

The Mercury Photosensitized Reactions of 1Butene and 2Butene

H. E. Gunning and E. W. R. Steacie

Citation: *The Journal of Chemical Physics* **14**, 581 (1946); doi: 10.1063/1.1724068

View online: <http://dx.doi.org/10.1063/1.1724068>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Primary Reactions in the Mercury Photosensitized Decomposition of Butene2 at Low Pressures](#)

J. Chem. Phys. **38**, 700 (1963); 10.1063/1.1733726

[Molecular Rearrangement in the Mercury Photosensitized Reaction of Butene1](#)

J. Chem. Phys. **37**, 543 (1962); 10.1063/1.1701371

[The Mercury Photosensitized Reactions of Isobutene](#)

J. Chem. Phys. **16**, 1146 (1948); 10.1063/1.1746747

[The Mercury Photosensitized Reactions of Ethane](#)

J. Chem. Phys. **16**, 381 (1948); 10.1063/1.1746894

[Mercury Photosensitized Reactions of Propane](#)

J. Chem. Phys. **8**, 571 (1940); 10.1063/1.1750716



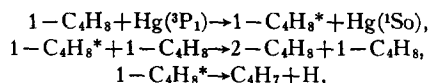
The Mercury Photosensitized Reactions of 1-Butene and 2-Butene*

H. E. GUNNING AND E. W. R. STEACIE

Division of Chemistry, National Research Laboratories, Ottawa, Canada

(Received July 25, 1946)

An investigation has been made of the reactions of 1-butene and 2-butene with mercury (3P_1) atoms at 30°C in a static system. The main products of the 1-butene reaction are 2-butene and liquid polymer. A large number of other products are also formed especially at low pressures. The rate of isomerization increases rapidly with pressure in the region of complete quenching, while the rate of polymerization falls off rapidly. The over-all rate of consumption of 1-butene increases very slightly with increasing pressure. The over-all quantum yield of 1-butene consumption is 0.32 at 20-mm pressure. The principal steps in the mechanism proposed for the reaction are:



followed by polymerization reactions of the type



It is therefore possible for the first time, to obtain a direct measurement of the rate of collisional deactivation merely by determining the rate of formation of 2-butene. 2-butene is much less reactive than 1-butene. The over-all quantum yield of 2-butene consumption has a maximum value of 0.11 at an initial pressure of 1-2 mm. Above this pressure the rate of 2-butene consumption falls off rapidly. The main product of the reaction is a liquid polymer. Smaller amounts of hydrogen and methane are also formed. An activated molecule mechanism is proposed which accounts for the essential aspects of the reaction.

INTRODUCTION

IN earlier papers from this laboratory it has been shown that ethylene,¹ butadiene,² propylene,³ and isoprene³ all react with mercury (3P_1) atoms, at room temperature, by an activated molecule mechanism. Isobutene,⁴ on the other hand seems to decompose initially into C_4H_7 radicals and H atoms. In other words, with isobutene, the activated molecule formed by collision of the hydrocarbon molecule with the mercury (3P_1) atom seems to have a shorter life than the interval between successive collisions.

The present investigation on 1-butene and 2-butene was undertaken in order to investigate further the relation between structure and mechanism of reaction in the unsaturated hydrocarbons.

EXPERIMENTAL

A general description of the apparatus employed, and the experimental technique has already been given in a previous paper.²

* Contribution No. 1414 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).

⁴ H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 534 (1946).

The cylindrical quartz cell had a volume of 240 cc, and was immersed in a water thermostat, maintained at $30.00 \pm 0.01^\circ\text{C}$. The total volume of the system was 1050 cc.

The analyses of the condensible products of the reaction reported in this paper were made on the mass spectrometer through arrangement with the National Bureau of Standards. The sampling technique employed, as well as the method of analysis of the products, non-condensibles in liquid air, have been previously described.⁴

The 1-butene and 2-butene were the C.P. grade manufactured by the Matheson Company, East Rutherford, New Jersey. After several trap-to-trap distillations, the middle fractions were collected and stored in one-liter flasks provided with Warrick-Fugassi valves.⁵

TABLE I. Composition of original reactants.

