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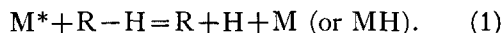
The Cadmium (3P_1) Photosensitized Reactions of the Lower Olefins*

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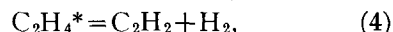
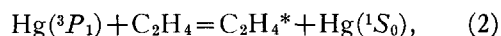
(Received September 3, 1942)

An investigation has been made of the cadmium (3P_1) photosensitized reactions of ethylene, propylene, butene-1, and butene-2. The low quantum yields are attributed to the influence of the C=C bond on the actual quenching process and are not inconsistent with the data on C-H bond strengths.

SEVERAL investigations have been made on the reactions of the lower paraffins with $Hg(^3P_1)$ and $Cd(^3P_1)$ atoms.¹ In every case the primary step was found to be



On the other hand the olefins react somewhat differently. The reaction of $Hg(^3P_1)$ atoms with ethylene involved the steps



as well as the reaction corresponding to (1). $Cd(^1P_1)$ and $Zn(^1P_1)$ atoms appeared to react in the same way, the importance of (1) relative to (2), (3), and (4) decreasing in the order $Zn(^1P_1) > Cd(^1P_1) > Hg(^3P_1)$. The reaction with $Cd(^3P_1)$ atoms was found to have a very low quantum yield (*ca.* 0.01).² These reactions have been discussed in relation to the corresponding excitation energies.¹

The difference between the paraffins and ethylene would seem to be closely connected with the presence of the C=C bond in the latter as compared to the C-C bonds in the paraffins, and the effect of these bonds on the C-H bond strength. The problem then presented itself of investigating the reactions of hydrocarbons having C-C as well as C=C bonds, namely, the other olefins. With this in mind a series of runs was made using $Cd(^3P_1)$ atoms with propylene, butene-1, and butene-2, as well as ethylene.

* Contribution No. 1083 from the National Research Laboratories, Ottawa, Canada.

¹ See D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 676 (1942) for a summary of these reactions as well as those of $Na(^2P)$, $Hg(^3P_1)$, $Cd(^3P_1)$, $Cd(^1P_1)$, $Zn(^3P_1)$ and $Zn(^1P_1)$ atoms with ethylene.

² E. W. R. Steacie and R. Potvin, *Can. J. Research* **B18**, 47 (1940).

In every case reaction was found to be slow, so most of the measurements were made in a static system similar to that described previously.³ For this purpose cadmium turnings were placed directly in the cell. The apparent volume of this system was 558 cc. Some runs were made in a circulating system in an attempt to collect products.

The results of the static runs are shown in Fig. 1. In every case the initial pressure was 225 ± 2 mm. The runs were made in the order Δ , \bullet , \square , \circ , \bullet , \circ , so the variations in rate cannot be attributed to a progressive decrease in

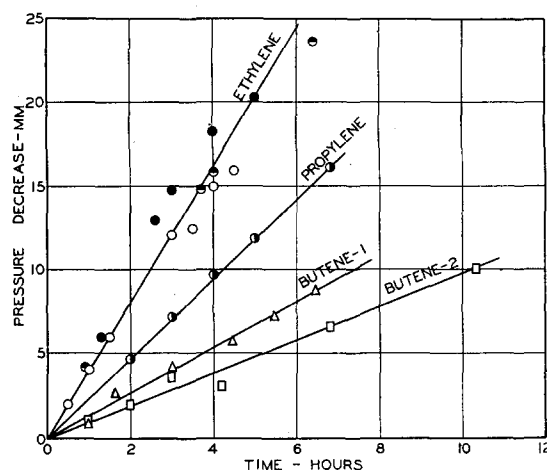


FIG. 1. Pressure decrease vs. time for the four olefins. Initial pressure 225 ± 2 mm.

light intensity. As shown by the curves, the rates are in the order ethylene $>$ propylene $>$ butene-1 $>$ butene-2.

PRODUCTS

In view of the small amount of reaction a complete analysis of the products offered con-

³ E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.* **10**, 22 (1942).

siderable difficulty. However a limited amount of significant data was obtained.

(a) Ethylene

One run was made in which acetylene was measured. It was found to be present to the extent of 0.16 percent, but since the pressure decrease for the same run was 8.8 percent the reaction leading to acetylene formation must be of small importance compared to that leading to polymerization. No measurable quantity of non-condensable gas (hydrogen or methane) was found.

(b) Propylene

No non-condensable gas was found in a $7\frac{1}{2}$ -hour run in the circulating system, and the entire sample distilled as propylene, although cyclopropane or propane could have been detected if present.

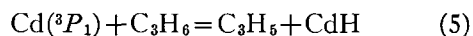
(c) Butene-1

A 23-hour run was made in the circulating system. The initial pressure was 335 mm and the final pressure was 287 mm. No non-condensable gas was found and only 26 cc of gas were distilled over before the temperature reached that of boiling butene-1. Most of this was probably butene. There were 573 cc of gas distilling in the butene-1 range and approximately 45 cc in the trans-butene-2 range. There remained a residue of higher boiling liquid which was not distilled. The indication of butene-2 may or may not be significant.

