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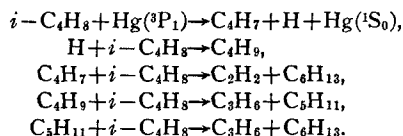
The Mercury Photo-Sensitized Reactions of Isobutene*

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An investigation has been made of the reaction of isobutene with mercury (3P_1) atoms at 30°C. The main products of the reaction are propylene, liquid polymer, and acetylene. Smaller amounts of a large number of other products are also formed. The over-all rate of consumption of isobutene, as well as the rates of formation of propylene, acetylene, and propane are independent of pressure in the region of complete quenching. Furthermore the rate of formation of propylene is just double the rate of formation of acetylene. The maximum quantum yield of consumption of isobutene is 0.59. The principal steps in the mechanism proposed for the reaction are



On the above mechanism the initial step would be only about 16 percent efficient. Polymerization is considered to be initiated mainly by the C_6H_{13} radical. The average molecular weight of the polymer would then be approximately 240.

INTRODUCTION

THE investigation of LeRoy and Steacie on ethylene,¹ and of Gunning and Steacie on butadiene,² propylene,³ and isoprene,³ would seem to suggest that these molecules all react with mercury (3P_1) atoms, at room temperature, mainly by an activated molecule mechanism of the type



TABLE I. Analysis of original isobutene.

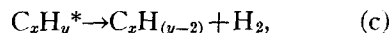
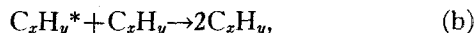
Component	Mole, percent
Propylene	0.97
Propane	0.09
Isobutene	95.65
Butanes	2.39
Methyl butenes	0.14
Pentadienes	0.06
Neopentane	0.44
Cyclohexane	0.01
Methyl cyclohexenes	0.02
Dimethyl pentenes	0.06
Ethyl cyclohexenes	0.04
Di-isobutylene	0.13

* Contribution No. 1409 from the National Research Laboratories, Ottawa, Canada.

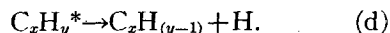
¹ D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. 9, 829 (1941).

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, 57 (1946).



or



The activated ethylene and butadiene molecules decompose by reaction (c) into hydrogen molecules and a more unsaturated hydrocarbon: while the activated propylene and isoprene molecules seem to split mainly into radicals by reaction (d). In a previous paper³ the present authors suggested that the difference in behavior between ethylene and butadiene, on the one hand, and propylene and isoprene, on the other might be caused by the presence in the latter of weak C-H bonds in a position once-removed from a double bond.

Isobutene offers interesting possibilities for testing further the generality of the mechanism cited above, since it possesses six C-H bonds in positions once-removed from a double bond. The results of this investigation are reported below.

EXPERIMENTAL

For a general description of the apparatus employed, and the experimental technique, reference should be made to the paper of Gunning

TABLE II.

P_0 mm	$\frac{\Delta p}{\Delta t}$ mm/min. $\times 10^2$	$\frac{A}{d[H_2]}$	$\frac{B}{d[CH_4]}$	A/B
		$\frac{dt}{moles/min. \times 10^6}$	$\frac{dt}{moles/min. \times 10^6}$	
1.49	0.95	0.0110	0.0344	0.32
5.05	1.05	0.0142	0.0140	1.0
9.50	1.23	0.0210	0.0101	2.1
11.94	1.05	0.0239	0.0077	3.1
14.29	1.15	0.0199	0.0104	1.9
18.14	1.28	0.0255	0.0100	2.6
26.63	1.17	0.0233	0.0083	2.8
45.90	1.20	0.0185	0.0079	2.3
51.28	1.15	0.0183	0.0081	2.3
69.93	1.20	0.0163	0.0080	2.0
83.91	1.32	0.0135	0.0059	2.3

TABLE III.

