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The Mercury $({}^{3}P_{1})$ Sensitized Decomposition of Normal and Iso-Butane at High Temperatures

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The mercury $({}^{3}P_{1})$ sensitized decomposition of normal and iso-butane at high temperatures is described. The reactions of both hydrocarbons result in the formation of decomposition products of butyl radicals at temperatures above 250°C. In the case of normal butane this reaction gives methane, ethane, ethylene, and propylene; and with iso-butane, only methane and butane. Activation energies are assigned to the various radical decomposition steps.

INTRODUCTION

THE investigation of the mercury photosensitized decomposition of propane¹ and ethane² at high temperatures has yielded information on the thermal stability of the ethyl and propyl radicals.

Previous work on the photosensitized decomposition of normal butane³ and iso-butane⁴ was carried out at temperatures below 250°C. Under these conditions the various butyl radicals showed no signs of decomposition. The reaction has here been carried out up to 400°C in order to obtain products of the butyl radical decomposition.

EXPERIMENTAL

The reaction has been carried out using a static system of conventional design. Unreversed $\lambda 2537$ was obtained from a low pressure mercury arc with neon (3 mm) as carrier gas. The light was roughly collimated by a quartz lens and passed through a quartz reaction cell contained in a concentric aluminum block furnace. The intensity of the incident light was found to be 1.38×10^{-5} einstein/hr as previously described.



FIG. 1. Normal butane: Hydrogen production at various temperatures.

* National Research Council of Canada Postdoctorate Fellow.
¹ S. Bywater and E. W. R. Steacie, J. Chem. Phys. 19, 319 (1951).
² S. Bywater and E. W. R. Steacie, J. Chem. Phys. 19, 326 (1951).
³ A. Hay and C. A. Winkler, Can. J. Research B21, 149 (1943).
⁴ B. deB. Darwent and C. A. Winkler, J. Phys. Chem. 49, 150 (1945).

Normal and iso-butane were obtained in cylinders from the Phillips Petroleum Company (research grade). These were certified as being 99.78 percent and 99.88 percent pure, respectively, traces of impurity being saturated hydrocarbons. The gas used was therefore subjected to only bulb-to-bulb distillation and rigorous degassing before use. The apparatus was exactly as described by Bywater and Steacie¹ except that the gas analysis system was altered to include a low temperature still similar to that described by LeRoy.⁵ This consisted of a primary trap immersed in liquid nitrogen, maintained at -125° C by means of a heating coil, followed by a long columnar trap with a temperature gradient along its length. After removal of noncondensible gases with the latter at liquid nitrogen temperature, ethane and ethylene were pumped off by maintaining the base of the column at -160° and the top some 20° higher. Blank experiments showed a 96 percent recovery of a small amount (0.150 cc N.T.P.) of ethane mixed with a large amount (50 cc N.T.P.) of normal butane. The recovered ethane was found by mass spectrometer analysis to be completely uncontaminated by butane. It was impossible to recover more than 60 percent of a similar amount of propane in a large excess



⁵ D. J. LeRoy, Can. J. Research **B28**, 492 (1950).

of butane with this apparatus. Propane and propylene were therefore not normally analyzed, but typical experiments were fractionated in a more efficient still closer in design to that of Savelli, Seyfried, and Filbert.⁶ The C₂ fraction was analyzed for ethylene by means of the Blacet-Leighton microanalysis apparatus. The noncondensible fraction was analyzed for methane by combustion over copper oxide at 280°C.

RESULTS

Experiments were carried out at a constant pressure of butane or iso-butane of 20 cm. This high pressure was chosen by consideration of the results obtained using propane. Under these conditions the reaction was shown to be much simpler than at lower pressures, where the results are complicated by some of the products quenching the $({}^{3}P_{1})$ mercury atoms. Using higher pressures also makes the occurrence of radical recombination reactions less important. At this pressure

TABLE I.

F	Production of	of methan at 20 c	e and hydrogen fr m total pressure.	om iso-bu	tane
Iso-butane Temp. cc °C CH4/hr		cc H2/hr	cc/hr non-chain (by extrapo- lation)	∆(chain H₂)	all quantities cc N.T.P.
26°		0.154		•••	
100°	•••	0.181		•••	
200°		0.197			
300°	0.040	0.212			
325°	0.088	0.219	0.214	0.005	
350°	0.145	0.270	0.217	0.053	
375°	0.248	0.402	0.219	0.183	
400°	0.436	0.801	0.233	0.568	
Productio	on of metha	ne and tot	al C ₂ hydrocarbor	ns from no	rmal butane.
Normal but	tane				
Temp.	CH ₄ production		C ₂ production	Tall quantities	
°C	(cc/	/hr)	(cc/hr)		N.T.P. 🔟
250°	0.0	39	0.030		
275°	0.1	36	0.085		
300°	0.3	360	0.214		
350°	1.7	4	1.07		
375°	3.2	22	2.05		

the quantum yield of hydrogen formation at room temperature for both iso-butane and normal butane is 0.50. This value is identical with the quantum yield from propane at high pressures.

