liquid in chloroform was found to discolor a dilute solution (0.05*M*) of bromide in glacial acetic acid, suggesting the presence of one or more double bonds in the compound.

The polymer formed in the reaction was a clear, colorless, viscous liquid, completely soluble in benzene. The fact that the polymer is both liquid and soluble would suggest that the molecules are of the linear type, and of relatively low molecular weight.

Quantum Yield

A relative determination of the quantum yield was made by comparison with the initial pressure rise in the mercury photosensitized reaction of ethylene. LeRoy and Steacie² obtained the value 0.37 at 13 mm for the quantum yield of the ethylene reaction. The average of four runs gave the value 0.15 ± 0.05 at 14 mm for the propylene reaction.

II—Isoprene

Eight runs were made with isoprene over the pressure range from 40 to 225 mm. The rate of pressure decrease *vs.* initial pressure is plotted in Fig. 3. The rate falls off in a similar manner to propylene, but not quite as rapidly.

A complete analysis of the products has not yet been made. However, preliminary analyses show that well over 90 percent of the isoprene decomposed forms polymer. A small amount of

gas, non-condensable in liquid air, was formed, which upon analysis proved to be pure hydrogen. At 40 mm initial pressure, 0.0014 mole of hydrogen was formed per mole of isoprene decomposed, in a one-hour run.

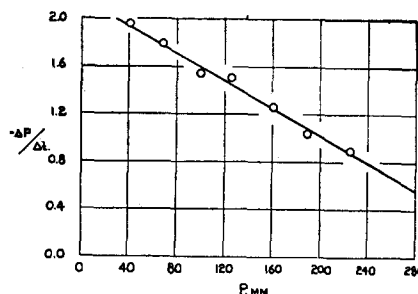


FIG. 3. The rate of pressure decrease in mm per minute *vs.* the initial pressure.

Since the same light intensity was used in both the isoprene and the propylene runs, the quantum yield for the isoprene reaction must be in the neighborhood of 0.2.

DISCUSSION

I—Propylene

Any mechanism proposed to explain the reaction of propylene with mercury (3P_1) atoms must be consistent with the following facts.

(a) The pressure-time curve is linear even in the initial stages of the reaction. The rate of pressure decrease diminishes owing simply to accumulation of polymer on the window of the cell.

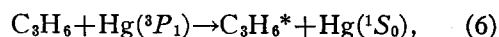
(b) Polymer is present even in the initial stages of the reaction.

(c) The products of the reaction are a liquid polymer, soluble in benzene and hydrogen, together with smaller amounts of methane, ethylene, and possibly hexene.

(d) The rate of propylene consumption, and the rates of hydrogen and methane formation decrease with increasing pressures above 10 mm.

(e) The quantum yield is 0.15.

The decrease in rate with increasing pressure over the range of complete quenching suggests, by analogy with ethylene and butadiene, a primary step of the type:

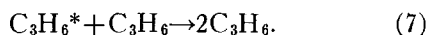


where $C_3H_6^*$ represents either an activated

TABLE I.

P_0	$-d(C_3H_6)/dt$	$d(H_2)/dt$	$d(CH_4)/dt$	B/C
mm	Moles per min. $\times 10^7$			
1.06	5.3 ₃	0.46 ₂		
1.91	7.6 ₃	0.51 ₁	0.08 ₉	5.7
4.23	8.6 ₃	0.53 ₉		
9.62	9.7 ₈	0.56 ₄	0.13 ₄	4.2
24.9	8.2 ₄	0.40 ₉	0.10 ₂	4.0
47.3	6.1 ₇	0.22 ₉	0.035	6.5
70.0	4.9 ₅	0.12 ₇	0.036	3.5

molecule, or perhaps an activated propylene-mercury complex. Both the decreasing rate and the low quantum yield could then be satisfactorily accounted for by the collisional deactivation reaction

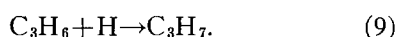


The absence of either an initial pressure rise, or a period of induction in the pressure-time curve, together with the fact that polymer is present even in the early stages of the reaction, suggests that free radical processes must occur early in the reaction. The reaction



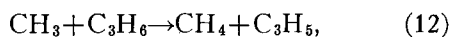
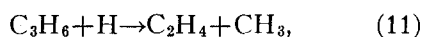
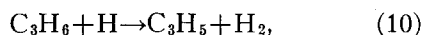
would have the net effect of generating two radical chains for each mole of propylene decomposed. Indeed in view of the presence of the weak C-H bonds in propylene,⁴ which differentiate propylene from ethylene and butadiene, reaction (8) might be expected to be faster than the corresponding reaction for butadiene and ethylene.

The H atoms generated in (8) would react rapidly with propylene generating propyl radicals



The activation energy of this reaction is low, probably less than 5 kcal.⁶

As Rabinovitch, Davis, and Winkler⁷ pointed out, reaction (9) is exothermic to the extent of about 40 kcal. Consequently the hydrogen, methane, and ethylene found in the products could be explained by the reactions



where (10) and (11) involve an energy-rich propyl radical as intermediate. Reaction (12) has an activation energy of 3.1 kcal.,⁴ and it is likely that reaction (10), which is the analogous reaction with H atoms, would have approximately the same activation energy. In addition to forming methane, the methyl radicals would

generate polymer chains by the reaction



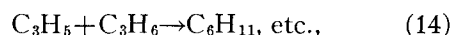
By analogy with the reaction of methyl radicals with ethylene,⁶ this reaction should have an activation energy of about 1.5 kcal.