P_0 mm	$\frac{-d[i-C_4H_8]}{dt}$	$\frac{d[C_2H_2]}{dt}$	$\frac{d[C_3H_6]}{dt}$	$\frac{d[C_3H_8]}{dt}$
	Moles per min. $\times 10^6$			
1.49	0.82 ₅	0.036	0.077	0.0085
5.05	1.42	0.164	0.33 ₂	0.020
9.50	2.00	0.31 ₆	0.61	0.029
11.93	1.72	0.40 ^o	0.77	0.031
14.29	1.98	0.51 ^o	0.88	0.052
18.14	3.80	1.00	1.94	0.086
26.63	4.18	1.17	2.43	0.087
45.90	4.15	1.33	2.46	0.110
51.28	4.15	[0.59]	2.37	0.090
69.93	4.03	1.30	2.49	0.162
83.91	4.14	0.98	2.04	0.046

and Steacie on the mercury photo-sensitized reactions of butadiene.² The cylindrical quartz cell used had a volume of 240 cc. The cell was immersed in a water thermostat maintained at $30.00 \pm 0.01^\circ\text{C}$. The total volume of the system was 1052 cc.

In order to obtain more complete information about the products of the reaction and their variation with the initial pressure, arrangements were made with Dr. A. Keith Brewer, Chief of the Mass Spectrometry Section of the National Bureau of Standards, to have analyses of the products performed on the mass spectrometer. After considerable experimentation on gaseous mixtures of known composition, the following technique was finally adopted for obtaining a representative sample of the gaseous mixture of unreacted isobutene and products present in the system at the end of each run.

A 100-cc bulb was first sealed to the system through a U-type mercury cut-off, which contained a small glass check-valve in each arm. After the system had been pumped down to a pressure of 10^{-5} mm, the cut-off was closed and a definite amount of isobutene was then admitted to the system and its pressure determined. The cut-off was then opened again, and the system was allowed to stand for three hours before starting the run.

At the end of each run the system was left for two hours in order to allow diffusion to equalize the composition throughout the system. The cut-off was then closed and Dewar flasks of liquid air were placed around the sample bulb, and around a trap in the system. When the

McLeod gage showed that the pressure in the system had fallen to a constant value, the sample bulb was sealed off and removed from the system. The gas, non-condensable in liquid air, present in the system was pumped into the gas burette for measurement. The hydrogen was determined by circulation through a tube containing finely-divided cupric oxide deposited on glass wool. The tube was maintained at 300°C by a small resistance heater. The residue from the hydrogen determination was identified as methane by combustion in excess oxygen over a small electrically-heated platinum spiral.

The isobutene used in the measurements was the C.P. grade manufactured by the Matheson Company, East Rutherford, New Jersey. After several trap-to-trap distillations, the middle fraction was collected and stored in a one-liter flask provided with a Warrick-Fugassi valve.⁴ Mass spectrometric analysis showed that the gas had the composition shown in Table I.

RESULTS

Isobutene shows a similar behavior to propylene in that the pressure begins to fall linearly with time as soon as the cell is exposed to radiation from the mercury resonance lamp. At the same time the window of the cell gradually becomes covered with tiny colorless droplets of liquid polymer. The gas, non-condensable in liquid air, which remained in the system at the end of each run, was shown to be a mixture of hydrogen and methane. These data are sum-

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

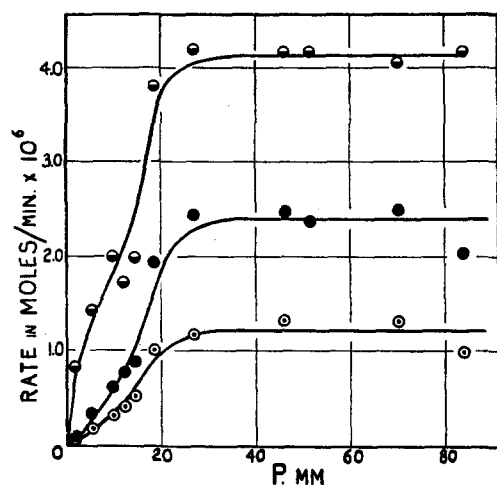


FIG. 1. ○ Rate of consumption of isobutene vs. initial pressure. ● Rate of formation of propylene vs. initial pressure. ○ Rate of formation of acetylene vs. initial pressure.

marized in Table II. From the table, it can be seen that, in contrast to propylene, the rate of pressure decrease is independent of the initial pressure, in the complete quenching region, i.e., above 15–18 mm. The rates of formation of hydrogen and methane, however, seem to fall off with increasing pressure in the same pressure region. Furthermore the ratio of these two rates, as given in the last column of Table II, appears to be constant, within experimental error. Runs were also made wherein the actual amounts of methane and hydrogen formed were determined as functions of the time, at a constant initial pressure of isobutene. Two sets of runs were made, the first set at an initial pressure of 15 mm, and the second at an initial pressure of 30 mm. 10-, 20-, 30-, 50-, and 80-minute runs were made at these pressures and the amount of methane and hydrogen determined in each case. These quantity-time curves were all straight lines passing through the origin.

