FREE RADICALS BY MASS SPECTROMETRY

XIII. THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF ALLENE AND BUTADIENE: THE C_3H_3 RADICAL[1]

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ABSTRACT

The $Hg(^3P_1)$ photosensitized decomposition of allene leads to the formation of a C_3H_3 radical. The reaction of this radical with added methyl radicals shows it to have the propargyl ($\dot{C}H_2—C{\equiv}CH$) structure rather than the alternative allenyl ($CH_2{=}C{=}\dot{C}H$) structure. The dissociation of 1,2-butadiene proceeds by two modes, one to give $H_2+C_4H_4$, and the other a split into CH_3 and C_3H_3 radicals. The dissociation of 1,3-butadiene leads to the same final products, a shift of a hydrogen atom being required for the split into free radicals. No evidence was found for a dissociation of 1,3-butadiene into two vinyl radicals. Considerable polymer formation occurred with all three compounds.

INTRODUCTION

The reaction of butadiene, presumably 1,3-butadiene, with $Hg(^3P_1)$ atoms was found by Gee (6) to give mainly an insoluble non-volatile polymer which was deposited on the walls of the reactor. Other products identified were hydrogen and butane. A dimer, assumed to be of cyclic form, was also produced. He concluded that hydrogen played no part in the polymerization but hydrogenated the butadiene to form butane. The primary steps of the mercury photosensitized reaction were postulated to be:

$$CH_2{=}CH—CH{=}CH_2 + Hg^* \rightarrow \dot{C}H_2—CH{=}CH—\dot{C}H_2 + Hg \qquad [1]$$

or alternatively

$$CH_2{=}CH—CH{=}CH_2 + Hg^* \rightarrow Hg—CH_2—CH{=}CH—\dot{C}H_2. \qquad [2]$$

This reaction of butadiene was later examined by Gunning and Steacie (7), who found the pressure–time curve in static runs to have an induction period, followed by a period of linear pressure decrease. The slope of the latter increased with increasing pressure, except below 2 mm. where quenching was probably incomplete. In the static runs the reaction products, aside from polymer formed on the walls, were hydrogen, ethane, an acetylenic compound probably C_4H_4, and a compound with a boiling point of about 95° C. Analysis of the latter for C and H gave a ratio corresponding to $(C_2H_3)_n$, the same ratio as in butadiene, and it was concluded that the compound was a dimer of butadiene. The yield of dimer was found to be 0.6 mole per mole of butadiene reacted. This amount is stoichiometrically too large, and it is possible that the fraction isolated contained dissolved butadiene. A number of runs were made in a flow system, in which the yields of H_2 and C_4H_4 were considerably higher than in static runs. This suggested that H_2 and C_4H_4 were consumed in the later stages of the reaction. In the static runs the induction period could be prolonged by pumping off the hydrogen produced and eliminated by adding hydrogen initially to the butadiene. The period of linear pressure decrease was consequently considered to be an H-atom initiated polymerization. The following primary steps were suggested:

$$C_4H_6 + Hg^* \rightarrow C_4H_6^*, \qquad [3]$$

$$C_4H_6^* \rightarrow H_2 + C_4H_4, \qquad [4]$$

$$C_4H_6^* + C_4H_6 \rightarrow 2C_4H_6, \qquad [5]$$

$$C_4H_6^* + C_4H_6 \rightarrow (C_4H_6)_2. \qquad [6]$$

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The rate of reaction was found to be proportional to the light intensity and the quantum yield was approximately unity, in agreement with Gee.

The reaction at pressures above 50 mm. was examined by Volman (15), who found the principal product to be a light yellow oil. Some solid white polymer was produced, and also a non-condensable gas, presumably hydrogen. The reaction was also investigated at pressures of about 2.5 mm. using a flow system and metallic mirrors. Volman found that antimony mirrors were removed, the half-life of the radicals being about the same as for the radicals produced from acetone under the same conditions. Experiments with a guard mirror of lead showed no indication of the presence of hydrogen atoms. He therefore suggested that at low pressures the polymerization is induced by vinyl radicals produced in a primary step rather than by H atoms, and proposed the following modes of decomposition:

$$C_4H_6^* \rightarrow 2C_2H_3, \qquad [7]$$

$$C_4H_6^* + C_4H_6 \rightarrow H_2 + C_4H_4 + C_4H_6, \qquad [8]$$

followed by

$$C_4H_6 + C_2H_3 \rightarrow C_6H_9 \text{ etc.} \qquad [9]$$

Thus reaction [7] would predominate at low pressures, and reaction [8] at high pressures. The unimolecular decomposition (reaction [4]) was considered not to occur.