Component	1-butene	2-butene
	mole percent	
C_3H_4	—	0.3
Propylene	—	0.4
1-Butene	98.91	—
2-Butene	0.87	99.0
Butanes	0.13	0.2
2-methyl-2-butene	—	0.03
Methyl pentenes	—	0.02
Dimethyl pentanes	—	0.05
Carbon dioxide	0.09	—

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

TABLE II. 1-Butene.

Run No.	Po (mm)	$\frac{-\Delta P}{\Delta t} \times 10^2$ mm/min.	$\frac{d(\text{CH}_4)}{dt} \times 10^6$ moles/min.	$\frac{d(\text{H}_2)}{dt} \times 10^6$ moles/min.	A/B
80G	2.12	1.45	0.0280	0.0186	1.50
81G	4.92	1.82	0.0540	0.0290	1.86
76G	6.03	1.73	0.0719	0.0427	1.68
77G	7.91	1.88	0.0686	0.0504	1.36
83G	8.66	1.83	0.0762	0.0599	1.27
73G	9.90	2.02	0.0704	0.0585	1.26
84G	15.35	1.83	0.0712	0.0536	1.33
79G	16.36	1.86	0.0619	0.0422	1.47
75G	17.49	1.87	0.0550	0.0426	1.29
71G	20.92	1.73	0.0520	0.0375	1.39
85G	22.52	1.70	0.0579	0.0416	1.39
74G	23.67	1.71	0.0522	0.0377	1.39
78G	24.74	1.62	0.0542	0.0429	1.27
86G	44.81	1.28	0.0340	0.0273	1.25
82G	62.38	1.00	0.0286	0.0227	1.26
87G	67.23	0.92	0.0257	0.0208	1.24

The compositions of the gases used, as determined on the mass spectrometer, are given in Table I.

RESULTS

1-Butene

1-butene shows a similar behavior to propylene,³ isoprene,³ and isobutene⁴ in that the pressure decreases linearly with time even in the initial stages of the reaction. The polymer forms in colorless droplets on the window of the cell through which the light enters. The gas, non-condensable in liquid air, present at the end of each run was shown to be a mixture of hydrogen and methane. These data are summarized in Table II.

From Table II we see that the rate of pressure decrease as well as the rates of formation of hydrogen and methane all reach a maximum at an initial pressure of 10 mm. Measurements of the actual amounts of methane and hydrogen formed, as functions of the time, were made at initial pressures of 15 mm and 30 mm. These quantity-time curves were all straight lines passing through the origin.

The last column of Table II shows that the ratio $[d(\text{CH}_4)]/dt/[d(\text{H}_2)]/dt$ is constant, within experimental error, at 1.39 ± 0.12 .

THE PRODUCTS OF THE REACTION

A detailed analysis of the products of the reaction has been made on the mass spectrometer at the National Bureau of Standards by Dr. A.

TABLE III. 1-butene. Mass spectrometric analysis—run 80G. Po=2.12 mm.

Product	Moles products formed per mole 1-butene decomposed
Hydrogen	0.0166
Methane	0.0250
Ethane	0.1372
Propane	0.0230
2-Butene	0.00204
<i>n</i> -Butane	0.00353
Pentenes	0.00676
Pentanes	0.0366
Benzene	0.00101
Methyl cyclopentane	0.00605
Hexanes	0.00524
Methyl cyclohexanes	0.00232
Ethyl cyclohexenes	0.00030
Heptanes	0.00434
Octenes	0.00040

Keith Brewer⁶ and these results are reported in Tables III, IV, V, VI, and VII. There are a large number of products at the lower pressures owing undoubtedly to radical recombination reactions. At the higher pressures, the main products are 2-butene and polymer. The polymer is a clear, viscous, colorless liquid, completely soluble in benzene.

The data in Table VII on the composition of the polymer, and the rate of polymerization of 1-butene, were obtained by a carbon-balance calculation.

In Fig. 1 the over-all rate of consumption of 1-butene, the rate of formation of 2-butene, and the rate of polymerization are plotted as

TABLE IV. 1-butene. Mass spectrometric analysis—run 81G. Po=4.92 mm.

