

441. *The Photolysis of Diazoethane and the Reactions of Ethylidene.*

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The photolysis of diazoethane has been investigated in the gas phase at various pressures with 4358 Å radiation. The products are explained in terms of a mechanism involving the production and reactions of ethylidene. The reactions of ethylidene with propylene, *cis*- and *trans*-but-2-ene, propane, and butane have been studied, and the reactivity of ethylidene has been compared with that of methylene. Results obtained in this work have been compared with some earlier investigations on the photolysis of diazoethane with light of shorter wavelength.

IN comparison with the extensive work on the photolysis of diazomethane and the subsequent reactions of the methylene produced,¹ the photolysis of diazoethane and the reactions of ethylidene have received little attention. Early experiments by the "Paneth mirror technique" indicated that thermal decomposition of diazoethane led to the production of ethylidene.² Then preliminary experiments (discontinued because of repeated explosions) suggested that ethylidene was produced in the photolysis of diazoethane.³ In the present work a more comprehensive investigation of the photolysis of diazoethane was undertaken, and some reactions of ethylidene were studied.

EXPERIMENTAL

Diazoethane was prepared by the action of sodium in ethylene glycol on 2-(*N*-ethyl-*N*-nitrosoamino)-2-methylpropyl methyl ketone. The diazoethane was swept out of the reaction

¹ Kirkbride and Norrish, *J.*, 1933, 119; Doering, Buttery, Laughlin, and Chaudhuri, *J. Amer. Chem. Soc.*, 1956, **78**, 3224; Frey, *Proc. Roy. Soc.*, 1959, *A*, **250**, 409; *J. Amer. Chem. Soc.*, 1960, **82**, 3217; Butler and Kistiakowsky, *J. Amer. Chem. Soc.*, 1960, **82**, 759.

² Barrow, Pearson, and Purcell, *Trans. Faraday Soc.*, 1935, **35**, 880.

³ Brinton and Volman, *J. Chem. Phys.*, 1951, **19**, 1394.

mixture in a stream of nitrogen, through a trap cooled to -20° , and condensed in a trap cooled in liquid oxygen. The crude diazoethane so obtained contained three major impurities which totalled $\sim 10\%$. That present in largest amount ($\sim 6\%$) was shown by gas-chromatography to be isoprene. The other two, formed in approximately equal amounts, were *cis*- and *trans*-penta-1,3-diene. Distillation under a high vacuum reduced the amount of these impurities to $\sim 2\%$.

Propene, *cis*- and *trans*-but-2-ene, propane, and butane were obtained from cylinders (Matheson Inc.) and subjected to several trap-to-trap distillations before use.

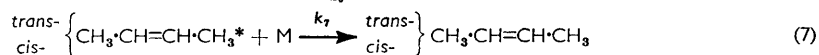
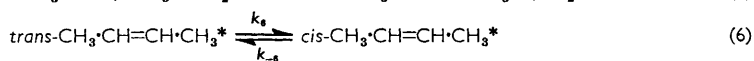
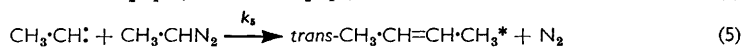
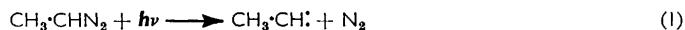
Analysis.—Analysis was by gas-chromatography and mass spectrometry. In some analyses a 20 ft. \times 0.17 in. (internal diameter) coiled copper column filled with 40—60-mesh Chromosorb containing 20% w/w of hexane-2,5-dione was used. In others a similar column but with di-(2-cyanoethyl) ether as the liquid phase was used. Hydrogen was the flow gas and the columns were operated at 0° . A Gow-Mac tungsten-filament katharometer was used as the detector in conjunction with a 0-1 MV recorder which was fitted with a retransmitting slide-wire for integration purposes. Integration of chromatographic peaks was carried out with a Perkin-Elmer model 194 integrator.

Photolysis.—Photolyses were carried out in cylindrical Pyrex reaction vessels at $\sim 65^\circ$. A medium-pressure mercury arc (Hanovia U.V.S. 500) was used in conjunction with filter solutions⁴ to isolate the 4358 Å band in the mercury spectrum. Reaction vessels were isolated from the rest of the vacuum-system by Fluon-glass diaphragm valves to avoid the troubles associated with the absorption of hydrocarbons in grease which occurs when conventional stopcocks are employed.

