30%, producing a significant amount of cyclohexadienyl radical. Photobleaching of the remaining 70% of the electrons, however, caused only very slight increase of the radical. If the trapped electron is photoreleased to be scavenged by reaction 3, one would expect more prominent increase of the radical, considering the comparatively high concentration of benzene.

As shown in Figure 8, the epr spectrum of radicals from *t*-BuCl in methanol agrees well with that in 3-MP. In both solutions *t*-BuCl scavenges electrons by dissociative electron attachment

$$RX + e^- \longrightarrow R + X^- \qquad (9)$$

giving the *t*-Bu radical, which has a well-defined epr spectrum.[22,23] The same spectrum was also obtained in the isobutene solution in methanol (Figure 8, middle). Since isobutene does not yield an anion nor depress the solvent-trapped electron band at 520 mμ, the formation of *t*-Bu radical in the isobutene solution must be attributed to the H-atom addition to the olefin. The radical is produced both during γ irradiation and subsequent bleaching of the 520-mμ band since the epr signal increases significantly by illumination. The latter effect might be accounted for by reaction 8. However, the following photolytic experiment with TMPD solutions indicates reaction 5 rather than 8 to be the effect of photobleaching. It is well known that ultraviolet excitation of TMPD gives TMPD cations and photoejected electrons which are trapped by the solvent in MTHF or 3-MP solutions.[24] In the methanol glass also, the electron would be trapped by the solvent as in the case of radiolysis, but then bleached almost immediately under the intense AH-6 lamp. The epr spectra of Figure 9 demonstrate that when both TMPD and isobutene were present in ultraviolet-excited methanol glass, *t*-Bu radicals form. Since in the photolyzed sample there is no $CH_3OH_2^+$, it must be concluded that the *t*-Bu radical is formed *via* reaction 5. Parallel photolytic runs with isobutene and TMPD in 3-MP, MTHF, and triethylamine yielded TMPD cation radical but no *t*-Bu radicals, indicating the specific effect of methanol.

Alger, Anderson, and Webb failed to detect photoconductivity in the irradiated alcohol.[18] This can be accounted for by reaction 5, but not easily by the neutralization reaction 8.

Reaction 5 may be exothermic from the following argument. In the mass spectrometer, the appearance potential (AP) of negative ions from dissociative electron attachment correlates with bond dissociation energy (*D*) and electron affinity (*A*) as follows.

$$AP = D - A \qquad (10)$$

Methanol produces CH_3O^- ion by

$$CH_3OH + e^- \longrightarrow CH_3O^- + H \qquad (11)$$

Direct observation of AP(CH_3O^-) gave 2.3 ev[25] while calculation based on $A(CH_3O) = 2.6$ ev and $D(CH_3O\text{–}H) = 4.3$ ev[26] gives 1.7 ev. The average of these two would be the optical threshold for reaction 5 *in vacuo*. It was found that light >700 mμ (1.8 ev) was ineffective in reaction 5. The proposed mechanism is exothermic provided that the solvation energy of CH_3O^- exceeds that of the electron.

It is rather surprising that butene-1 adds an H atom while pentene-1 does not, as described above, but similar differences among simple olefins have been observed by Klein and Scheer. For example, butene-1 produces *sec*-butyl radical at −196° whereas pentene-1 does not yield any radical.[27] They found that an H atom adds to the terminal carbon of olefin, producing *sec*- and not *n*-butyl radical from butene-1. This was confirmed by us since the epr signals from propylene, butene-1, and isobutene agreed with those from isopropyl-, *sec*-butyl-, and *t*-butyl chlorides in methanol, respectively.

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[22] D. W. Skelly, R. G. Hayes, and W. H. Hamill, *J. Chem. Phys.*, **43**, 2795 (1965).

[23] H. Shields and P. Hamrick, *ibid.*, **42**, 443 (1965).

[24] J. B. Gallivan and W. H. Hamill, *ibid.*, **44**, 1279 (1966).

[25] G. F. Hennion, Jr., private communication.

[26] R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

[27] R. Klein and M. D. Scheer, *J. Am. Chem. Soc.*, **80**, 1007 (1958).

