method of locating the positions of chelated groups in aromatic systems. Fig. 4 shows that the $\Delta\delta$ values are linearly related to the $\Delta\nu(C{=}O)$ values to a striking degree. The deviations of the points from the straight lines in this figure are much smaller than either the deviations from linearity in Fig. 3 or the corresponding deviations in the plot of $\Delta\nu(C{=}O)$ values.[5] This again indicates that, in addition to the C=C mobile bond orders, some other effects are concerned in exact descriptions of the factors which influence the $\Delta\delta$ values and that these effects also influence the $\Delta\nu(C{=}O)$ values. We believe that these other factors are mainly steric in nature.

Work is in progress in these Laboratories designed to determine $\Delta\nu(C{=}O)$ values and proton shifts for chelated derivatives of the simple 5-membered heterocyclic rings.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, RIVER CAMPUS STATION, ROCHESTER, NEW YORK]

The Photochemistry of 1,3-Butadiene and 1,3-Cyclohexadiene[1]

BY R. SRINIVASAN

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The photolysis of 1,3-butadiene at 4 mm. pressure and room temperature with an unfiltered medium pressure mercury arc (mainly 2000–2500 Å.) led to hydrogen, acetylene, ethylene, ethane, 1-butyne, 1,2-butadiene, dimer(s) and a polymer as the major products and numerous minor products. A consideration of the stoichiometry, the effects of added gases and of increasing pressure, suggests that three primary processes which may arise from an excited state of the butadiene molecule are important. These are (1) $C_4H_6^* \rightarrow CH_2{=}C{=}CH{-}CH_3^*$ (the "hot" 1,2-butadiene molecule may subsequently decompose to give $CH_3\cdot$ and $C_3H_3\cdot$ radicals unless it is stabilized by a deactivating collision); (2) $C_4H_6^* \rightarrow C_2H_2 + C_2H_4$; (3) a process which leads to the formation of hydrogen. This may be $C_4H_6^* \rightarrow C_4H_4 + H_2$, although the formation of C_4H_4 was not proven. Preliminary results on the photolysis of 1,3-cyclohexadiene suggest that three analogous primary processes which lead to 1,3,4-hexatriene, $2C_2H_2 + C_2H_4$, and benzene and hydrogen are important. A second isomer also was observed to be formed in poor yield.

Introduction

The mercury photosensitized decomposition of 1,3-butadiene has been the subject of several studies.[2–5] The present study of the photochemistry of butadiene[6] was started in an attempt to see whether this compound would isomerize photochemically to cyclobutene. It may be stated even at this point that such a reaction was not observed. However, it became apparent that many of the products of the photochemical decomposition were common to the mercury photosensitized decomposition.[3,5] The present study was undertaken to find the primary processes in the photochemistry of butadiene and also to clarify some of the secondary processes in the mercury sensitized decomposition. An exploratory study of the photochemistry of cyclohexadiene was attempted in order to compare this with butadiene.

Experimental

Butadiene of 99.4% purity was obtained from The Matheson Co., Inc. It was distilled from −78 to −159° and degassed at about −110° before use. Cyclohexadiene from Farchan Research Laboratories was dried and distilled once *in vacuo*. By vapor phase chromatography, it was found to be free from impurities.

A conventional high vacuum apparatus in which the reactants did not come in contact with stopcock grease was used. Since the photolysis of either diene led to the deposition of a polymer on the walls of the cell, reproducible results were obtainable only in clean cells. Hence two identical quartz cells of 5.0 cm. diameter an 4.4 cm. length were used alternately. At the end of each experiment, the used cell was detached from the line and replaced by a clean one. The alignment of the cell in the optical path was made reproducible by the use of a jig. The used cell was cleaned with a hot mixture of concentrated nitric and sulfuric acids followed by hot concentrated sulfuric acid alone and washed with distilled water.

The light source was a Hanovia type S-100 medium pressure mercury arc lamp, used without filters. This lamp does not give the mercury resonance radiation in detectable amounts.