RESULTS AND DISCUSSION

Photolysis of Diazoethane.—The diazoethane was found to contain dienes as impurities. However, preliminary experiments with material containing 10% and 2% of total impurity yielded identical results. Accordingly, no attempt was made to reduce the impurities to below 2%. Brinton and Volman³ reported that the tendency for diazoethane to decompose explosively increases as its purity increases. It is possible that the freedom from such decomposition in the present work was due to the diene impurity. In all cases photolyses were continued until virtually 100% decomposition of the diazoethane. This was necessary since it was found that diazoethane decomposed on the analytical (gas-chromatography) column to yield various butenes. Although it would have been possible to remove the excess of diazoethane before analysis by the use of various liquid absorbents it was felt that such a procedure would lead to selective absorption of some of the products. In some cases the very small quantities involved might have made such errors relatively large.

The results for the photolysis of diazoethane at various pressures can be accounted for by the following mechanism:



In qualitative agreement with this mechanism it was found that the yield of ethylene rose, and the yields of the but-2-enes fell as the pressure was decreased. The yield of

⁴ Burawoy and Roach, *Nature*, 1958, **181**, 762.

acetylene rose more rapidly than that of ethylene as the pressure was decreased. A stationary-state treatment of the postulated mechanism yields the equation:

$$[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_2] = k_4\text{M}/k_3. \quad (8)$$

Hence a plot of the yield of ethylene divided by the yield of acetylene against the total pressure should result in a straight line passing through the origin. Such a plot, shown in Fig. 1, indicates that in the pressure range from 14 to 140 mm. this relation is accurately obeyed. At higher pressure the very small relative yields of acetylene lead to large errors in the determination of the required ratio. The slope of the line gives the magnitude of k_4/k_3 , which is found to be 0.86 mm.⁻¹. Since the composition of the reaction mixture changes during the photolysis this ratio contains a mean value of k_4 . However, in view of the high energy content of the excited ethylene it is unlikely that the collision efficiencies for deactivation of the various gases present vary by more than a small amount. In a similar way it can be shown that:

$$\frac{[\text{cis-} + \text{trans-CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CH}_3]}{[\text{C}_2\text{H}_4 + \text{C}_2\text{H}_2]} = k_5[\text{CH}_3\cdot\text{CHN}_2]/k_2. \quad (9)$$

If the mean concentration of the diazoethane is taken as proportional to one-half of the initial pressure, then the left-hand ratio should be directly proportional to this pressure. This ratio has a value of ~0.058 at 100 mm. and rises to 0.18 at 370 mm. In this pressure range the ratio was found to be directly proportional to the pressure. Below 100 mm. the ratio decreases less rapidly than expected. However, small amounts of undecomposed diazoethane remaining at the end of the photolysis will have a very large effect, at low pressures (owing to decomposition on the column), on the measured ratio, and it is felt that results for this ratio are unreliable in this region.

The postulated mechanism requires that the initial attack of ethylidene on diazoethane yields an excited molecule of *trans*-but-2-ene. This molecule may undergo a subsequent *trans-cis*-isomerization. It is, therefore, to be expected that at high pressures the but-2-ene will be predominantly the *trans*-isomer, and that at lower pressures the relative yield of the *cis*-isomer will increase. Stationary-state treatment yields the equation:

$$\frac{[\text{trans-CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CH}_3]}{[\text{cis-CH}_3\cdot\text{CH}=\text{CH}\cdot\text{CH}_3]} = \frac{k_{-6}}{k_6} + \frac{k_7}{k_6}\text{M}. \quad (10)$$

Hence a plot of the observed ratio of *trans*- to *cis*-but-2-ene against the pressure should yield a straight line with an intercept equal to k_{-6}/k_6 . Such a plot is shown in Fig. 2. It yields a value for k_{-6}/k_6 of unity. Thus $k_{-6} = k_6$, *i.e.*, for the highly activated but-2-ene molecule there is an equal probability of isomerization in either direction. This suggests that the activated molecules must initially have energy well in excess of the minimum required for isomerization⁵ (*ca.* 63 kcal. mole⁻¹) and must lose much of this energy on their first deactivating collision.

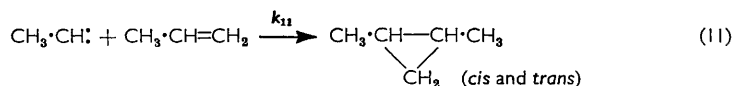
Lifetime of the Ethylidene.—In the pressure range investigated, most of the ethylidene produced by photolysis isomerizes to ethylene. To obtain the value of k_2 and hence determine the life-time of the ethylidene it is necessary to know the collision efficiency of reaction (5). The maximum value for this is unity, which leads to a value for k_2 of 1.36×10^{10} sec.⁻¹. In fact it is highly improbable that the collision efficiency is as high as 0.1,⁶ but assuming this to be the value gives an average life-time for ethylidene of 7×10^{-10} sec.