The Products of the Reaction

The principal products of the reaction, condensible in liquid air, were propylene, liquid polymer, acetylene, and propane, in order of decreasing importance. Smaller amounts of a large number of other products are also present, especially at lower pressures where radical recombination reactions assume a more important role.

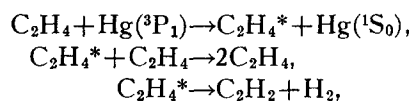
These minor products were ethane, propadiene and/or methyl acetylene, *n*-butane, methyl butenes, neopentane, benzene, cyclohexadiene, cyclohexene, cyclohexane, toluene, heptadiene, heptanes, methyl cyclohexenes, dimethyl pentenes, dimethyl pentanes, ethyl cyclopentene, ethyl cyclopentane, trimethyl pentene, trimethyl pentanes, dimethyl hexene, dimethyl hexane, diisobutylene, and octanes. The rates of formation of these minor products were all less than 0.01 micromole per minute.

In Table III the over-all rate of consumption of isobutene, together with the rates of formation of acetylene, propylene and propane, are tabulated as functions of the initial pressure. These results are represented graphically in Fig. 1. From a study of Table III, we see that the four rates tabulated all seem to be constant and independent of the pressure, within experimental error, above 18 mm. Above this pressure there are approximately 0.54 mole of propylene, and 0.28 mole of acetylene formed for each mole of isobutene decomposed. Furthermore the ratio $(d[C_2H_2]/dt)/(d[C_3H_6]/dt)$ has a constant value over the entire pressure range of 0.51 ± 0.02 .

Quantum Yield

Four determinations were made of the quantum input to the cell from the mercury resonance lamp by filling the cell with ethylene at an initial pressure of 13 mm and measuring the initial rate of production of hydrogen.

LeRoy and Steacie¹ have shown that the initial stages of the mercury photo-sensitized reaction of ethylene at room temperature can be represented by the sequence



and that the initial quantum yield is 0.37 at 13 mm. On this basis the mean quantum input to the cell was 7.07×10^{-6} einstein per minute. The values for the over-all quantum yield of isobutene consumption, $\phi(i-C_4H_8)$, are given for each pressure in Table IV.

Rate of Polymerization

By a carbon balance calculation, an estimation was made of the rate of polymerization of

isobutene, $-d[i-C_4H_8] \text{ poly.}/dt$ at the various initial pressures. These results are tabulated in Table IV. From this table, it will be seen that the rate of polymerization of isobutene seems to reach a maximum at an initial pressure of about 18 mm, and above that pressure it seems to show a slight trend downward.

The polymer formed was a clear, colorless, viscous liquid, completely soluble in benzene, in all these respects exactly similar to the polymer formed in the mercury photo-sensitized reaction of propylene.³

DISCUSSION

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

(a) The pressure *vs.* time curve is linear even in the initial stage of the reaction.

(b) The rate of pressure decrease is independent of pressure in the complete quenching region, i.e., above 18 mm.

(c) The products of the reaction are propylene, liquid polymer, acetylene, and propane, together with smaller quantities of hydrogen, methane, and a large number of other hydrocarbons.

(d) The polymer is a viscous liquid, completely soluble in benzene and present even in the initial stages of the reaction.

(e) The rate of isobutene consumption, as well as the rates of formation of propylene, acetylene, and propane are independent of pressure in the complete quenching region.

(f) Above 18 mm there are approximately 0.54 mole of propylene and 0.28 mole of acetylene formed for each mole of isobutene decomposed. Furthermore the ratio $(d[C_2H_2]/dt)/(d[C_3H_6]/dt)$ has a constant value over the entire pressure range of 0.51 ± 0.02 .