From the products, two fractions were removed at −195 and −159°, respectively. These were analyzed mass spectrometrically on a Consolidated Engineering Co. type 21-620 instrument. The remaining products along with the unreacted butadiene were introduced into a Perkin–Elmer Vapor Fractometer type 154-B fitted with a 3-meter Perkin–Elmer column material "D." This column material gave a satisfactory resolution of 1,2-butadiene from butadiene but not the latter from 1-butyne, especially when butadiene was present in great excess. Hydrocarbon products of molecular weight 78 or more had such high retention times on this column that analysis for them was not practical. A 2-meter column of material "A" (Perkin–Elmer) had to be used if the higher boiling products were to be separated and analyzed. A complete analysis to include compounds as complex as 4-vinylcyclohexene (b.p. 129°) involved two identical experiments.

Qualitative analysis of the products was based on the cracking pattern in the mass spectrometer[7] and the retention time on the vapor phase chromatograph. Quantitative analyses for 1,2-butadiene and 1-butyne were based on the areas under the peaks in the chromatogram.

In some of the results reported here, when an initial pressure of butadiene of 4 mm. was used, the conversions ranged from 10 to 15%. At higher pressures of butadiene and in the presence of added gases, the conversions were less than 10%. While these conversions are high in terms of accepted photochemical practice, they were made necessary by the need to obtain reasonable amounts of products for analysis and to establish the amount of butadiene which had reacted. A further discussion of this will be reserved for a later section.

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[1] The author wishes to thank the National Science Foundation for a grant to the Department of Chemistry, University of Rochester, in support of this work.

[2] G. Gee, *Trans. Faraday Soc.*, **34**, 712 (1938).

[3] H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **12**, 484 (1944).

[4] D. H. Volman, *ibid.*, **14**, 467 (1946).

[5] J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).

[6] The name butadiene or cyclohexadiene used without any prefixed numerals will hereafter refer to the 1,3-compounds.

[7] The author wishes to express his thanks to Dr. F. P. Lossing of the National Research Council of Canada for the mass spectrometric identification of a sample of 1,2-butadiene.

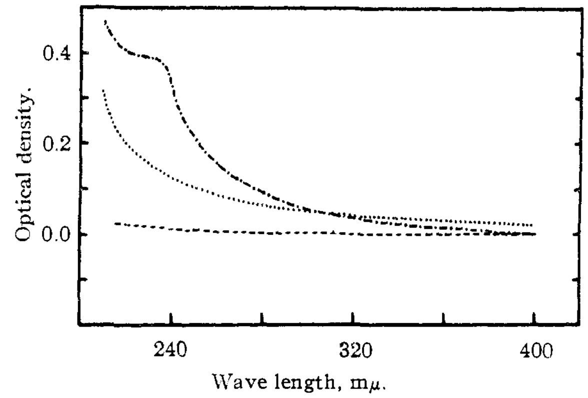

Fig. 1.—Absorption curves for cell after photolysis of: --------, butadiene, P = 4 mm.; ......, butadiene, P = 29 mm.; —·—·—, cyclohexadiene, P = 5 mm. Optical density (log I_0/I) of empty cell has been arbitrarily set at zero.

Results

Products.—The photolysis of butadiene at about 4 mm. initial pressure was found to lead to a profusion of products, not one of which was formed in a yield greater than 0.15 mole (of product) per mole of butadiene. Those products which amounted to 0.05 to 0.15 mole will be termed the major products and these were: hydrogen, 0.06: acetylene 0.14: ethylene 0.14: ethane 0.08: 1-butyne 0.05: 1,2-butadiene 0.05. On the basis of the peaks in the vapor phase chromatogram, there were no less than 17 minor products which included the following: methane, 2-butyne, a pentene, two compounds of mass 84 (C_6H_{12}), two compounds of mass 78 (C_6H_6) and one compound of mass 94 (C_7H_{10}). Two approximate checks on the completeness of the detection of the products could be made. One, which was based on the fact that even at 30% conversion of butadiene, the total pressure in the system did not change (with an uncertainty of ±30%) required that the total count of molecules in the gas phase should remain the same. On the basis of reasonable assumptions for the sensitivity of the minor products in the gas chromatograph, it can be estimated that these add up to 0.21 mole. Together with the major products, these account for 0.73 mole to replace every mole of butadiene that reacted. These figures were obtained as an average of several runs in each of which about 3.4 μmoles of butadiene reacted. Since it was found that dimers of butadiene boiling higher than 4-vinylcyclohexene (*e.g.*, 1,5-cyclooctadiene) were not included in this analysis, and since all the dimers and even trimers may contribute to the total pressure of the products, the estimated value is bound to be low. It is hence believed that no major product among the C_1 to C_7 hydrocarbons has been overlooked in the analysis. A check of the carbon balance indicated that only 0.6 of each butadiene molecule appeared in the C_1–C_7 products. Transmission curves for the cell (sealed with a vacuum inside) before and after photolysis (Fig. 1) showed that a solid was deposited on the wall during the photolysis even at 4 mm. initial pressure. After prolonged photolysis at this pressure in a flow system, a white solid was clearly seen on the windows of the cell.