Vapor Phase Photochemistry of 1,3-Butadiene-1,1,4,4-d_4

I. Haller and R. Srinivasan

Contribution from the IBM Watson Research Center,
Yorktown Heights, New York. *Received April 5, 1966*

Abstract: The mechanisms of the three primary processes in the vapor phase photolysis of 1,3-butadiene have been investigated by the use of deuterium labeling on the end carbon atoms. None of the processes proceeds by the obvious pathway exclusively. Thus ethylene and acetylene are formed not only by a 1,3 shift but also *via* an intermediate cyclobutene and a third path which gives $C_2H_2D_2$ and C_2D_2. Two mechanisms seem to be applicable to the other two primary processes which give 1,2-butadiene and $H_2 + C_4H_4$, respectively.

The primary processes in the mercury-photosensitized decomposition of 1,3-butadiene were first identified by Collin and Lossing.[1] The reactions which can be represented as

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[Hg]{h\nu} CH_3{-}CH{=}C{=}CH_2 \qquad (1)$$

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[Hg]{h\nu} C_4H_4 + H_2 \qquad (2)$$

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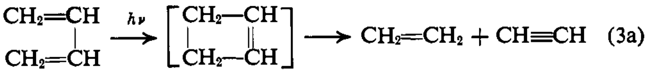
[1] J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).

were both hydrogen migration processes taking place probably *via* four-center intermediates. In the direct photolysis of butadiene,[2] it was observed that in addition to (1) and (2), a third primary process gave rise to ethylene and acetylene.[3,4] The nature of the excited

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{h\nu} C_2H_4 + C_2H_2 \qquad (3)$$

states of butadiene which participate in these processes has been recently reviewed.[5] The occurrence of (3) in the direct photolysis, but not in the sensitized photolysis, suggested the possibility that this process may proceed by the intermediate formation of cyclobutene.



$$\begin{matrix}CH_2{=}CH\\ |\\ CH_2{=}CH\end{matrix} \xrightarrow{h\nu} \left[\begin{matrix}CH_2{-}CH\\ | \qquad \|\\ CH_2{-}CH\end{matrix}\right] \longrightarrow CH_2{=}CH_2 + CH{\equiv}CH \qquad (3a)$$

In order to test this hypothesis, the photolysis of butadiene-1,1,4,4-d_4 was undertaken. It can be seen that this compound would give only C_2D_4 and C_2H_2 if (3a) were operative, while if (3) were a four-center hydrogen migration it would lead to C_2HD_3 and CHCD. Actually, the present study demonstrates that none of these primary processes proceeds exclusively by a single mechanism.

Experimental Section

Butadiene-1,1,4,4-d_4 was obtained from Merck Sharp and Dohme of Montreal, Canada. Its isotopic purity was stated to be 98%. Mass spectrometric analysis confirmed that this was so. It was more difficult to establish what fraction of the material was deuterated in the 2 and/or 3 positions instead of 1 or 4. The infrared spectrum was consistent with the structure butadiene-1,1,4,4-d_4 for the major component. Since the conversions that were used in this study ranged from 10 to 30%, it is unlikely that the observed results were in major part due to a second (differently) deuterated butadiene-d_4.

Photolyses were carried out in the gas phase in a 2.5-l. quartz reaction vessel. For direct photolysis, a 100-w high-pressure mercury arc was used with a chlorine filter, while for the mercury sensitized reaction a bank of 16 germicidal lamps arranged in a circle was used.

The analytical methods that were used have been described before.[3,4] In addition, a column packed with silica gel was found to be useful in the gas chromatographic separation of ethylene, acetylene, and ethane. Unfortunately, acetylene underwent extensive exchange of its deuterium atoms in passage through this column. Acetylene, however, is trapped in preference to the other C_2 hydrocarbons by the frozen starting material. This made it possible to obtain a sufficient amount of acetylene free from ethylene and ethane by separating it from the higher boiling products on a tetraisobutylene column without any H-D exchange.

The deuterium content of the various fractions were analyzed by a Consolidated Electrodynamics 21-620A mass spectrometer modified to vary the ionizing voltage, and in one instance a Cary White Model 90 infrared spectrophotometer.

Results

The deuterium content of the various products in the direct and sensitized photolysis of butadiene-1,1,4,4-d_4 are listed in Tables I and II.

It was established that the deuterium content, as well as its distribution inside the molecule of butadiene-1,1,4,4-d_4, did not change during the course of its photolysis.

