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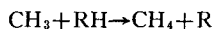
The Reaction of Methyl Radicals with Butadiene and Isoprene*

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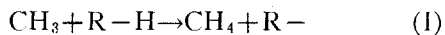
An investigation of the reaction of methyl radicals with butadiene and isoprene has been made by photolyzing admixed mercury dimethyl. In each case the amount of methane formed by the reaction



was small relative to the accompanying polymerization. For butadiene the activation energy of methane formation is 6.5 kcal. This value is, however, rather unreliable on account of the small amount of methane formation.

INTRODUCTION

THE reaction



has been studied by H. S. Taylor and his co-workers,¹ with various hydrocarbons. The methyl radicals were generated, *in situ*, by the photolysis of admixed mercury dimethyl. One of the most interesting results of these investigations was that the activation energy of reaction (1) is low, if the hydrocarbon has a C-H bond in a β -position to a double bond. Thus, for example, propylene and methyl radicals form methane with an activation energy of 3.1 kcal. per mole, while with ethylene and benzene, E for reaction (1) is greater than 10 kcal. per mole.

Taylor and Smith² suggest that the low activation energy for the reaction of propylene with methyl radicals might be caused by the weak C-H bond in the methyl group of propylene. Since $E=8$ kcal. for ethane in reaction (1), they conclude that the weakest C-H bond in propylene has a bond strength 5 kcal. less than the C-H bond strength in ethane, or about 91-93 kcal. per mole.³ The present work extends the study of reaction (1) to butadiene and isoprene.

EXPERIMENTAL

The mercury dimethyl used was prepared by the method of Gilman and Brown,⁴ which yields

* Contribution No. 1408 from the National Research Laboratories, Ottawa, Canada.

¹ See Hugh S. Taylor, *Ann. N. Y. Acad. Sci.* **41**, 231-240 (1941).

² H. S. Taylor and J. O. Smith, Jr., *J. Chem. Phys.* **8**, 543-546 (1940).

³ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 683-685 (1942).

a product of high purity. Traces of water were removed with fused calcium chloride, and the dried product was stored in a glass bulb, connected to the system through a Warrick-Fugassi valve.⁵

Owing to the high solubility of mercury dimethyl in stopcock grease, mercury valves were used exclusively in the system. The cell was similar in shape to the one used by Taylor and Smith,² and was made entirely of quartz except for the narrow neck which was made of Pyrex and sealed to the quartz portion by a graded seal. The cell was provided with a small thermocouple well, and a side tube with an internal glass tip for introducing the products of the reaction into the analytical unit. The cell had a volume of 252 cc, and was sealed off from the system after the introduction of the sample. The partial pressures of the mercury dimethyl and the hydrocarbon were measured with a constant volume manometer.

In making a run, the cell was sealed to the system by means of a short piece of 2-mm capillary tubing. After evacuation, the mercury dimethyl was admitted until the pressure reached 40 mm, which corresponds to the vapor pressure of mercury dimethyl at 18°C. 200 mm of hydrocarbon were then introduced, after which the cell was immersed in liquid air and sealed off from the system.

The reaction was studied at various temperatures by placing the cell in a small furnace which

⁴ H. Gilman and R. E. Brown, *J. Am. Chem. Soc.* **52**, 3314-3317 (1930).

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

TABLE I.

Furnace temperature °C	Butadiene			Isoprene		
	$k(\text{CH}_4) \times 10^3$	$-\Delta P \times 10^3$	$-\Delta P/k(\text{CH}_4)$	$k(\text{CH}_4) \times 10^3$	$-\Delta P \times 10^3$	$-\Delta P/k(\text{CH}_4)$
106	0.105 ± 0.011	0.61 ± 0.03	5.8	0.17 ± 0.012	7.2 ± 0.2	42
140	0.245 ± 0.015	7.2 ± 0.2	29			
232	1.01 ± 0.02	53 ± 0.8	53			

contained a quartz window 4×4 cm through which the cell could be irradiated. The temperature of the cell was followed with the thermocouple in the cell.

The absorption spectrum of mercury dimethyl exhibits a continuum beginning at 2800Å, and extending into the far ultraviolet. Since mercury vapor is always present in the cell, it was necessary to choose a mercury arc source in which the $\lambda 2537$ resonance line was completely reversed. Otherwise mercury photo-sensitized decomposition of the reactants would occur. A Hanovia Alpine sun lamp proved to be a satisfactory source for photolyzing the mercury dimethyl. Plates taken of the radiation from the lamp with a large Hilger quartz spectrograph showed almost complete reversal of the $\lambda 2537$ resonance line. Furthermore, there was no indication of mercury photo-sensitized decomposition when a cell containing ethylene and mercury vapor was exposed to the lamp for 12 hours.

After exposure, the cell was sealed to an analytical unit, similar to one previously employed.⁶ After evacuation, the cell was immersed in liquid air and the glass tip broken by a small iron hammer, actuated by a solenoid. The gas, non-condensable in liquid air, was pumped into a gas burette, designed for the accurate measurement of small quantities of gas. After measuring its volume, the gas was burned to carbon dioxide and water, in a small combustion tube containing an electrically heated platinum spiral. By this means it was conclusively shown that the gas was pure methane.

At the end of each run, the pressure of residual hydrocarbon was determined, in order to obtain some indication of the extent of polymerization.

⁶ H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. 12, 484-493 (1944).

RESULTS

The quantities of methane formed were extremely small, and consequently the measurements were heavily influenced by experimental error. The results for butadiene and isoprene are summarized in Table I. Each value is the average of three determinations. $k(\text{CH}_4)$ and $-\Delta P$ the decrease in pressure, are expressed in cc per minute at 760 mm and 0°C. Above 100°C thermal polymerization of isoprene becomes appreciable.

The plot of $\log [k(\text{CH}_4)]$ vs. $1/T$ is roughly linear for butadiene. From the slope of this line the activation energy of methane formation is about 6.5 kcal. per mole.

In general the chain length of the polymer radical will be given by the expression

$$-d \frac{[\text{R}-\text{CH}=\text{CH}_2]}{dt} \bigg/ \frac{-d(\text{CH}_3)}{dt},$$

and the ratio $-\Delta P/k(\text{CH}_4)$ will represent a maximum value for the chain length, provided there is no other source of methane than the reaction under investigation. Consequently the quantity is of considerable interest.

The values of $-\Delta P/k(\text{CH}_4)$ for butadiene would suggest that, as in case of propylene, the chain length increases with temperature. The measurements made at 100°C on isoprene indicate a longer chain length than butadiene under the same conditions.

The activation energy of 6.5 kcal. for butadiene seems altogether too low. In view of the small amount of methane formed, and the large amount of polymerization, the possibility of complicating factors is considerable and too much reliance should not be placed on this value.