Steacie (13) has suggested that the failure to detect H atoms in the above experiments was not conclusive in view of the very rapid rate of the addition reaction:

$$H + C_4H_6 \rightarrow C_4H_7^* \qquad [10]$$

and that a polymerization initiated by vinyl radicals would not explain the induction period.

From the work discussed above, it would appear that of the excited 1,3-butadiene molecules which dissociate, some do so by loss of H_2 to form C_4H_4, and others form free radicals of unknown composition. The mercury photosensitized decompositions of the related compounds allene and 1,2-butadiene do not appear to have been studied previously. It was thought that an examination of these reactions using a mass spectrometer adapted for free radical studies might provide more direct evidence as to the nature of the primary dissociation steps. This technique has been useful in determining modes of decomposition in the mercury photosensitized reactions of C_2–C_4 olefins (9) and of acetone and acetaldehyde (8). The low pressures used in this method are advantageous in that deactivation and polymerization steps are less favored, and the increased lifetime available to excited molecules favors dissociation processes.

EXPERIMENTAL

The arrangement of reaction cell, mercury resonance lamp, and mass spectrometer has been described in previous publications (8, 9). The reactant, at a partial pressure of a few microns, was carried in a stream of helium at 10 mm. pressure over a surface of mercury in a saturator at 55° C., and through an illuminated zone. From a point 1.5 cm. downstream from the illuminated zone, a small fraction of the gas stream was sampled directly into the ionization chamber of the mass spectrometer. The operation of the reactor and the method of measurement of the concentrations of free methyl radicals and stable species have been described in detail in earlier papers of this series (8, 9). The sensitivity of the instrument to C_3H_3 radicals was not measured.

In the reaction of the butadienes, considerable difficulty was caused by the rapid formation of polymeric material on the walls of the reactor and the consequent decrease in illumination during the time taken to record the spectra. In order to obtain the relative intensity of illumination for a given experiment, the amount of decomposition of ethylene in the reactor under the same conditions was used as a standard of comparison. It was found that in a "non-clean" reactor, when the length of the illuminated zone was reduced to one-half by using the movable shutter, less than half as much ethylene was decomposed. This meant that the deposition of polymer was unequal over the length of the reactor, a proportionally greater amount being deposited at the downstream end. A calibration with ethylene was consequently performed each time the shutter was moved. From these data, an effective "length" of illuminated zone was obtained for each position of the shutter. After a considerable amount of polymer had been deposited, a situation then arose in which equal "lengths" were not quite equal intervals of time. The curves for formation of combination products in Figs. 2 and 3 are therefore slightly distorted.

At the flow rates used, the time of residence in the illuminated zone was 0.34 millisecond per cm. at 55° C.

Materials

A sample of allene was obtained through the courtesy of Dr. L. C. Leitch of these laboratories. The mass spectrum showed the presence of a few per cent of propylene. The effect of this on the course of the reaction was considered to be negligible. Samples of 1,2-butadiene and 1,3-butadiene were Phillips Research Grade gases.

RESULTS AND DISCUSSION

Allene

Three products only were produced by the mercury photosensitized decomposition of allene: hydrogen, a radical of mass 39 (C_3H_3), and a substance of mass 78, evidently the dimer of this radical. In a contact time in which ethylene was decomposed to the extent of 40%, allene was 23% decomposed. A considerable amount of polymer was also formed. The primary step is probably the formation of an excited allene molecule,

$$CH_2{=}C{=}CH_2 + Hg^* \rightarrow CH_2{=}C{=}CH_2^* + Hg. \qquad [11]$$

The excited molecule then dissociates as follows:

$$CH_2{=}C{=}CH_2^* \rightarrow C_3H_3 + H. \qquad [12]$$

This mode of dissociation appears to be the only one, and no products corresponding to a C—C rupture were found. The spectrum of the dimer was similar to that of 1,5-hexadiyne (di-propargyl). Since the spectra of the other C_6H_6 species, 1,2,4,5-hexatetraene and 1,2-hexadiene-5-yne, were not available for comparison, the identity of the dimer could not be established.