(g) The rates of formation of methane and hydrogen seem to fall off slightly with increasing pressure in the complete quenching region.

(h) The over-all quantum yield of isobutene consumption is constant above 18 mm at 0.59.

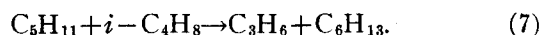
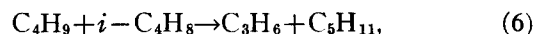
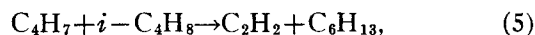
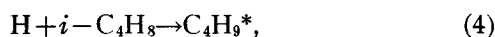
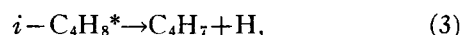
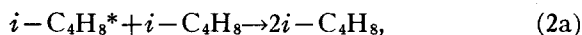
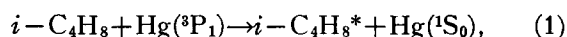
(i) The rate of polymerization seems to fall off slightly with increasing pressure in the complete quenching region.

The reactions of mercury (3P_1) atoms at room temperature with ethylene,¹ propylene,³ isoprene,³

TABLE IV.

P_0 mm	$\phi(i-C_4H_8)$	$-d[i-C_4H_8] \text{ poly.}$ $\frac{dt}{\text{Moles/min.} \times 10^6}$
1.49	0.12	0.57
5.05	0.20	0.70
9.50	0.28	0.81
11.93	0.24	0.91
14.29	0.28	0.99
18.14	0.54	1.69
26.63	0.59	1.66
45.90	0.59	1.49
51.28	0.59	
69.93	0.57	1.33
83.91	0.59	1.40

butadiene,² 1-butene,⁵ and 2-butene⁵ can all be explained on the assumption that an activated molecule is formed initially on the collision of a mercury (3P_1) atom with the hydrocarbon molecule, the mercury (3P_1) atom reverting thereby to the ground state. A similar mechanism can be proposed for isobutene. Consider the sequence



Proroguing for the moment, a discussion of the individual reactions, the rate of formation of acetylene, on the above scheme, using a steady-state calculation, would be given by the expression,

$$\frac{d[C_2H_2]}{dt} = Iab \left[1 / 1 + \frac{k_{2a}[i-C_4H_8]}{k_3 + k_{2b}[i-C_4H_8]} \right].$$

Now, it has been found that $d[C_2H_2]/dt$ is independent of pressure in the complete quenching region, and consequently we must assume that $k_3 \ll k_{2a}[i-C_4H_8]$ in the above expression in order to make the rate of acetylene formation independent of pressure. This is true, at least,

⁵ H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. (to be published).

so long as we assume that the initial quenching act is 100 percent efficient. Effectively this assumption would mean that the activated isobutene molecule has an extremely long life compared to the interval between collisions, and therefore that it would disappear in the main by bimolecular reactions rather than undergo unimolecular decomposition. On this basis

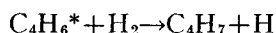
$$\frac{d[\text{C}_2\text{H}_2]}{dt} = \left[Iab \frac{k_{2b}}{k_{2a} + k_{2b}} \right],$$

and similarly for the rate of formation of propylene we obtain

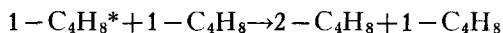
$$\frac{d(\text{C}_3\text{H}_6)}{dt} = 2Iab \left[\frac{k_{2b}}{k_{2a} + k_{2b}} \right].$$

This mechanism would account for the fact that the rate of formation of propylene is just double the rate of formation of acetylene.

Radical disproportionation reactions in general are considered to be rather slow. However there seems to be no exact precedent for a reaction of the type of (2b). Gunning and Steacie found it necessary to assume that the reaction



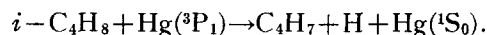
occurred to some extent in the mercury photo-sensitized hydrogenation of butadiene.² In the mercury photo-sensitized reaction of 1-butene,⁵ there is very good evidence for collisional reaction between activated molecule and molecule since the reaction



appears to be very fast. Certainly reaction (2b) is quite possible from an energetic standpoint, since the net effect of the reaction is merely the degradation of a C=C to a C-C, which would certainly require less energy than the 112.2 kcal. possessed by the activated isobutene molecule.