Product	Moles product formed per mole 1-butene decomposed
Hydrogen	0.0141
Methane	0.0263
Ethane	0.1126
Propane	0.0240
2-Butene	0.2124
<i>n</i> -Butane	0.0207
Pentadienes	0.00296
Pentenes	0.0416
Pentanes	0.0124
Benzene	0.00104
Hexenes	0.0108
Hexanes	0.0137
Methyl cyclohexenes	0.00226
Ethyl cyclohexenes	0.00191
Heptenes	0.00330
Heptanes	0.00834
Octanes	0.00070

⁶For a description of the method of analysis, see A. Keith Brewer and Vernon H. Dibeler, J. Research Nat. Bur. Stand. **35**, 125 (1945).

TABLE V. 1-butene. Mass spectrometric analysis—
run 87G. $P_0=67.23$.

Product	Moles product formed per mole of 1-butene decomposed
Hydrogen	0.0091
Methane	0.0113
2-Butene	0.742

functions of the initial pressure, using the data of Tables VI and VII.

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. LeRoy and Steacie¹ have shown that this reaction has a quantum yield of 0.37 at this pressure. The mean quantum input to the cell, on this basis, was $7.07 \pm 0.11 \times 10^{-6}$ einstein per minute. The values of the over-all quantum yield of 1-butene consumption are given for each pressure in the last column of Table VI.

RESULTS

2-Butene

The results for the runs on 2-butene are summarized in Table VIII.

It is apparent from Table VIII that 2-butene is considerably less reactive than 1-butene. The main product of the reaction is a liquid polymer. Smaller amounts of hydrogen and methane are

TABLE VI. 1-butene.

Run No.	P_0 mm.	$-d(1-C_4H_8)$ $d(2-C_4H_8)$		Quantum yield $\phi(1-C_4H_8)$
		$\frac{dt}{moles/min. \times 10^6}$	$\frac{dt}{dt}$	
80G	2.12	1.12	0.00229	0.159
81G	4.92	2.06	0.437	0.291
83G	8.66	1.71	0.526	0.242
84G	15.35	2.23	0.967	0.316
85G	22.52	2.25	1.115	0.318
86G	44.81	2.13	1.285	0.301
87G	67.23	2.28	1.693	0.323

TABLE VII. 1-Butene.

Run No.	Polymer composition	Rate of polymerization of 1-butene moles per min. $\times 10^6$
80G	$n(C_4H_{7.4})$	0.92
81G	$n(C_4H_{7.2})$	1.10
83G	$n(C_4H_{7.8})$	1.16
84G	$n(C_4H_{7.8})$	1.24
85G	$n(C_4H_{7.8})$	1.12
86G	$n(C_4H_{7.9})$	0.83
87G	$n(C_4H_{7.8})$	0.58

also formed. The maximum rate of consumption of 2-butene seems to occur at an initial pressure of 1–2 mm corresponding to the maximum over-all quantum yield of approximately 0.11.

DISCUSSION

1-Butene

Before attempting to devise a mechanism for this reaction, it might be well to summarize briefly the salient results of our investigation. These are:

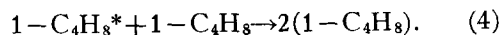
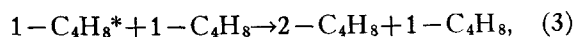
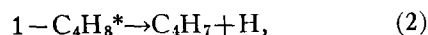
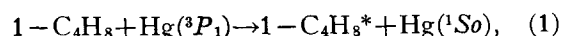
- The pressure *vs.* time curve is linear even in the initial stages of the reaction.
- The rate of pressure decrease is maximum at 10 mm.
- The main products of the reaction are 2-butene and a liquid polymer. Smaller amounts of a large number of other substances are also formed, including methane and hydrogen.
- The rate of isomerization increases rapidly with pressure in the region of complete quenching, while the rate of polymerization falls off rapidly.
- The over-all rate of consumption of 1-butene increases only very slightly with increasing pressure in the complete quenching region. The quantum yield is approximately constant in this region at 0.32.
- The rates of formation of methane and hydrogen reach a maximum at 10-mm pressure. Furthermore the ratio

$$\frac{[d(CH_4)/dt]}{[d(H_2)/dt]}$$

is constant throughout the entire pressure range at 1.39 ± 0.12 . These products are only of minor importance compared to isomerization and polymerization.