The deuterium content of the products was found to be insensitive to the conversion in the range from 10 to 50%.

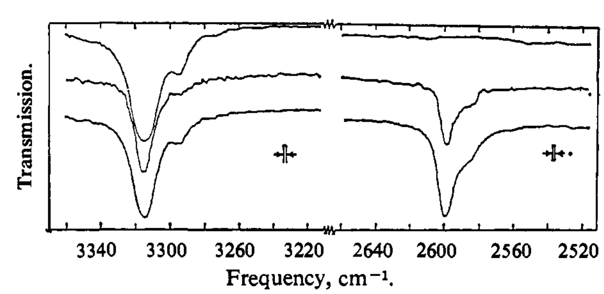


Figure 1. Infrared spectra of 1-butyne: top, standard sample of 1-butyne; middle, 1-butyne formed in the direct photolysis of butadiene-1,1,4,4-d_4; bottom, 1-butyne formed in the mercury-sensitized photolysis of butadiene-1,1,4,4-d_4.

In Figure 1 sections of the infrared spectra of (a) 1-butyne, (b) 1-butyne obtained in the direct photolysis of butadiene-1,1,4,4-d_4, and (c) 1-butyne isolated from the mercury-photosensitized decomposition of butadiene-d_4, are compared. An estimate of the ratio of deuterium and hydrogen atoms in the 1 position in 1-butyne can be obtained from the ratio of the integrated

Table I. Deuterium Content of the Products from the Photolysis of 1,3-Butadiene-1,1,4,4-d_4 in the Vapor Phase

Deuterium content	Products, %					
	Ethane	Ethylene	Acetylene	1-Butyne[c]	1,2-Butadiene	Vinylacetylene
			Direct Photolysis[a]			
d_0	0	0	35.9	0	0	0
d_1	0	0	39.5	0	0	0
d_2	0	26.0	24.6	0	0	64.6
d_3	0	39.2	...	17.3	16.4	28.3
d_4	80.5	34.6	...	69.6	73.0	7.0
d_5	18.5	...	...	13.1	10.5	...
Yield, μmoles	7.9[b]	11.5	~12	62	40	12
		Direct Photolysis in Presence of Oxygen[d]				
d_0	...	0	39.3	0	0	0
d_1	...	0	37.9	0	0	0
d_2	...	26.2	22.7	0	0	73.6
d_3	...	38.1	...	7.0	1.1	25.4
d_4	...	35.6	...	90.0	94.0	1.0
d_5	...	...	...	2.9	4.9	...
Yield, μmoles	0.1	13.6	~14	1.4	6.9	2.1

[a] High-pressure mercury arc; Cl_2 filter, p = 4.0 mm; t = 45 min. [b] Ethane-d_6 = 1.0%. [c] The d_6 isomer was undetectable. [d] p_{oxygen} = 3.8 mm; $p_{butadiene}$ = 4.0 mm; t = 45 min.

Table II. Deuterium Content of the Products from the Mercury-Sensitized Photolysis of 1,3-Butadiene-1,1,4,4-d_4[a]

Deuterium content	Products, %					
	Ethane	Ethylene	Acetylene	1-Butyne	1,2-Butadiene	Vinylacetylene
d_0	0	0	22.0	0	0	...
d_1	0	0	37.4	0	0	...
d_2	0	40.6	40.6	0	0	...
d_3	0	34.1	...	4.8	4.2	...
d_4	0	25.4	...	94.1	94.8	...
d_5	17.1	...	...	1.1	1.1	...
d_6	82.9	...	...	0	0	...
Yield, μmoles	8.4	3.0	~3	94	43	<1

[a] $p_{butadiene}$ = 4.1 mm; t = 2.0 min.

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[2] The term butadiene without any prefix will hereafter refer to 1,3-butadiene.

[3] R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 5063 (1960).

[4] I. Haller and R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964).

[5] R. Srinivasan, *Advan. Photochem.*, **5**, 113 (1966).