(d) Butene-2

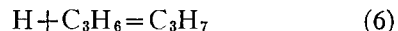
This reaction was even slower than that of butene-1. A $21\frac{1}{2}$ -hour run was made in the circulating system using an initial pressure of 327 mm. The pressure decrease was only about 6 mm. Approximately 4 cc of non-condensable gas were found, which is not very significant since a small amount of air may have leaked in during the transfer of the gas to the still. No other gas of smaller molecular weight than butene was found; consequently it is not surprising, in view of the small pressure change, that no appreciable amount of higher boiling liquid was found.

The most striking result of this investigation is the slow rates observed for propylene and the two butenes. As mentioned before, the initial step in the reaction of $\text{Cd}(^3P_1)$ atoms with the paraffins is the breaking of the C—H bond with the formation of CdH and the corresponding alkyl radical. Taylor and Smith⁴ found a very low activation energy (3.1 kcal.) for the reaction of methyl radicals with propylene and attributed it to a low C—H bond strength on the carbon remote from the double bond. They suggested that the strength of this bond was about 5 kcal. less than that in ethane. Since recent estimates of the C—H bond strength in ethane are in the range 96 to 98 kcal.,⁵⁻⁷ this would place the corresponding value for propylene in the range 91 to 93 kcal., a value close to that of the weakest C—H bond in propane.⁵ Consequently one would expect that the reaction



would take place readily. Similar considerations should obtain for butene-1 and butene-2.

It is known that the reaction



takes place readily,⁸ leading to the formation of hexane and propane, together with smaller amounts of methane, ethane, butane, and pentane. Also Taylor and Smith⁴ found considerable polymerization of propylene which they stated

TABLE I.

Olefin	Quenching efficiency	Paraffin	Quenching efficiency
C_2H_4	26.3 mm^{-1}	C_2H_6	} <i>ca.</i> 0.04 mm^{-1}
C_3H_6	26.5	C_3H_8	
C_4H_8-1	29.0	<i>n</i> - C_4H_{10}	
C_4H_8-2	25.0	<i>iso</i> - C_4H_{10}	

may be due to the sensitized polymerization of propylene by the allyl radical. At any rate one would expect that if reaction (5) did occur it

⁴ H. S. Taylor and J. O. Smith, *J. Chem. Phys.* **8**, 543 (1940).

⁵ E. C. Baughan, M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.* **37**, 377 (1941).

⁶ D. P. Stevenson, *J. Chem. Phys.* **10**, 291 (1942).

⁷ H. G. Andersen, G. B. Kistiakowsky, and E. R. Van Artsdalen, *J. Chem. Phys.* **10**, 305 (1942).

⁸ W. J. Moore and H. S. Taylor, *J. Chem. Phys.* **8**, 504 (1940).

would lead to a relatively rapid polymerization. Since this is not the case the efficiency of reaction (5) must be quite low. We must then attribute the low rate to the influence of the C=C bond on the actual quenching process rather than to the strength of the C-H bond.

The quenching efficiencies of propylene, butene-1, and butene-2 are in the same range as that of ethylene so we cannot attribute the slow reaction to this cause. Table I gives the quenching efficiencies of the four olefins together with the corresponding values for the lower paraffins.⁹ These values are given by the slope of the curve obtained by plotting the reciprocal of the actual quenching against the pressure.¹⁰

It would appear from this table that the actual quenching process is responsible for the inefficiency of the ultimate reaction. The excitation energy of Cd(³P₁) atoms is such that reaction (1) cannot take place unless CdH is formed ($\Delta H = 15.5$ kcal.). Consequently if this energy is absorbed by the C=C bond, as seems to be the case, most of it will be dissipated as vibrational and rotational energy and not lead to reaction. Assuming that the quenching efficiency of a double bond is 600 times as great as that of a single bond, the probability of removing an H atom from the methyl group in propylene, for

example, compared to the probability that the excitation energy will be absorbed by the olefinic part of the molecule will be of the order 1 : 600. The actual ratio may be even smaller than this due to steric effects. The small amount of reaction that does occur may be the result of the removal of an H atom from either the olefinic or the paraffinic part of the molecule, with the formation of CdH; or it may even be due to a pseudo-thermal polymerization resulting from collisions of activated olefin molecules with normal ones. In this connection it is worth noting that the temperature used in these experiments (285°C) is not far from the lower limit where thermal reaction begins.

The fact that Hg(³P₁) atoms react readily with ethylene to form activated ethylene molecules capable of dissociating into acetylene and hydrogen, while very little acetylene is formed with Cd(³P₁) atoms is probably due simply to the difference in excitation energy.¹¹ What little acetylene is formed is probably the result of reactions analogous to (2), (3), and (4).

In view of the above remarks our results are not inconsistent with those of Taylor and Smith⁴ in as much as collisions of methyl radicals with propylene involve processes of quite a different character.

⁹ E. W. R. Steacie and D. J. LeRoy, unpublished.

¹⁰ A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge, 1934).

¹¹ E. W. R. Steacie, *Ann. New York Acad. Sci.* **41**, 187 (1941).