NORMAL BUTANE

Up to 250°C no reaction product is detectable other than hydrogen and a heavy fraction. The hydrogen production reaches a maximum at 200°C. Thereafter the initial rate is equal to that at 200°C but begins to fall off with time (Fig. 1). Presumably an equal amount of octane is produced,^{2,3} corresponding to the heavy fraction present.

Above 250° C with normal butane, appreciable amounts of methane, ethane, ethylene, and propylene are formed (Table II). Double bond analyses made on twelve typical C₂ fractions from various runs showed



FIG. 3. Normal butane: Methane production at various temperatures.

that an average of 55 percent of the C_2 fraction was ethylene, variation between 53 and 57 percent being normal. The C_3 fraction is roughly equivalent to the amount of methane formed. Exact estimation of the quantity of this fraction was difficult since it was always contaminated with butane. Usually it was found to be around 85 percent propylene. A further cut was found to produce further small quantities of propylene contaminated heavily with butane. The agreement between methane and propylene production has therefore partially resulted by cancellation of these two factors.

The rate of total C_2 fraction and methane formation with time at various temperatures is shown in Figs. 2 and 3 and Table I. The activation energy calculated from these results (Fig. 4) corresponds to 23 kcal for both C_2 and methane formation. Although the experi-



FIG. 4. Activation energy plots for the formation of CH_4 and total C_2 fraction for the two butanes.

⁶ Savelli, Seyfried, and Filbert, Ind. Eng. Chem. (Anal.) 13, 868 (1941).



FIG. 5. Iso-butane: Hydrogen production at various temperatures.

ments were carried out at constant pressure rather than constant concentration, no appreciable error will result from using concentration units in this calculation. Thermal blank experiments at 375°C show that only 0.5 percent of the products are due to thermal reaction at this temperature.

ISO-BUTANE

With iso-butane, the hydrogen production increases continuously with temperature (Fig. 5). At a temperature of 300°C, appreciable quantities of methane are formed. No appreciable amounts of ethane or ethylene could be detected at any temperature. Complete product analysis (Table II) gave erratic results for the formation of C₃ hydrocarbons. From the results, it is clear that in some cases the C₃ was incompletely removed and in others appreciable amounts of butane were carried over. No thermal reaction could be detected even at 400°C.

The rate of methane formation at various temperatures is shown in Fig. 6, an activation energy of 18.5 kcal (Fig. 4) is obtained from the Arrhenius plot. Above 350°C the quantum yield of hydrogen rises sharply and has values above unity. A chain mechanism producing hydrogen atoms must occur. The activation

TABLE II. Complete analyses on several typical experiments with *n*-butane and iso-butane.

· Normal butane Temp. °C	Time (min)	H2	Сн₄	C2	C2	[all quantities] cc N.T.P.
275° 300° 350° 375°	60 30 7 6	0.182 0.108 0.034 0.024	0.136 0.174 0.200 0.282	0.082 0.091 0.109 0.178	0.104 0.195 0.204 0.307	C ₃ 83% double bond C ₃ 83% double bond C ₃ 77% double bond C ₃ 82% double bond
Iso- butane Temp. °C 325° 350° 375° 400°	Time (min) 80 70 40 20	H ₂ 0.278 0.279 0.259 0.259	CH4 0.119 0.167 0.161 0.147	C3 0.079 0.088 0.63 0.167	[all quantities] cc N.T.P. Cs 46% double bond Cs 50% double bond C 21% double bond C 30% double bond	

energy for this step has been calculated by subtracting the amount of hydrogen produced by the non-chain mechanism from the total hydrogen production (Fig. 7), by extrapolation of the low temperature results (Table I). This extra hydrogen production plotted logarithmically (Fig. 8) vs reciprocal temperature gives an apparent activation energy for the chain step of 40 kcal.