A much simpler mechanism can be devised, however, if we assume (1) that the activated isobutene molecule has a shorter life than the interval between successive collisions and (2) that the initial quenching process is very inefficient. The result would be that instead of reactions (1), (2a), (2b), and (3), we would

essentially have only the single initial step



The C-H bond split would likely occur at one of the six weak C-H bonds in isobutene in a position once-removed from a double bond.³ The rates of formation of acetylene and propylene would then be simply

$$\frac{d[\text{C}_2\text{H}_2]}{dt} = K \cdot Iab \quad \text{and} \quad \frac{d[\text{C}_3\text{H}_6]}{dt} = 2K \cdot Iab,$$

where K is a constant, less than unity, representing an inefficiency in the initial quenching process.

From Table III, we find that the rate of formation of acetylene in the complete quenching region has the average value of 1.16×10^{-6} mole per min. and similarly the average value for propylene is 2.29×10^{-6} mole per minute. Whence with $Iab = 7.07 \times 10^{-6}$ einstein per minute.

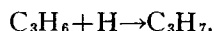
$$K = \frac{d[\text{C}_2\text{H}_2]}{dt} / Iab = \frac{d[\text{C}_3\text{H}_6]}{dt} / 2Iab = 0.16.$$

In other words, only 16 percent of the mercury ($^3\text{P}_1$) atoms colliding with the isobutene molecules lead to decomposition. There is a good deal of evidence in support of the assumption of an inefficiency in the primary quenching process in the mercury photo-sensitized reactions of the unsaturated hydrocarbons. In the first place, the quantum yields for all the hydrocarbons that have been investigated so far are less than unity, in spite of the fact that all these reactions involve the formation of free radicals which are capable of propagating polymer chains. The assumption of an inefficiency in the primary process would clarify the situation considerably. In reference (3) the authors pointed out that the zone of reaction in the mercury photo-sensitized reaction of the unsaturated hydrocarbons must be limited to a layer a few millimeters in thickness at the window. Under these conditions it is probable that if some quenching of mercury ($^3\text{P}_1$) atoms to the metastable ($^3\text{P}_0$) state occurs, the mercury ($^3\text{P}_0$) atoms, on account of their long life, could be deactivated at the window. Another very important possibility, with the unsaturated hydrocarbons especially, is physical

quenching. The high quenching efficiency of these molecules renders it quite possible that the excitation energy transferred from the mercury (3P_1) atom on collision might simply be disseminated over the various vibrational and rotational modes of the hydrocarbon molecule, without sufficient energy ever accumulating in one bond to bring about decomposition. 2-butene seems to afford an excellent example of physical quenching since the quantum yield of the mercury photo-sensitized reaction seems to be considerably lower than any of the other unsaturated molecules that have been investigated so far.⁵

Since there seems to be very good evidence for an inefficiency in the primary quenching process, the assumption of an initial C—H bond split seems to be the more plausible mechanism.

Returning now to a discussion of the individual reactions leading to the formation of acetylene and propylene, reaction (4) should be exothermic to the extent of about 30–40 kcal., by analogy with the reaction



which, as Rabinovitch, Davis, and Winkler pointed out,⁶ is exothermic to about 40 kcal. It is therefore likely that the butyl radical formed is rich in energy by this heat of hydrogenation.

Reaction (5) should be endothermic, since the net effect of the reaction is the formation of a $C \equiv C$ from a $C = C$, and the degradation of a $C = C$ to a $C - C$. Only semi-quantitative data exist on the values for the carbon-carbon double and triple bond strengths,⁷ but in general the increment in carbon-carbon bond strength in passing from single to double, appears to be greater than from double to triple. The six C—H bonds on the methyl groups in isobutene should each have a bond strength not exceeding 93 kcal. by analogy with propylene (3). And therefore it is quite probable that the C_4H_7 radical formed in the initial C—H bond split may be richer in energy by the difference between the excitation energy of the $Hg(^3P_1)$ state and the

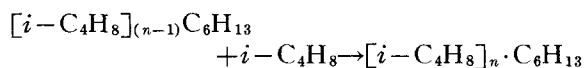
C—H bond strength, or, in other words, by about 20 kcal. Consequently reaction (5) may occur readily, even though it may have an activation energy of upwards of 20 kcal., owing to the activated C_4H_7 radical.