The nature of the C_3H_3 radical is of considerable interest. From the structure of allene it might at first sight be assumed that the C_3H_3 radical would necessarily have the form $H_2C{=}C{=}\dot{C}H$ (allenyl). However, an alternative structure differing in electronic configuration is also possible: $H_2\dot{C}{-}C{\equiv}CH$ (propargyl). A C_3H_3 radical, thought to be propargyl, has been detected by mass spectrometry in the thermal decomposition of propargyl iodide (2). If the two structures may in fact be regarded as resonance hybrids, the actual structure will be an intermediate one, and it is of interest to know whether the radical reacts as a propargyl or as an allenyl radical or as both. If it reacts predominantly as one of these forms, it is then not unreasonable to conclude that the actual structure of the radical more closely approximates this form, which is consequently the more stable one.

An identification of the radical from the nature of the dimer was not possible, as mentioned above. It was possible, however, to distinguish between the two forms in the following way. If methyl radicals were to be added to the reaction mixture, the combination of these with C_3H_3 radicals would result in the formation of either 1,2-butadiene,

$$CH_3 + \dot{C}H{=}C{=}CH_2 \rightarrow CH_3{-}CH{=}C{=}CH_2, \qquad [13]$$

or 1-butyne,

$$CH_3 + \dot{C}H_2{-}C{\equiv}CH \rightarrow CH_3{-}CH_2{-}C{\equiv}CH, \qquad [14]$$

depending on the structure of the C_3H_3 radical. The identification of the C_4H_6 product as 1,2-butadiene or 1-butyne could then be made on the basis of the ratio of the peaks at mass 53 and 54. A convenient way of bringing about this reaction was to allow a small concentration of mercury dimethyl to flow through the reactor with the allene–helium mixture. The mercury photosensitized decomposition of the mercury dimethyl provided a source of methyl radicals. It was found that in this way a mass 54 peak several centimeters in height could be produced. The mass 53/54 ratio obtained for this product of combination of CH_3 and C_3H_3, together with ratios for pure samples of 1,2-butadiene and 1-butyne, is given in Table I. It is evident that the combination product is mainly, if not entirely, 1-butyne, and consequently that the C_3H_3 radical reacts as if it had the propargyl ($\dot{C}H_2{-}C{\equiv}CH$) form. It is interesting to speculate as to why the reaction appears to proceed so exclusively by this form, although considerations of resonance suggest that the C_3H_3 radical would have a form intermediate between propargyl and allenyl. A possibility to be considered is that the activated complex resulting from the collision of CH_3 and C_3H_3 can rearrange to form the more stable product. This can be ruled out since the heat of formation of 1-butyne (39.48 kcal./mole) is slightly larger than that of 1,2-butadiene (38.77 kcal./mole) (12), although the difference is not large. The observation that only one product is formed although the heats of formation are so similar suggests that the identity of the product is already implicit in the activated complex, and consequently that the C_3H_3 radical is much more reactive at the CH_2 end. This is consistent with a configuration of C_3H_3 which is nearer to $\dot{C}H_2{-}C{\equiv}CH$ than to $CH_2{=}C{=}\dot{C}H$, if one assumes that the reactivity is associated with the position of maximum free electron density. This assumption appears to be valid since, if reaction could occur at either end of the radical regardless of the free electron distribution, both butyne and butadiene would be formed whatever the structure of C_3H_3 might be. A further possibility to be considered is that the structure is indeed intermediate between propargyl and allenyl, but the rate of reaction at the "fraction" of the free electron associated with the CH end of the radical is some 20–40 times slower than at the CH_2 end. Since it is hard to see how such a large difference in rate could arise between such similar combination processes, the interpretation given above is to be preferred.