Table III. Yields of Ethylene and Acetylene in the Mercury-Sensitized Photolysis of 1,3-Butadiene and Cyclobutene

	1,3-Butadiene				Cyclobutene			
Pressure,[a] mm	1.0	4.1	4.7	16.4	2.4	5.2	10.4	19.9
Time, sec	30	60	189	240	30	60	60	128
Conversion, %	16	15	33	11	16	16	8	13
Ethylene, μmole/min	0.36	0.14	0.20	0.067	1.38	1.01	0.66	0.62
Acetylene, μmole/min	0.34	0.22	0.19	0.060	1.16	0.80	0.62	0.62

[a] Hanovia, spiral-shaped low-pressure mercury arc; 2-cm water filter; 252-ml quartz vessel.

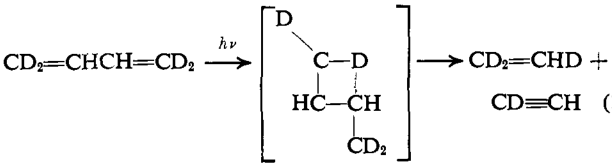
intensities of the ≡CD and ≡CH stretching absorptions by assuming that the quantity I/ν^2 is invariant under isotopic substitution. This relation is strictly valid[6] only as a sum rule for all vibrations belonging to the same symmetry class, but due to the large separation of the frequencies in question from other vibrational frequencies of the molecule, it can be expected to hold. The resulting estimates are 44 and 53% deuterium in the 1 position of 1-butyne obtained in the direct and mercury-photosensitized photolysis, respectively.

In Table III, the yields of ethylene and acetylene in the mercury-sensitized photolysis of butadiene and cyclobutene are compared.

Discussion

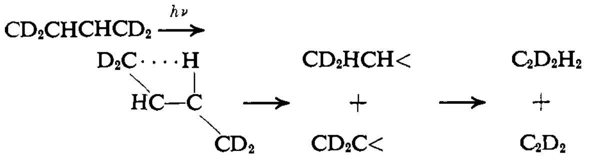
The results are best discussed in terms of the different primary processes and the two modes of photolysis. The one generalization that is possible is that no primary process seems to proceed by a unique pathway.

(i) **Formation of Ethylene and Acetylene.** Earlier studies[3,4] have already shown that this is an intramolecular process. The deuterium balance between the two products is observed to be quite satisfactory. The obvious mechanism, *viz.*, a 1,3 migration from carbon 1 to carbon 3 (3b) would give only ethylene-d_3



(3b)

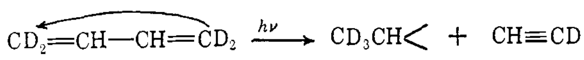
so that mechanism 3a must also be operative in order to give C_2D_4 and CH≡CH. The formation of C_2D_2 suggests yet another primary process which may be



(3c)

The initial rearrangement is obviously the same one that gives rise to 1,2-butadiene in reaction 1. The formation of ethylene from $CD_2HCH<$ and acetylene from $CD_2C<$ have analogies in the vacuum ultraviolet photolysis of ethane and ethylene, respectively.[7]

There is a fourth possibility for the formation of ethylene and acetylene which is indicated by (3d). It is suggested by analogy to (3c), but there is no independent evidence for its presence since ethylene-d_3 can be formed by (3b) as well. The data indicate that the relative importance of (3a), (3b–3d), and (3c) are in the ratio 7:8:5.



$$CD_2{=}CH{-}CH{=}CD_2 \xrightarrow{h\nu} CD_3CH< + CH{\equiv}CD \quad (3d)$$

The results in Table III show that at moderate pressures (1–10 mm) of butadiene primary process (3) does occur in the mercury-sensitized photolysis. The work of Collin and Lossing was performed in a flow system at butadiene pressures of only a few microns and a carrier gas (helium) pressure of several millimeters. The present data indicate that the trend with a decrease in pressure favors the formation of ethylene and acetylene. There is a discrepancy between the two sets of data which can be eliminated only with further study.

Investigations on the irradiation of 1,3-butadiene in the condensed phase have shown that direct irradiation (which gives the singlet and possibly only the singlet) gives cyclobutene[8] but sensitization to the triplet state does not give any cyclobutene.[9] The present data show that at a given pressure of cyclobutene or butadiene, reaction 3 is more important in the former system than in the latter, which would suggest that (3a) is an important source of ethylene and acetylene in the direct decomposition of butadiene. This is supported by the observed distribution of deuterium between ethylene and acetylene, namely that there is more ethylene-d_4 in the direct photolysis than in the sensitized decomposition.