From the standpoint of steric hindrance, the C_6H_{13} radical formed in (5) would most probably have the structure $(CH_3)_2C \cdot C_3H_7$. Such a highly

branched structure would likely have a relatively long life, and since it does not possess sufficient energy to split off another acetylene molecule, it may either react further with isobutene to form a longer polymer chain or diffuse to the wall and become deactivated.

As we pointed out above the C_4H_9 radical formed in (4) should be "hot" owing to the 30–40 kcal. to which the reaction is exothermic. Consequently the C_4H_9 radical must have at least twice as much excess energy as the C_4H_7 radical formed in the initial quenching process. Now the net effects of reactions (6) and (7) from an energetic standpoint are approximately the same. Namely the formation of a $C = C$ from a $C - C$, and the degradation of a $C = C$ to a $C - C$. Therefore, in this case, it may be quite possible for two molecules of propylene to split off the growing polymer chain. The C_6H_{13} radical formed in reaction (7) will be sterically protected against further reaction with isobutene molecules. This radical may either diffuse to the wall or it may add on another molecule of isobutene through a favorable collision. But, in any event it will not possess sufficient energy to split off another molecule of propylene.

In Table IV, data are given for the actual rate of polymerization, $-d[i-C_4H_8]_{poly.}/dt$, as a function of the initial reaction pressure. On the basis of the mechanism outlined above, we were led to the conclusion that the growing polymer radical, which we can represent by the formula $[i-C_4H_8]_n \cdot C_6H_{13}$ decreases in its rate of growth owing to steric factors. That is to say, the steric factor for the reaction



decreases rapidly with increasing n . And under these conditions the radical tends to diffuse to the wall where it is deactivated by some zero-

⁶ B. S. Rabinovitch, S. G. Davis, and C. A. Winkler, *Can. J. Research* **B21**, 251 (1943).

⁷ For a discussion of hydrocarbon bond strengths, see E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946), Chapter III.

order reaction. Now we can make a rough calculation of the average value of n , i.e., \bar{n} , from our data, since \bar{n} can be represented by the expression

$$\bar{n} = \frac{-d[i-C_4H_8] \text{ poly.}/dt}{\left[\frac{d[C_2H_2]}{dt} + \frac{1}{2} \frac{d[C_3H_6]}{dt} \right]}$$

In the complete quenching region, the mean value of the above quantities from Tables III and IV are $-d[i-C_4H_8] \text{ poly.}/dt = 1.5$, $d[C_2H_2]/dt = 1.16$, and $d[C_3H_6]/dt = 2.29$, all in micromoles per minute, and therefore $\bar{n} = 0.6$. This calculation shows that the chain length of the polymer is very short, in agreement with the observation that the polymer is liquid and completely soluble in benzene. If the polymer is finally formed by a zero-order recombination at the wall, the polymer should have an average molecular weight of only 240.

If the slight falling off in the rate of polymerization with pressure is a real effect, and not just experimental error, it may indicate that chain decomposition, which should increase with the collision frequency, is a significant factor.

The rate of formation of propane seems to be the same type of function of the initial pressure as the rate of formation of acetylene and propylene. This could be explained by assuming that the reaction



occurs to some extent. This reaction would probably only occur with isobutyl radicals, whereas on steric grounds reaction (4) should form predominately tertiary butyl radicals. The rate of formation of propane would then be represented by

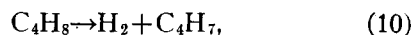
$$\frac{d[C_3H_8]}{dt} = \frac{k_8}{2k_6} \frac{d[C_3H_6]}{dt}$$

Hence, from Table III, we see that

$$\frac{k_8}{k_6} = \frac{1}{12}$$

The small amounts of hydrogen and methane formed probably arise from the unimolecular

decomposition of the activated butyl radicals formed in (4). This radical may decompose to some extent by the reactions



whence

$$(d[H_2]/dt)/(d[CH_4]/dt) = k_{10}/k_9 = 2.4$$

from Table II.