- The polymer is a clear, colorless liquid, completely soluble in benzene.

The fact that the rate of isomerization increases with pressure, in the complete quenching region, while the rate of polymerization decreases, suggests the sequence



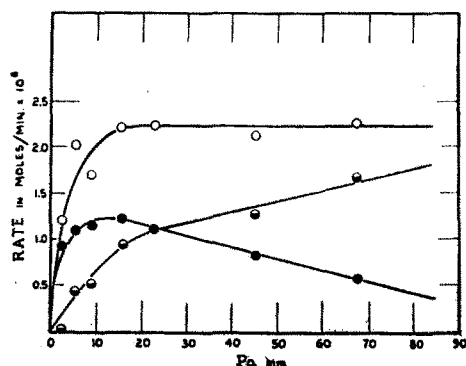
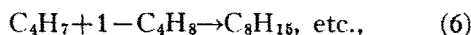
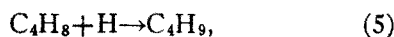


FIG. 1.

Polymerization will then be initiated by the radicals formed in (2)



On this basis, isomerization would be virtually the only reaction occurring at high pressures. An examination of Table VI will show that this conclusion is consistent with our findings. At $P_0 = 15.35$ mm, $0.967/2.23$ or 0.43 mole of 2-butene are formed per mole of 1-butene decomposed. While at $P_0 = 67.23$, $1.693/2.28$ or 0.74 mole of 2-butene are formed per mole of 1-butene decomposed. Consequently one would expect that at pressures above, say, 150 mm, free radical formation, and hence polymerization would be of negligible importance, the only reaction occurring being the isomerization of 1-butene to 2-butene. It is interesting to note at this point that LeRoy and Steacie⁷ found that 2-butene was a significant product in the cadmium (3P_1) sensitized reaction of 1-butene.

With increasing pressure, then, reaction (2) will eventually become completely suppressed and under these conditions the rate equations assume the asymptotic form

$$\begin{aligned} \frac{d(2 - \text{C}_4\text{H}_8)}{dt} / I_{ab} &= \frac{-d(1 - \text{C}_4\text{H}_8)}{dt} / I_{ab} \\ &= k_1 \left(\frac{k_4}{k_3 + k_4} \right) = 0.32 \end{aligned}$$

⁷ D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **10**, 683 (1942).

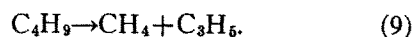
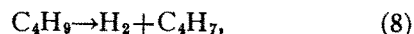
from Table VI or

$$\frac{k_4}{k_3} = \left(\frac{k_1 - 0.32}{0.32} \right).$$

Now if all collisions between activated 1-butene molecules and normal 1-butene molecules lead to isomerization $k_4 = 0$, and hence $k_1 = 0.32$. This is not an improbable assumption in view of the fact that it has been shown that the initial step in the mercury photo-sensitized reaction of isobutene⁴ is only about 16 percent efficient. In other words, if we assume that reaction (1) is only 32 percent efficient, the rate of formation of 2-butene becomes a direct measure of the rate of deactivation of the excited molecules.

This conclusion is of considerable interest. Collisional deactivation has been postulated in a large number of reactions in order to explain, for example, a decrease in rate with increasing pressure. Now, for the first time, it becomes possible to follow deactivation directly simply by measuring the rate of formation of 2-butene.

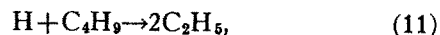
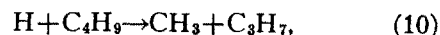
The small amounts of methane and hydrogen formed probably arise from the unimolecular decomposition of the activated butyl radical formed in (5). This radical will contain excess energy of hydrogenation⁴ and may decompose to some extent by the reactions



These reactions would explain the fact that the ratio of the rates of formation to methane to hydrogen is constant, since under these conditions

$$\frac{d(\text{CH}_4)}{dt} / \frac{d(\text{H}_2)}{dt} = \frac{k_8}{k_9} = 1.39 \text{ from Table II.}$$

At low pressures atomic cracking reactions of the type



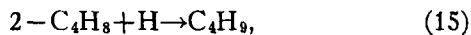
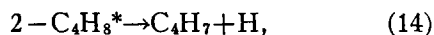
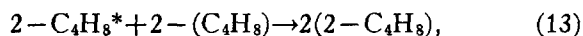
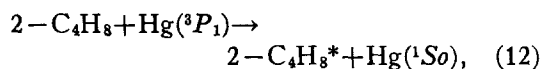
would become significant. The important products listed in Tables III and IV could easily be accounted for by radical recombination reactions involving CH_3 , C_2H_5 , C_3H_7 , C_4H_7 , and C_4H_9 radicals.