A careful effort was made to see whether a product of mass 54 (C_4H_4) was formed. While it is impossible to say that no such product was formed, it is reasonably certain that it was not a major product.

The formation of the major products and the disappearance of butadiene are plotted as a function of time in Figs. 2 and 3. The wide scatter in the data for 1-butyne and for butadiene disappearance are due to difficulties in analysis. The linearity of these plots may be questioned as a subtle change in slope would not be emphasized by the scatter. It may be concluded that no sharp change in the rate of formation of any of the products occurred over the large range of conversion (0–30%) represented in these figures.

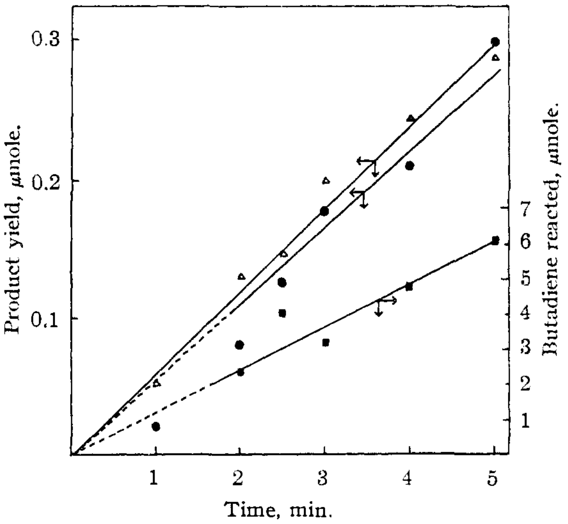

Fig. 2.—Products and butadiene reacted as function of time: △, 1,2-butadiene; ●, 1-butyne; ■, butadiene.

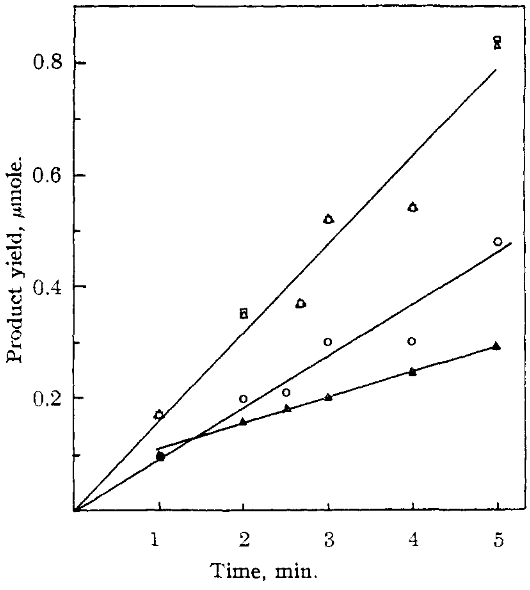

Fig. 3.—Products as function of time: □, ethylene; △ acetylene; ○, ethane; ▲, hydrogen.

The influence of filters and added gases on the photolysis is shown in Table I.

TABLE I

EFFECT OF FILTERS AND ADDED GASES ON THE PHOTOLYSIS OF BUTADIENE

Butadiene pressure, 4.1 ± 0.2 mm. (except d); room temperature; cell volume, 82.4 ml.; dead space 55.2 ml.; Hanovia S-100 medium pressure mercury arc.