(ii) **Formation of Ethane, 1,2-Butadiene, and 1-Butyne.** The secondary processes which follow primary process 1 were clearly unraveled by Collin and Lossing.[1] Thus (1) leads to a "hot" 1,2-butadiene which, unless it is stabilized by a collision, decomposes to two radicals. The C_3H_3 radical can react from both

$$CH_3CH{=}C{=}CH_2 \longrightarrow CH_3\cdot + \cdot C_3H_3 \quad (4)$$

the allenyl ($\cdot CH{=}C{=}CH_2$) and the propargyl ($\cdot CH_2{-}C{\equiv}CH$) resonant structures. The major secondary products are formed as shown (eq 5–7). The nature of

$$2\cdot CH_3 \longrightarrow C_2H_6 \quad (5)$$

$$\cdot CH_3 + \cdot CH{=}C{=}CH_2 \longrightarrow CH_3CH{=}C{=}CH_2 \quad (6)$$

$$\cdot CH_3 + \cdot CH_2{-}C{\equiv}CH \longrightarrow CH_3CH_2{-}C{\equiv}CH \quad (7)$$

the hydrogen migration in (1) can be inferred from the distribution of deuterium in all three of the products that are formed in (5), (6), and (7). The formation of C_2D_6, C_2D_5H, and $C_2D_4H_2$ indicates that the methyl radicals consist of both CD_3 and CD_2H. Their ratio can be calculated from one-half of the ratio of C_2D_5H to $C_2D_4H_2$ or from the square root of the ratio of C_2D_6 to $C_2D_4H_2$. This is found to be 1:9. Evidently (4)

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[6] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[7] J. R. McNesby and H. Okabe, *Advan. Photochem.*, 3, 210, 230 (1964).

[8] R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).

[9] G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, 83, 4674 (1961).

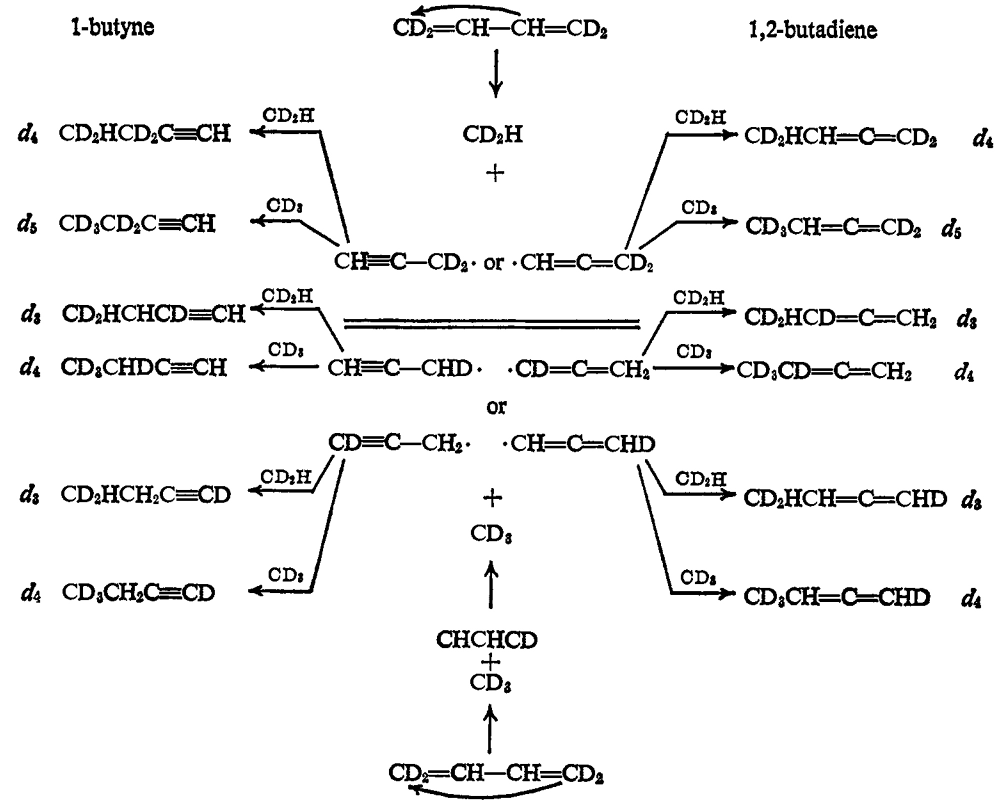
can proceed in one of two ways (eq 4a and 4b). It has