DISCUSSION

The low temperature results are consistent with the basic mechanisms postulated by Hay and Winkler¹ and Darwent and Winkler.⁴

$$\mathrm{Hg}({}^{1}S_{0}) + h\nu = \mathrm{Hg}({}^{3}P_{1}) \qquad 0$$

$$Hg(^{3}P_{1})+C_{4}H_{10}=C_{4}H_{9}+H+Hg(^{1}S_{0})$$
 ΦI_{abs}

$$+C_4H_{10}=C_4H_9+H_2$$
 K₂

 $2C_4H_9 = C_8H_{18}$ k3

together with a quenching step which results in $({}^{3}P_{0})$ mercury atoms and no C-H bond split. This has been expressed as a factor Φ in the quenching step



FIG. 6. Iso-butane: Methane production at various temperatures.

which is temperature dependent. The reactions

$$H+C_{4}H_{9}=C_{4}H_{10}$$

$$H+C_4H_8=C_4H_9$$
 k₆

which can conceivably occur but are unlikely by analogy with the experimental evidence on propane decomposition are not here considered. If they caused the low quantum yield rather than quenching inefficiency, the rate of hydrogen production would be again ΦI_{abs} , where Φ has a different significance being a ratio of rate constants.

At higher temperatures, radical decomposition products appear. By analogy with the previous work on propane and ethane we may expect the following reactions

$$C_4H_9 = C_2H_4 + C_2H_5 \qquad k_7$$

$$C_4H_9 = C_3H_6 + CH_3$$
 k₈
 $C_4H_9 = C_4H_8 + H$ k₉

k۵

followed by

$$C_{2}H_{5}+C_{4}H_{10}=C_{2}H_{6}+C_{4}H_{9} \qquad k_{10}$$

$$CH_{3}+C_{4}H_{10}=CH_{4}+C_{4}H_{9} \qquad k_{11}$$

The methyl radical produced will not decompose further since it is known to be thermally stable up to very high temperatures. The ethyl radical will not appreciably decompose until 425°C and so will also be thermally stable in these experiments.

The experiments described earlier confirm that these reactions occur, ethane and ethylene being formed in roughly equal quantities. Similarly, the rates of formation of methane and propylene are roughly equivalent. On the basis of the aforementioned mechanism, neglecting terms such as $\frac{1}{2}E_{\Phi}$ or $\frac{1}{2}E_3$ which will be small compared to the experimental error, $E_7=E_8=23$ kcal, for normal butane; and $E_8=18.5$ kcal, $E_9=40$ kcal for iso-butane.

The two possible branched chain radicals produced by the decomposition of iso-butane could not split to form C_2 fragments without an extensive rearrangement of the carbon skeleton. Thus reaction (7) would be impossible in this case. This is confirmed by the absence



FIG. 7. Iso-butane: Activation energy plot for the total hydrogen production.

of ethane and ethylene in these experiments. There appears no obvious reason why the two straight chain radicals produced from normal butane should not decompose via reaction (9) but the products are not found experimentally. With normal butane reaction (8) is found to be approximately 3.3 times as fast as reaction (7). On the simplest possible basis one would expect a factor of two in the rates since there are two possible bonds to break for reaction (8) and only one for reaction (7). There must, therefore, be some other effect in the steric factor which increases this ratio still further.

No previous estimate appears in the literature for the activation energies of reactions (7), (8), (9). It is possible to estimate the heats of these reactions if the various carbon-hydrogen bond strengths in the butanes are known. Butler and Polanyi⁷ estimate the primary

⁷ E. T. Butler and M. Polanyi, Trans. Faraday Soc. 38, 19 (1942).



FIG. 8. Iso-butane: Activation energy plot for the chain step.

C-H bond strength in normal butane and the tertiary C-H bond strength in iso-butane. No estimate is available for the other two C-H bond types however, and in any case Butler and Polanyi's values must be considered inaccurate. It is certain that the various C-H bond strengths in the butanes cannot be greater than the value in ethane which is known with more certainty. Thus we can estimate minimum heats of reaction using heats of formation from tables.⁸

In this way $\Delta H_7 = \Delta H_8 \ge 21$ kcal (normal butane) and $\Delta H_9 \ge 33$ kcal (iso-butane). The experimental activation energies are thus reasonable assuming approximately 2 kcal for the activation energy of the back reaction. The values suggest a mean C-H bond strength in normal butane very little lower than in ethane and in iso-butane a value some 5 kcal lower. This confirms the impression gained from the propane results¹ that the mean C-H bond strength in propane is only around 2 kcal lower than in ethane and suggests that all Butler and Polanyi's bond strengths with the exception of the ethane values are too low, particularly for the secondary and tertiary C-H bonds.

The experimental value of E_8 for iso-butane is much too low since the true value cannot be less than the corresponding value for normal butane. It may be that in this case side reactions have complicated the mechanism to some extent.

ACKNOWLEDGMENTS

The complete Ward-still analyses described in Table II and double bond analysis were carried out by Mr. R. Pilon to whom our thanks are due.

⁸Selected values of the properties of hydrocarbons. U. S. National Bureau of Standards, Washington, D. C.