Time, min.	Filter or gas added P, mm.	μmole					
		H_2	C_2H_2	C_2H_4	C_2H_6	1-Butyne	1,2-Butadiene
3	None	0.20	0.48	0.49	0.28	0.17	0.18
3	Hg vapor filter	.15	.33	.34	.20	.08	.13
3[b]	O_2 3.9	.08	.30	.41	0	0	.01
5[a,b]	O_2 2.5	.26	.09	.60	0	n.d.[f]	n.d.[f]
2[a]	NO 4.2	.06	.11	.21	0	0	0.02
3	CO_2 8.5	.24	.40	.40	0.22	0.14	.18
1035[d]	Corex D filter[e]	.06	.08	.08	0	0(?)	.04

[a] Both C_6H_8 compounds absent. [b] CO, CO_2 and H_2O present in products. [d] P = 97.1 mm. [e] Corning clear glass filter which transmitted 60% at 3000 Å.; 16% at 2800 Å. and 0.1% at 2500 Å. [f] n.d., not determined.

In Table II, the effect of the pressure of butadiene on the products is presented. Since the estimation of 1-butyne in the presence of large amounts of butadiene is difficult, this product is not listed in Table II, but its yield definitely decreased with an increase in the pressure of butadiene.

TABLE II

EFFECT OF PRESSURE ON THE PHOTOLYSIS OF BUTADIENE

Room temperature; cell volume, 82.4 ml.; dead space, 55.2 ml.; time, 5 min.

P, mm.	μmole				
	H_2	C_2H_2	C_2H_4	C_2H_6	1,2-Butadiene
4.1	0.30	0.81	0.81	0.46	0.30
11.8	.30	(.59)	.72	.31	.36
26.6	.27	.68	.69	.23	.39
43.8	.25	.50	.50	.14	.38
91.0	.24	.38	.39	.06	.40

In the photolysis of cyclohexadiene at 4 mm. pressure, the observed products were hydrogen, ethane, ethylene, acetylene, 1,3,4-hexatriene, benzene and a compound of mass 80 (C_6H_8) other than 1,3,4-hexatriene. Transmission curves for the cell before and after photolysis (Fig. 1) established the formation of a solid deposit on the window in considerable amount. Mass and pressure balance showed that these volatile products accounted for about 70 mole % of gaseous products but only 25% of the cyclohexadiene that reacted. In view of such a large discrepancy in the mass balance, only a few exploratory runs were made on this compound. These are listed in Table III. The yield of benzene was subject to a large uncertainty since it was poorly separated from the parent compound on the chromatographic column that was used. At high conversions it could be observed that the yield of benzene equalled that of hydrogen.

TABLE III

PHOTOLYSIS OF CYCLOHEXADIENE VAPOR

Room temperature; P, 4.4 mm.; cell volume, 82.4 ml.; dead space, 55.2 ml.; yields of products in μmoles.

Gas added or filter	None	Oxygen[a]	Nitric oxide[b]	Corex D[c] filter
Time (min.)	5	5	5	975
H_2	1.14	0.48	0.63	0.81
C_2H_2	.13	.09	.10	.05
C_2H_4	.08	.09	.02	.03
C_2H_6	.06	0	0	0
C_6H_8	.19	0.10	0.10	0.24
Benzene	.8	.7	.9	1.2
1,3,4-Hexatriene	.18	.28	.26	1.86

[a] P = 2.4 mm. [b] P = 4.8 mm. [c] See Table I for characteristics.

Discussion

The absorption spectrum of butadiene gas above 2000 Å.[8,9] may be divided into two regions although there is no sharp separation between them. From 2000 to about 2500 Å. the absorption is very intense (log ϵ, the molar absorption coefficient = 1 to 3.5) while from 2500–3000 Å. the absorption is relatively weak[10] (log $\epsilon < 1$). At 4 mm. pressure of the gas for a path length of 4.4 cm., absorption in the second region will be negligible while in the first region it will range from 10 to 90%. Further, in the experiment in which a Corex D filter was used, the irradiation time had to be increased by a factor of 1000 to obtain the same degree of decomposition as without the filter. Hence it may be concluded that in those experiments in which an unfiltered light source was used, the photochemically effective wave length region was below 2500 Å.