TABLE I

Substance	Ratio 53/54
$CH_3+C_3H_3$	0.474±0.006
1-Butyne	0.478±0.006
1,2-Butadiene	0.420±0.006

From these considerations it might be expected that the stabilization of the C_3H_3 radical by resonance is considerably less than in the allyl radical, where the resonating structures are identical in energy. The dissociation energies for the propargyl halides, as measured by electron impact (2), are 8–10 kcal./mole greater than those of the corresponding allyl halides (see, for example, Ref. 13). A study of the appearance potentals of $C_3H_3^+$ ions formed from propyne and other compounds, which is to be published shortly, indicates however that the C_3H_3—H bond is only a few kcal./mole greater than the allyl—H bond.

1,2-Butadiene

Using low energy electrons suitable for detecting free radicals, methyl radicals and a radical of mass 39 (C_3H_3) were found to be produced abundantly in the decomposition of 1,2-butadiene. Other parent molecular ions found were those of ethane, hydrogen, and mass 52, presumably C_4H_4. A small amount of mass 40, allene or propyne, was also produced. No indication of the C_4H_5 radical could be found. A compound of mass 78 was also produced, evidently the dimer of C_3H_3. Using 50-v. electrons, the spectrum of this dimer was seen to be similar to, but not identical with, that of 1,5-hexadiyne. The formation of considerable amounts of polymer also occurred. The first step in the reaction is probably the formation of an excited 1,2-butadiene molecule:

$$CH_3{-}CH{=}C{=}CH_2 + Hg^* \rightarrow CH_3{-}CH{=}C{=}CH_2^* + Hg. \qquad [15]$$

From the products found, two modes of decomposition can occur:

$$CH_3{-}CH{=}C{=}CH_2^* \rightarrow H_2 + C_4H_4, \qquad [16]$$

$$CH_3{-}CH{=}C{=}CH_2^* \rightarrow CH_3 + C_3H_3. \qquad [17]$$

The ethane and C_6H_6 evidently arose by the dimerization reactions:

$$2CH_3 \rightarrow C_2H_6, \qquad [18]$$

$$2C_3H_3 \rightarrow C_6H_6. \qquad [19]$$

Since both CH_3 and C_3H_3 radicals were present, the combination reaction

$$CH_3 + C_3H_3 \rightarrow C_4H_6 \qquad [20]$$

might be expected. As discussed above in the case of allene, the combination reaction would form 1-butyne or re-form 1,2-butadiene depending on the structure of the C_3H_3 radical. In either case the decrease, on illumination, of the mass 54 peak (using 50-v. electrons) would be less than expected, particularly at the longer contact times where the combination reaction would be favored. This effect is clearly shown by curve I in Fig. 1. This curve was obtained by plotting the percentage decrease in the mass 54 peak (measured using 50-v. electrons) against the effective length of the illuminated zone. The percentage decrease was not proportional to the length but fell off as the length was increased. Since the ionization potential of 1-butyne (10.34 v. (4), 10.32 v. (5)) is considerably greater than that of 1,2-butadiene (9.57 v. (5)), a measurement of the mass 54 peak using electron energies between these values permitted a measurement of the amount of 1,2-butadiene without interference from 1-butyne. The relation between the height of the mass 54 peak at low electron energies and the effective length of the illuminated zone is shown by curve 2 in Fig. 1. This relation is much more nearly linear than is curve 1, showing that the curvature of the latter was caused by the formation of 1-butyne. If the curvature of 1 were caused by recombination to form 1,2-butadiene, curve 2 would of course have the same shape as curve 1. It may be concluded, therefore, that the

C_3H_3 radical, as in the case of allene, reacts as if it had the propargyl structure. The measurements at low electron energy consequently give approximately the actual percentage of decomposition of the 1,2-butadiene.

The composition of the products, excepting C_3H_3, C_6H_6, and C_4H_4, at different lengths of the illuminated zone were measured using 50-v. electrons. These concentrations, together with the amount of 1,2-butadiene decomposed, are given in Table II.