$$CD_2CHCHCD_2 \rightarrow CD_2H + CHCCD_2 \qquad (4a)$$

$$CD_2CHCHCD_2 \rightarrow CD_3 + CHCHCD \qquad (4b)$$

already been shown that in the direct photolysis (7) is the sole source of 1-butyne,[1,3] while (6) is the major source of 1,2-butadiene. These reactions can occur in a number of ways when the reactant is butadiene-1,1,4,4-d_4, as shown in Scheme I. However, these do not exhaust all of the possibilities by any means. From the ratio of CD_3 to CD_2H, which must also be the ratio of C_3DH_2 to C_3D_2H, it can be calculated that the yield of butyne-d_3, -d_4, and -d_5 in the direct photolysis should be in the ratio 9:82:9 which does not correspond to the experimental ratio in Table I. Furthermore, if the sole source of butyne with a $-C{\equiv}CD$ grouping is the C_3H_2D radicals formed in (4b), then such molecules cannot exceed 10% of the whole, as (4b) is only $^1/_9$ of (4a). Therefore, the $CHCCD_2$ radicals formed in (4a) must also undergo a redistribution of hydrogen (and deuterium) atoms as well as valence tautomerization. The rearrangement from 1,3-butadiene to 1,2-butadiene is endothermic by about 12.8 kcal/mole, but the energy required to cause a split into two radicals, as in (4a) and (4b), is not easy to estimate. The interesting question which cannot be answered at present is whether the hydrogen and deuterium migrations occur in the C_3DH_2 and C_3HD_2 fragments which may carry over enough energy to be "hot" or whether the migrations take place after the recombination reactions 6 and 7.

Scheme I. Possible Distribution of Deuterium in 1-Butyne and 1,2-Butadiene



If (6) is the sole source of 1,2-butadiene, its deuterium distribution should also be d_3:d_4:d_5, 9:82:9. The experimental value (Table I) seems to agree with that found for 1-butyne, but is clearly different from the calculated value. Such calculations would fail if the steric factors for the different recombination processes for labeled methyl and C_3H_3 radicals differ appreciably.

The ratio of CD_3 to CD_2H in the mercury-photosensitized reaction can be calculated to be 10, which indicates that process 4b is more favored than process 4a in this case. The calculated distribution of 1-butyne and 1,2-butadiene should be d_3:d_4:d_5, 0.8:8.4:0.8, which agrees poorly with the experimental values.

The relatively large yield of 1-butyne compared to 1,2-butadiene and ethane in the mercury-sensitized reaction (Table II) is an interesting point. Since the deuterium distribution between the 1,2-butadiene and 1-butyne is in reasonable agreement, the source of this "excess" 1-butyne cannot be an intramolecular rearrangement of butadiene. There appears to be no satisfactory explanation for this anomaly.

(iii) Formation of Hydrogen and Vinylacetylene. The separation and identification[10] of vinylacetylene (by comparison with an authentic sample) has been achieved in this study.[3,4] The formation of hydrogen has been known for a long time.[1,3,11] The isotopic composition of the hydrogen was not analyzed as earlier work[4] had shown that there is probably more than one source of hydrogen in this system. Further, in the presence of free radicals, scrambling of the different hydrogen molecules can be expected. This process must take place by three mechanisms (eq 2a and 2b). To give vinylacetylene-d_2, elimination of two deuterium atoms from one end carbon, or one atom apiece from two end carbons, is necessary. These reactions, as well as (2b) require a further shift of atoms to give a

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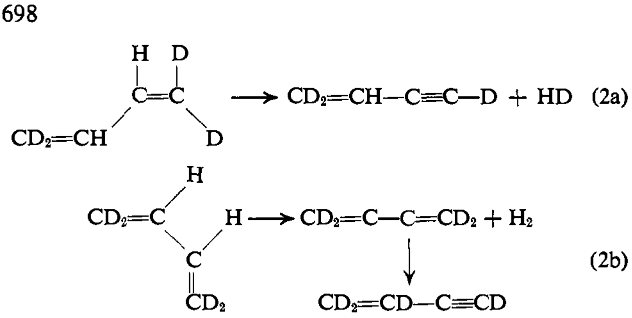
(10) In this study it was also possible to obtain enough of the product, tentatively designated in ref 4 as 2-butyne, to identify it positively on the basis of infrared and mass spectra as *trans*-2-pentene.