High conversions were used in some experiments in this study. Justification for this (experimentally necessary) procedure may be found in the facts that (i) no single compound predominated in the gaseous products, (ii) butadiene has a more intense absorption in the wave length region from 2000–2500 Å. than any of the major products, (iii) bimolecular processes that followed the primary absorption were not studied quantitatively, (iv) the rates of production of the major products appear to be nearly constant even up to 25% conversion. No suitable alternatives were available; a higher initial pressure was unacceptable as this would have limited the absorption to the front portion of the cell[11]; a flow system and a larger sample were ruled out by the need to monitor the disappearance of butadiene with reasonable accuracy.

Since the total yield of products appears to decrease with an increase in the initial pressure of butadiene or on the addition of carbon dioxide, it seems likely that the absorption of radiation by butadiene leads to an excited molecule which persists long enough to undergo collisions. These collisions may lead to deactivation or dimerization.

$$CH_2{=}CH{-}CH{=}CH_2 + h\nu \longrightarrow CH_2{=}CH{-}CH{=}CH_2^* \quad (1)$$

$$CH_2{=}CH{-}CH{=}CH_2^* + M \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + M \quad (2)$$

$$\longrightarrow C_8H_{12}\ (M = C_4H_6) \quad (3)$$

The excited molecules of butadiene may undergo one of three reactions. These are (i) rearrangement to a "hot" 1,2-butadiene molecule which may either decompose or be stabilized by a collision

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(8) American Petroleum Research Institute Project 44 Serial No. 65.

(9) R. F. Boyer, *J. Phys. Chem.*, **51**, 86 (1947). The spectrum is reported in solution (solvent?).

(10) The absorption from 2600–3000 is so weak that measurements in the gas phase are difficult. Part of this statement is based on the information in ref. 9.

(11) This study has also shown that self-quenching may be an important effect at higher pressures. See ref. 3.

$$CH_2{=}CH{-}CH{=}CH_2^* \longrightarrow CH_2{=}C{=}CH{-}CH_3^* \tag{4}$$

$$CH_2{=}C{=}CH{-}CH_3^* \longrightarrow CH_3\cdot + C_3H_3\cdot \tag{5}$$

$$CH_2{=}C{=}CH{-}CH_3^* + M \longrightarrow CH_2{=}C{=}CH{-}CH_3 + M \tag{6}$$

For normal molecules reaction 4 is endothermic by 12.8 kcal.[12] so that if the absorbed wave length is $\sim$2300 ($\equiv$ Å. 124 kcal./mole) sufficient energy may be available for (5). The presence of methyl radicals in the system can be inferred from the formation of methane and ethane. An increase in the pressure of butadiene would promote not only (6) which would favor the formation of 1,2-butadiene but also (2) and (3) which would act in the opposite way. Actually 1,2-butadiene increases and then levels off with an increase in the pressure of butadiene from 4 to 90 mm. The secondary reactions of methyl radicals may include recombination to give ethane, addition

$$CH_3\cdot + C_4H_6 \longrightarrow C_5H_9\cdot \tag{7}$$

which may ultimately lead to the pentene found as a product and abstraction of a hydrogen to give methane. The reactions of the $C_3H_3\cdot$ radical are less clear. Collin and Lossing[5] found that the C_3H_3 radical formed from allene by mercury photosensitized decomposition reacted with methyl radicals to give mainly 1-butyne. On this basis they favored $\cdot CH_2{-}C{\equiv}CH$ as the structure of the C_3H_3 radical. In the present study the facts that two[13] compounds of formula C_6H_6 are formed and that most of the 1,2-butadiene and all of the 1-butyne are eliminated by the addition of oxygen or nitric oxide suggest that methyl may add to C_3H_3 to give 1,2-butadiene as well as 1-butyne, but the evidence is not conclusive.[14]

$$CH_3\cdot + \cdot CH_2{-}C{\equiv}CH \longrightarrow CH_3{-}CH_2{-}C{\equiv}CH \tag{8}$$

$$CH_3 + CH_2{=}C{=}CH\cdot \longrightarrow CH_2{=}C{=}CH{-}CH_3 \tag{9}$$

$C_3H_3\cdot$ radicals may also attack the parent molecule $C_3H_3\cdot + C_4H_6 \rightarrow C_7H_9$. This may be the source of the C_7H_{10} found in the products.