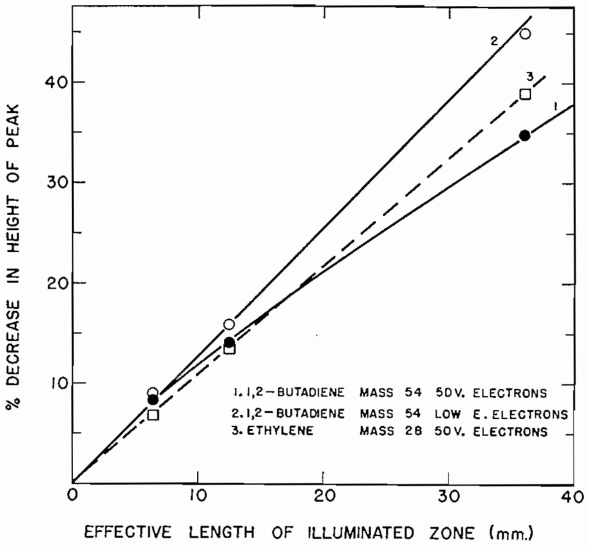


FIG. 1. The curvature of line 1, obtained using 50-v. electrons, shows that a product having a mass of 58 is formed at the longer contact times. The straightening of the line at low electron energies, line 2, shows that this product has a higher ionization potential than 1,2-butadiene. Line 3 shows the calibration of effective length using ethylene.

TABLE II

DECOMPOSITION OF 1,2-BUTADIENE

Butadiene (μ)		Effective length of zone	Butadiene decomposed		Ethylene decomposed	Products from butadiene (μ)					Yield of	Yield of
Lamp off	Lamp on	(mm.)	μ	%	(%)	H_2	CH_3	CH_4	C_2H_6	1-Butyne	CH_3	H_2
2.34	1.29	36	1.05	45.0	39.0	0.11	0.08_0	0.01_8	0.12_2	0.27_3	0.59	0.11
2.33	1.96	12.6	0.37	15.9	13.5	0.03_4	0.07_8	0.00_7	0.03_2	0.04_8	0.53	0.09_2
2.27	2.07	6.4	0.20	9.0	6.9_2	0.03_0	0.04_6	0.00_5	0.01_2	0.03_0	0.53	0.15

The change in the composition of the products with the length of the zone can be seen by reference to Fig. 2. Owing to the large amount of polymer formed it was not possible to get a complete mass balance. The amount of C_4H_4 could not be measured, no pure samples of butatriene or vinyl acetylene being available for calibration. An estimate of the proportion of the two modes of decomposition can be made, however, on the basis of the following mechanism:

$$CH_3—CH{=}C{=}CH_2^* \rightarrow C_4H_4 + H_2, \qquad [16]$$

$$CH_3—CH{=}C{=}CH_2^* \rightarrow CH_3 + C_3H_3, \qquad [17]$$

$$2CH_3 \rightarrow C_2H_6, \qquad [18]$$

$$CH_3 + C_3H_3 \rightarrow CH_3—CH_2—C{\equiv}CH, \qquad [14]$$

$$2C_3H_3 \rightarrow C_6H_6. \qquad [19]$$

The proportion of reaction proceeding by reaction [16] can be estimated from the production of H_2. As shown in Table II the yield of hydrogen per molecule of butadiene decomposed varies between 0.09 and 0.15. The proportion of reaction proceeding by reaction [17] can be estimated from the number of methyl radicals produced per molecule of butadiene decomposed. The total number of methyl radicals is given by the sum $[CH_3] + 2[C_2H_6] + [\text{1-butyne}] + [CH_4]$. From Table II it can be seen that the split into CH_3 and C_3H_3 accounts for 0.53–0.59 of the butadiene molecules decomposed. The remainder of the butadiene (~35%) presumably forms polymer.