2-Butene

The salient features of the 2-butene reaction are:

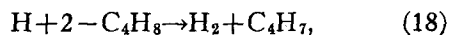
- The rate of pressure decrease, as well as the rate of consumption of 2-butene both fall off with increasing pressure above 2 mm.
- The maximum over-all quantum yield of 2-butene consumption is 0.11.
- The main product of the reaction is a liquid polymer. Smaller amounts of hydrogen and methane are also formed.

The falling off in the rate of consumption of 2-butene with increasing pressure again suggests an activated molecule mechanism.



A comparison of Tables VII and VIII shows that the maximum in the polymerization rate curves occurs at an initial pressure of 1-2 mm for 2-butene, and at about 10 mm for 1-butene. Now since the quenching cross sections for the two molecules should not be significantly different, we are led to conclude that the activated state has a longer life in the case of 2-butene than in 1-butene, i.e., $(1/k_{14}) > (1/k_2)$. This assumption would also offer a plausible explanation for the fact that the rate of polymerization of 2-butene is only about one-half that of 1-butene.

The small amounts of hydrogen formed suggest the step



which would involve an activated C_4H_9 radical as an intermediate.

The methane is present in significant amounts only at low pressures. The reaction



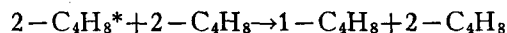
would require that the rate of methane formation fall off even more rapidly with pressure than the

TABLE VIII. 2-butene.

Po mm	$-\frac{\Delta P}{\Delta t} \times 10^2$ mm./min.	$-d(2-C_4H_8)$ dt	$d(H_2)$ dt moles/min. $\times 10^6$	$d(CH_4)$ dt	Quantum yield $\phi(2-C_4H_8)$
2.02	0.93	0.77	0.041	0.047	0.11
4.63	0.82	0.74	0.047	0.024	0.10
8.32	0.65	0.49	0.038	0.009	0.07
21.52	0.52	0.36	0.027	0.003	0.05
32.36	0.57	0.35	0.025	0.001	0.05
42.14	0.37	0.30	0.022	0.001	0.04
49.02	0.33	0.21	0.022	0.0008	0.03
61.14	0.27	0.28	0.020	0.0007	0.04
70.64	0.37	0.28	0.020	0.0002	0.04

rate of hydrogen formation, in agreement with our results.

It is interesting to note that the reaction



does not seem to occur, since no 1-butene was found in the products. Thermodynamically, of course, 2-butene is more stable than 1-butene, although their heats of formation differ only by 1-2 kcal.⁸

CONCLUSIONS

It is apparent that, with the striking exception of isobutene, the activated molecule mechanism seems to be common to all the lower olefines and alkadienes.

The collisional isomerization reaction of 1-butene to 2-butene is of considerable interest since it gives us a direct means of determining the extent of collisional deactivation. Virtually every activated molecule formed seems to undergo a deactivating collision above an initial pressure of 150 mm. We are therefore led to the important conclusion that, with the exception of isobutene, free radicals play an important part in the mercury photo-sensitized reactions of the lower olefines and alkadienes only at relatively low pressures.

ACKNOWLEDGMENT

It is a great pleasure to acknowledge our indebtedness to Dr. A. Keith Brewer and Dr. Fred L. Mohler of the Mass Spectrometry Section of the National Bureau of Standards for their kindness in performing the mass spectrometric analyses reported in this paper.

Our thanks are also due to Mr. Yves Lupien for assistance in making the measurements.

⁸ F. D. Rossini, Chem. Rev. 27, 1 (1940).