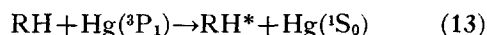
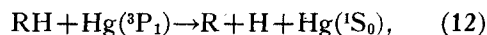
These rates should both fall off with increasing pressure in accordance with our findings. The increase in the rate of formation of methane at very low pressures suggests that the reaction



is occurring at the wall.

CONCLUSIONS

The most surprising result of the present investigation is the striking difference in behavior between isobutene and the other unsaturated hydrocarbons which have been previously investigated. Ethylene,¹ propylene,³ isoprene,³ butadiene,² 1-butene,⁵ and 2-butene⁵ all seem to form activated molecules in the initial quenching process. These activated molecules seem to have sufficiently long lifetimes to be able to undergo deactivating collisions, as well as decomposing unimolecularly into radicals or molecules. Isobutene, on the other hand, appears to decompose, in the main, initially into C_4H_7 radicals and H atoms. If we compare isobutene with propylene, which, of all the above molecules, it should most closely resemble, we see that the substitution of a methyl group for a hydrogen shortens the lifetime of the activated state to such an extent that it becomes less than the interval between collisions. This is true, at least, up to a pressure of 80 mm. Actually the difference in behavior between propylene and isobutene is probably more a matter of degree than kind. The reactions



undoubtedly occur in both cases, (12) predominating in isobutene and (13) in propylene.

The quenching efficiency of a double bond is

some six hundred times greater than that of a single bond. Now in isobutene there is a greater probability that quenching will occur at the paraffinic end than in propylene, and this should lead to reaction (12). On the other hand if quenching does occur at the olefinic end, reaction (13) may occur with propylene, whereas with isobutene, the increased number of degrees of freedom may cause the excitation energy of the mercury (3P_1) atoms to be dissipated as vibrational and rotational energy without leading to reaction. This argument is supported by the fact

that the initial quenching process seems to be only 16 percent efficient in isobutene.

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The Mercury Photo-Sensitized Reactions of Diethyl Ether*

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The mercury photo-sensitized reactions of diethyl ether have been investigated in a circulatory system at 35°C and between 9- and 193-mm pressure. The principal products are hydrogen and $C_2H_5O_2$; smaller amounts of CO, CH_4 , C_2H_6 , and aldehydes are formed. The quantum yield for ether disappearance is about 2.0 initially but decreases with the duration of the experiment. In low pressure experiments the hydrogen produced initially is consumed in the later stages of the experiment and ultimately vanishes. The decrease in rate and the consumption of hydrogen in the late stages of the reaction are not caused by the accumulation either of polymer on the wall or to hydrogen and/or CO in the system. The nature of the reaction is altered by interrupting the experiment thus indicating the occurrence of a dark reaction. The initial stages may be explained by either a C-H split followed by "atomic cracking" or by reactions involving an active ether molecule.

INTRODUCTION

THE thermal decomposition of diethyl ether has been investigated extensively and the indications¹ are that the reaction proceeds by a mixed free radical and molecular rearrangement mechanism. The only photochemical investigation of the decomposition of diethyl ether published is that of Berthelot and Gaudechon² who report that non-condensable gas consisting of 14.5

percent CO and 85.5 percent H_2 , CH_4 , and C_2H_6 (ethane predominating) was formed when diethyl ether was exposed in a quartz vessel to the light of a mercury lamp. In the same investigation they found that dimethyl ether behaved similarly but report that a liquid was formed as well as the non-condensable gas. Since both dimethyl and diethyl ethers are almost completely transparent to light of wave-length longer than about 2000Å and since Berthelot and Gaudechon do not mention any precautions to remove mercury vapour from their reaction vessel and used a Hg lamp which probably gave unreversed $\lambda 2537$, it seems likely that they investigated the mercury photo-sensitized reaction rather than the photolysis of diethyl ether.

Although much information is available on the

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¹ For comprehensive reviews see: (a) E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946). (b) H. J. Schumacher, *Chemische Gasreaktionen* (Theodor Steinkopff, Leipzig, 1938).

² D. Berthelot and H. Gaudechon, *Comptes rendus* (Paris) **153**, 383 (1911).