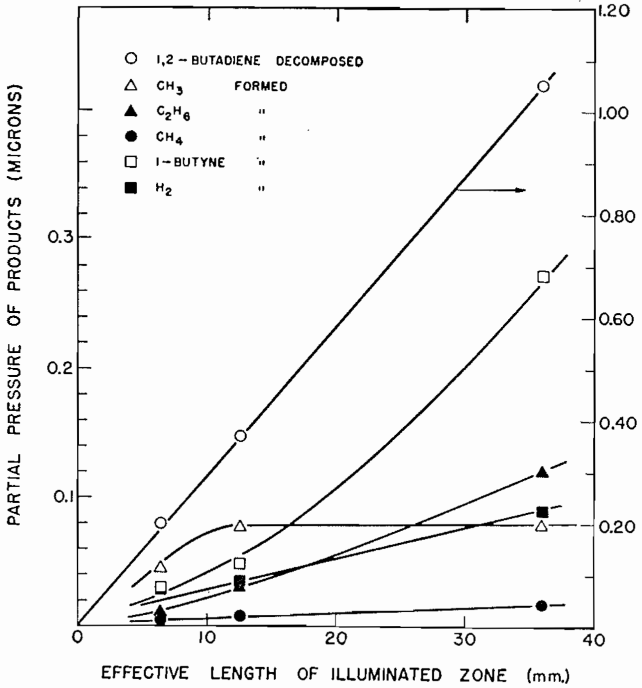


FIG. 2. Decomposition of 1,2-butadiene.

1,3-Butadiene

The dissociation of excited 1,3-butadiene molecules appears to be more complicated than that of allene or 1,2-butadiene. Using low energy electrons, the products of decomposition were found to be H_2, C_4H_4, CH_3 and C_3H_3 radicals, ethane, and C_6H_6. Using 50-v. electrons, the variation in composition of the products with increasing length of the illuminated zone was measured. These results are given in Table III. The effect

TABLE III

DECOMPOSITION OF 1,3-BUTADIENE

Butadiene (μ)		Effective length of zone	Butadiene decomposed		C_2H_4 decomposed	Products from butadiene (μ)					Yield of	Yield of
Lamp off	Lamp on	(mm.)	μ	%	(%)	H_2	CH_3	CH_4	C_2H_6	1,2-Butadiene + 1-butyne	CH_3	H_2
2.46	1.64	36	0.82	33.3	41.0	0.11	0.06_2	0.02_4	0.09_9	0.22	0.35–0.61	0.13
2.44	2.14	13.6	0.30	12.3	15.4	0.01_9	0.04_4	0.01_5	0.03_3	0.06_7	0.42–0.64	0.06_3
2.42	2.27	7.2	0.14_9	6.2	8.2	0.01_5	0.04_4	0.00_5	0.01_3	0.03_0	0.50–0.70	0.10

of varying the length of the zone can be seen in Fig. 3. From these data, there would appear to be two primary modes of decomposition of 1,3-butadiene, one to give H_2 and C_4H_4, and the other to give CH_3 and C_3H_3 radicals. The latter reaction does not at first sight appear very probable, since a hydrogen shift is required. When the configuration of butadiene is taken into account, such a shift appears less unreasonable.

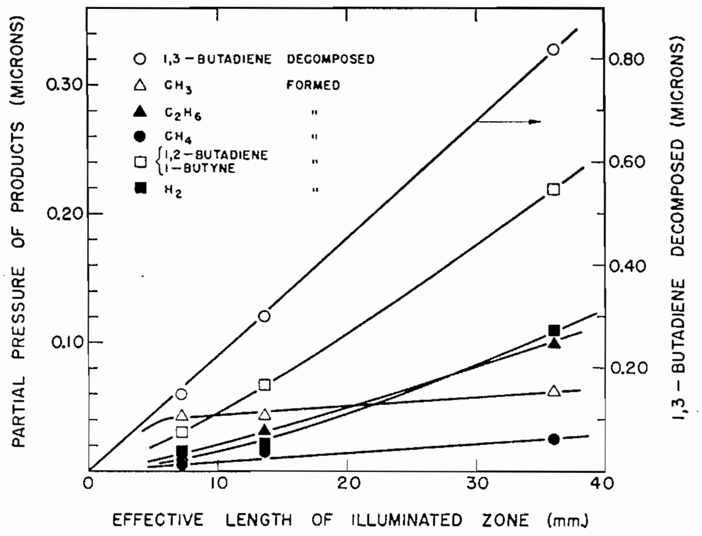
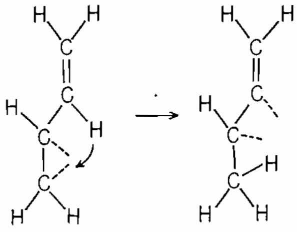


FIG. 3. Decomposition of 1,3-butadiene.