From Table I, it can be seen that the rates of both the hydrogen and the methane formation decrease with increasing pressure over the range of complete quenching. Moreover, the ratio of these two rates is a constant within experimental error, and equal to about 4.8. The sequence (9) to (13) satisfactorily accounts for these facts. We can express this ratio as a function of the individual rate constants by a steady-state calculation, from which we obtain the expression

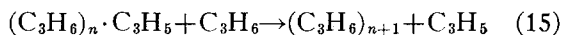
$$\frac{d(\text{H}_2)/dt}{d(\text{CH}_4)/dt} = 4.8 = \frac{k_{10}}{k_{11}} \left[1 + \frac{k_{13}}{k_{12}} \right].$$

If we assume that all these reactions have the same steric factor, and assign the values $E_{10}=3.1$, $E_{12}=3.1$, and $E_{13}=1.5$, to reactions (10), (12), and (13), respectively, reaction (11) would have the surprisingly low value of about 2-3 kcal. for its activation energy. Of course this reaction can occur only through the formation of an activated propyl radical.

Polymerization would be initiated in the main by the allyl radicals formed in (8), (10), and (12),



although, of course, the propyl radicals formed in (9), and the methyl radicals formed in (11), are both capable of forming polymer chains. The growing polymer chains formed by a continuation of reaction (14) could be represented by the formula $(\text{C}_3\text{H}_6)_n \cdot \text{C}_3\text{H}_5$. It is not likely that n would be very large, since as Taylor and Smith⁸ pointed out, propylene is an extremely efficient chain breaker, and, therefore, chain-transfer steps of the type



would be expected to occur before n became very large. Reaction (15), it will be observed, would have the net effect of breaking one chain and initiating another, and consequently the

⁶ *Annual Tables of Physical Constants*, Section 602(c) (1942).

⁷ B. S. Rabinovitch, S. G. Davis, and C. A. Winkler, *Can. J. Research* **B21**, 251 (1943).

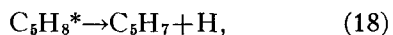
⁸ H. S. Taylor and J. O. Smith, Jr., *J. Chem. Phys.* **8**, 543 (1940).

short-chain liquid polymer isolated in the mercury-photosensitized reaction could be satisfactorily accounted for by reactions of this type.

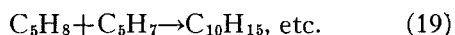
The small amount of liquid dimer found in the product might have been formed either by the dimerization of propylene, or by the recombination of allyl radicals.

II—Isoprene

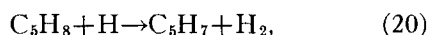
Both the low quantum yield and the decreasing rate with increasing pressure seem to suggest that isoprene follows the same general pattern of reaction as propylene,



followed by polymerization by the free radicals formed in (18),



The very small quantity of hydrogen formed would indicate that, if it is produced by a similar reaction to propylene, i.e.,



this reaction must occur only to a very small extent.

Since a detailed analysis of the products has not yet been made, it is not possible at this time to set up a complete mechanism for the reaction. However, it is fairly clear from the preliminary investigation that isoprene reacts with mercury ($^3\text{P}_1$) atoms in an essentially similar manner to propylene.

CONCLUSIONS

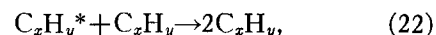
The investigations of LeRoy and Steacie on ethylene,² of Gunning and Steacie on butadiene,³ and the present investigation on propylene and isoprene seem to show that the substituted and the unsubstituted alkenes and alkadienes all

react with mercury ($^3\text{P}_1$) atoms at room temperature by an activated molecule mechanism. The essential difference between ethylene and butadiene, on the one hand, and propylene and isoprene, on the other, lies presumably in the presence in the latter of weakly bound hydrogens in their methyl groups.

If we allow C_xH_y to represent any of the above-mentioned hydrocarbons, we find that the two initial steps,

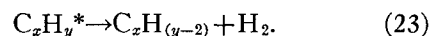


and



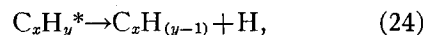
are common to all.

The activated molecules formed from ethylene and butadiene split mainly into hydrogen and a more unsaturated hydrocarbon,



The concentration of hydrogen builds up in the system until it quenches the mercury ($^3\text{P}_1$) atoms to an appreciable extent by reaction (5), thereby initiating polymerization.

The activated propylene and isoprene molecules, on the other hand, owing to their weak C—H bonds, split into an H atom and a radical,



initiating polymerization immediately thereby.

The low value for the quantum yield (0.15–1.0) found in all these reactions suggests that reaction (22) must be extremely efficient. However, there are probably other factors involved. Under static conditions the concentration of mercury atoms in the cell is always high enough to absorb all the resonance radiation within a few millimeters from the cell window. This fact, coupled with the high quenching efficiencies of the unsaturated hydrocarbons, would seem to limit the zone of reaction to a thin layer close to the cell window, rather than throughout the body of the cell. Under these conditions it is likely that wall effects would become significant.