(11) G. Gee, *Trans. Faraday Soc.*, **34**, 712 (1938); H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **12**, 484 (1944).



stable molecule. The diminution in the yield of vinylacetylene on the addition of oxygen is puzzling. Perhaps radicals such as the one formed in the first step of (2b) can react with oxygen.

The reactions described here are somewhat similar to the thermal rearrangements observed in 7-deuterio-1,3,5-cycloheptatriene.[12] Since the photochemical reactions of butadiene in the vapor phase have been shown[4] to take place from the vibrationally excited ground state that is formed by internal conversion from the initially produced singlet excited state, the rearrangements observed in the present instance are also thermal processes. The principal difference between the two systems is that in 1,3,5-cycloheptatriene there is no chemical change which accompanies the migration of deuterium (or hydrogen), whereas in butadiene there is always a chemical change. In butadiene one migration of hydrogen has to be followed by a second migration if the molecule is to be regenerated. This pathway may be prohibited to a highly excited (*ca.* 100 kcal/mole) molecule such as the one that is produced by internal conversion from the upper singlet state. The extension of these results to other conjugated diene and triene molecules should be of considerable interest.

[12] A. P. Ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962); *Rec. Trav. Chim.*, **82**, 717 (1963).

The Vapor Phase Photolysis of Benzene at 1849 A

J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr.[1]

Contribution from the Department of Chemistry, University of California, Riverside, California. *Received January 3, 1966*

Abstract: The quantum yield of disappearance of benzene vapor at 1849 A is 0.9 ± 0.3. The major irradiation product appears to be a valence isomer of benzene, tentatively identified as "benzvalene." Addition of diluent N_2 reduces the rate of formation of the product but, up to 50 mm total pressure, increases its maximum concentration. Small amounts of fragmentation products, *i.e.*, methane, ethane, ethylene, and acetylene, are also observed, as well as considerable amounts of polymeric or carbonaceous deposit on the cell walls. These products may be formed in the secondary photolysis of "benzvalene."

The photochemistry of benzene has been studied in the gas phase,[2-4] the liquid phase,[5-8] and the solid phase;[3] however, little is known of the products or mechanism of its decomposition. In the solid phase, Gibson suggested that 1,3,5-hexatriene was a product,[8] while Bryce-Smith reported the formation of fulvene in the liquid phase. In the gas phase Noyes[2a] reported that below 2000 A the only volatile products formed were hydrogen, acetylene, and methane. He also concluded that the only major nonvolatile product, the solid material always found on the windows of a benzene photolysis cell, was most probably an acetylene polymer similar to cuprene. Shindo and Lipsky[4] have recently observed the ultraviolet spectrum of a product of the 1849-A photolysis of benzene vapor which was similar in appearance to that of biphenyl vapor.

Recent work on the spectroscopy and energy-transfer processes of electronically excited benzene[9-12] and its simple homologs has shown that the energy absorbed by benzene in its first absorption band (2300–2700 A) is efficiently dissipated by photophysical processes (*i.e.*, internal conversion and/or emission), while that absorbed in its second and third bands (λ_{max} at 2200 and 1800 A), cannot be accounted for by such processes. For reference, a benzene spectrum complete with band assignments is shown in Figure 1. As the photochemical data for benzene are inadequate and even somewhat ambiguous in the lower wavelength regions, and in view of the implications of the recent spectroscopic data, we felt it desirable to attempt a new study utilizing the newer analytical methods which have become available since Noyes' early work.

Experimental Section

Two reaction cells and concomitant irradiation systems were used. Cell 1 was a 50-mm Pyrex tube, blown closed at one end, with a

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[1] Author to whom communications should be addressed.

[2] (a) J. E. Wilson and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **63**, 3025 (1941), and references included therein; (b) G. Porter and F. J. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).

[3] J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, *Photochem. Photobiol.*, **4**, 323 (1965).

[4] K. Shindo and S. Lipsky, International Conference on Photochemistry, Tokyo, Japan, 1965.

[5] J. McBlair and D. Bryce-Smith, *Proc. Chem. Soc.*, 287 (1957).

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