As shown, the excitation of a butadiene molecule probably results in the uncoupling of one pair of electrons in the double bond. The migration of an H atom would give rise to a configuration equivalent to an excited 1,2-butadiene molecule, which could then dissociate into CH_3 and C_3H_3 as was found for 1,2-butadiene. The probability also exists that such an excited molecule could be deactivated to form 1,2-butadiene. The identification of 1,2-butadiene in the presence of 1,3-butadiene and 1-butyne was not unambiguous. Since the ionization potentials of 1-butyne and 1,2-butadiene (see above) are both larger than that of 1,3-butadiene (9.24 (11), 9.18 (5)) low electron energy measurements of the mass 54 peak were not capable of distinguishing between 1,2-butadiene and 1-butyne. Measurements (using 50-v. electrons) of the ratio of the peaks at mass 53 and 54 gave for the product a value intermediate between the ratios for 1,2-butadiene and 1-butyne. Both were probably present. In Table III the two have been lumped together, and the amount calculated using the average of their sensitivities.

The following reactions would account for the products observed:

$$CH_2{=}CH{-}CH{=}CH_2 + Hg^* \rightarrow CH_2{=}CH{-}CH{=}CH_2{}^* + Hg, \qquad [20]$$

$$CH_2{=}CH{-}CH{=}CH_2{}^* \rightarrow H_2 + C_4H_4 \text{ (probably vinyl acetylene)}, \qquad [21]$$

$$CH_2{=}CH{-}CH{=}CH_2{}^* \rightarrow CH_3{-}CH{=}C{=}CH_2{}^*, \qquad [22]$$

$$CH_3{-}CH{=}C{=}CH_2{}^* \rightarrow CH_3 + C_3H_3, \qquad [17]$$

$$CH_3{-}CH{=}C{=}CH_2{}^* \, (+M?) \rightarrow CH_3{-}CH{=}C{=}CH_2, \qquad [23]$$

$$2CH_3 \rightarrow C_2H_6, \qquad [18]$$

$$2C_3H_3 \rightarrow C_6H_6, \qquad [19]$$

$$CH_3 + C_3H_3 \rightarrow CH_3{-}CH_2{-}C{\equiv}CH. \qquad [14]$$

As in the experiments with allene and 1,2-butadiene, the formation of 1-butyne shows that the C_3H_3 radical reacts as if it had the propargyl configuration. From the data in Table III, reaction [21] accounts for 0.06–0.13 of the butadiene disappearing. The fraction decomposing by reaction [17] depends on what fraction of the 1-butyne/1,2-butadiene product is 1-butyne. Assuming this product to be all 1,2-butadiene, a lower limit is obtained for the extent of reaction [17]. If it is all 1-butyne, an upper limit is obtained. Both limits are given in Table III in the column headed "yield of CH_3". The variation in the observed value of the limits with the length of the illuminated zone suggests that an intermediate value of 0.5 is the most probable. The remaining 20–30% of the 1,3-butadiene appears to form polymer.

No evidence could be found for the dissociation into two vinyl radicals proposed in earlier work (15). The radicals detected by Volman were therefore probably methyl radicals and C_3H_3 radicals. His observation that the radicals had a half-life about the same as the radicals from acetone is consistent with this interpretation. It is of interest in this regard to consider possible values for the dissociation energy of the $(CH_2{=}CH){-}(CH{=}CH_2)$ bond. From electron impact data two values of the heat of formation of vinyl radicals have been obtained: 51.6 kcal./mole (14) and 82.3 kcal./mole (3). From the heat of formation of 1,3-butadiene (26.3 kcal./mole) (12) these lead to two values for the C—C bond as follows:

ΔH_f vinyl	$D(C_2H_3{-}C_2H_3)$
51.6	76.9
82.3	138.3

Since two C_2H_3 radicals would be formed by rupture of this bond, the discrepancy in the heat of formation appears doubled in the bond dissociation energy. The lower value is considerably less than $D(C{-}C)$ in ethane (83.3 kcal./mole (1)) and appears to be much too low. The higher value is considerably higher than $D(C{-}C)$ in cyanogen (112 kcal./mole (10)). Such comparisons can be misleading, but a value of about 105 kcal./mole would be easier to understand. Since the energy corresponding to a $Hg(^3P_1)$ atom is 112 kcal., it is evident that a dissociation of 1,3-butadiene into two vinyl radicals could not occur if $D(C_2H_3{-}C_2H_3)$ were greater than 112 kcal. The non-occurrence of this reaction is not sufficient to prove that $D(C_2H_3{-}C_2H_3) > 112$ kcal., but on the other hand it would be surprising that it does not occur if, in fact, the bond were as weak as 77 kcal./mole. The present results may be taken as support for a considerably higher value than 77 kcal./mole for this bond.

It is interesting to note that in the earlier work on the mercury photosensitized reaction of 1,3-butadiene, the polymerization reaction seems to have predominated over the dissociation reactions. This is understandable on the basis of the great difference in the pressure of butadiene. At pressures above a few millimeters, the excited molecules may not have time to dissociate before suffering collisions leading to polymerization. In addition, the observation of the free radical mode of dissociation would be obscured by the addition of the free radicals to butadiene, resulting in induced polymerization. In static systems at moderate pressures quenching by hydrogen formed in the primary dissociation would, as pointed out by Gunning and Steacie (7), change the course of the reaction from a mercury photosensitized decomposition to an H-atom initiated polymerization. The simplification obtainable by studying such excited molecule reactions at very low pressures and high intensities of radiation is consequently of great assistance in determining the primary modes of dissociation.

Note added in proof.—The migration of a hydrogen atom is also found to occur in the 1,3-butadiene ion. The presence of a relatively large metastable peak at mass 28.2 in the mass spectrum of 1,3-butadiene shows that the following dissociative rearrangement must occur in the C_4H_8 ion:

$$C_4H_8^+(\text{mass } 54) \rightarrow C_3H_3^+(\text{mass } 39) + CH_3(\text{mass } 15).$$

This reaction appears to be analogous to that described above as occurring in a 1,3-butadiene molecule after excitation by a $^3P_1$ Hg atom.

REFERENCES

1. Cottrell, T. L. The strengths of chemical bonds. Butterworth Scientific Publications, London. 1954.
2. Farmer, J. B. and Lossing, F. P. Can. J. Chem. **33**, 861 (1955).
3. Field, F. H. J. Chem. Phys. **21**, 1506 (1953).
4. Franklin, J. L. and Field, F. H. J. Am. Chem. Soc. **76**, 1994 (1954).
5. Collin, J. and Lossing, F. P. To be published.
6. Gee, G. Trans. Faraday Soc. **34**, 712 (1938).
7. Gunning, H. E. and Steacie, E. W. R. J. Chem. Phys. **12**, 484 (1944).
8. Lossing, F. P. Can. J. Chem. **35**, 305 (1957).
9. Lossing, F. P., Marsden, D. G. H., and Farmer, J. B. Can. J. Chem. **34**, 701 (1956).
10. McDowell, C. A. and Warren, J. W. Trans. Faraday Soc. **48**, 1084 (1952).
11. Morrison, J. A. and Nicholson, A. J. C. J. Chem. Phys. **20**, 1021 (1952).
12. Rossini, F. D. *et al.* Selected values of physical and thermodynamic properties of hydrocarbons and related compounds. Carnegie Press, Pittsburgh. 1953.
13. Steacie, E. W. R. Atomic and free radical reactions. 2nd ed. Reinhold Publishing Corporation, New York. 1954.
14. Stevenson, D. P. J. Am. Chem. Soc. **65**, 209 (1943).
15. Volman, D. H. J. Chem. Phys. **14**, 467 (1946).