Primary process 4 may account for 0.3 of every mole of butadiene that disappears. This may be compared with the value of 0.5 estimated by Collin and Lossing for this set of reactions under their conditions.

(ii) A second mode of decomposition may be

$$CH_2{=}CH{-}CH{=}CH_2^* \longrightarrow CH_2{=}CH_2 + CH{\equiv}CH \tag{10}$$

The remarkable constancy in the equivalence of ethylene and acetylene under a wide variety of conditions, and the fact that both are still formed in the presence of oxygen or nitric oxide suggests a process such as (10). Thermochemical data[12] show that the reaction is endothermic (when the butadiene molecule is "cold") by 39.91 kcal./mole. The process involves a hydrogen transfer very similar to the rearrangement of butadiene to 1,2-butadiene. This primary process accounts for 0.14 of every mole of butadiene that reacted.

(iii) A third mode of decomposition may give rise to hydrogen. Gunning and Steacie[3] proposed that in the mercury photosensitized decomposition this reaction may be

$$CH_2{=}CH{-}CH{=}CH_2^* \longrightarrow C_4H_4 + H_2 \tag{11}$$

They also suggested that the acetylenic compound that they found in the products may be vinyl acetylene from reaction 11. Their estimate of this acetylenic compound, which was based on a specific reaction for the $-C{\equiv}CH$ group, showed that it was formed in only one fourth of the yield of hydrogen. The later work of Collin and Lossing[5] suggests that 1-butyne was also part of the acetylenic products, so that the discrepancy in the equivalence of hydrogen and C_4H_4 in the first work would be even greater. Collin and Lossing[5] noted that a product of mass 52 was formed but they did not estimate it quantitatively. In the present work, the hydrogen yield/butadiene reacted is 0.06[15] which compares well with the value of 0.06–0.13 quoted by Collin and Lossing,[5] but a product of formula C_4H_4 was not detected. The situation may be clarified if a sample of pure vinylacetylene is available for comparison.

Since the results obtained in this study on the photochemistry of cyclohexadiene are preliminary, an extensive discussion of the primary processes is not warranted. It suffices to say that the three reactions (12), (13), (14) appear to be important

(12)

$$\longrightarrow CH_3{-}CH{=}C{=}CH{-}CH{=}CH_2 \tag{13}$$

$$\longrightarrow 2C_2H_2 + C_2H_4 \tag{14}$$

When the radiation from an unfiltered arc was used, the amounts of these processes were in the order (14) < (13) < (12). When a Corex filter was used, (14) < (12) < (13). The similarity between these three processes and the corresponding processes in butadiene is obvious.

NOTE.—The identification of one of the products of the photolysis of cyclohexadiene as 1,3,4-hexatriene was made after this manuscript had been submitted for publication, and corrections to this effect were made in proof.

Acknowledgment.—The author wishes to express his thanks to Professor W. Albert Noyes, Jr., for his advice and encouragement in the course of this work.

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[12] American Petroleum Research Institute Project 44; quoted by "Handbook of Chemistry and Physics," 41st Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1959, p. 1907.

[13] If either end of the C_3H_3 radical can behave as a "free" end and if the two ends are equivalent, then combination of two C_3H_3 radicals can give rise to three compounds.

[14] Dr. F. P. Lossing has informed the author that the results of Collin and Lossing do not exclude the occurrence of (9) in the mercury photosensitized reaction of butadiene. Since a C–C rather than a C–H bond (as in allene) is broken in the formation of C_3H_3, more energy would be available for an excitation of the C_3H_3 radical.

[15] Gunning and Steacie also report a value of 0.06 for a one hour run in a static system at 25 mm. of butadiene.