Reactions of Ethylidene with Propene.—To determine whether ethylidene undergoes reactions similar to those of methylene, *viz.*, addition to carbon double bonds and insertion

⁵ Rabinowitch and Michel, *J. Amer. Chem. Soc.*, 1959, **81**, 5065; Cundall and Palmer, *Trans. Faraday Soc.*, 1961, **57**, 1936.

⁶ Kistiakowsky and Mahan, *J. Amer. Chem. Soc.*, 1957, **79**, 2412.

into carbon-hydrogen bonds, photolyses of diazoethane were performed in the presence of a large excess of propene. In this system two major new products were observed, which were identified as *cis*- and *trans*-1,2-dimethylcyclopropane. These results from the addition of ethylidene to the carbon double bond:



C_5 olefins which could result from the insertion of ethylidene into the carbon-hydrogen bonds in propene were found only in traces. Thus, unlike methylene, ethylidene does

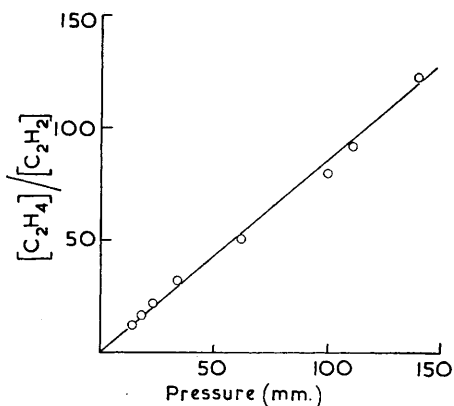


FIG. 1. Ratio of ethylene to acetylene as a function of pressure.

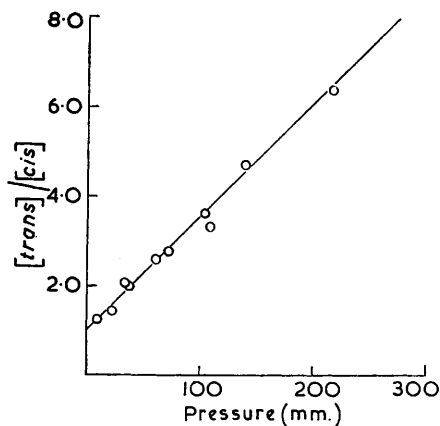
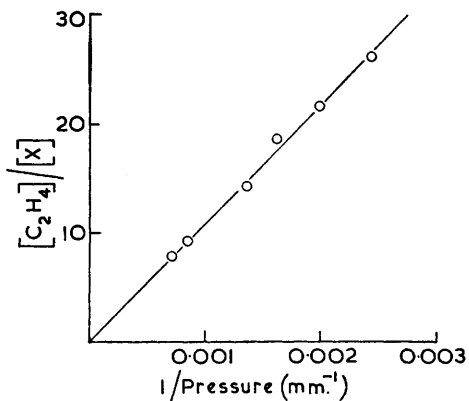


FIG. 2. Ratio of *trans*- to *cis*-but-2-ene as a function of pressure.

FIG. 3. Ratio of ethylene to the 1,2-dimethylcyclopropanes (X) as a function of pressure.



not appear to undergo an insertion reaction to any appreciable extent. In most reaction mixtures the initial ratio of propene to diazoethane was 10 : 1, and photolysis was again continued until virtually all the diazoethane had decomposed. Various initial pressures in the range 400—1400 mm. were used. The ratio of *cis*- to *trans*-dimethylcyclopropane was independent of the pressure, and had a value of 1.4 : 1. A stationary-state calculation for this system yields the equation:

$$\frac{[\text{C}_2\text{H}_4 + \text{C}_2\text{H}_2]}{[\textit{cis} + \textit{trans}\text{-}1,2\text{-Dimethylcyclopropane}]} = \frac{k_2}{k_{11}[\text{C}_3\text{H}_6]} \quad (12)$$

Since even at the lowest pressures used the yield of acetylene was negligible compared with

that of ethylene, and further since the mixture consisted almost entirely of propene, equation (12) may be simplified to give:

$$\frac{[\text{C}_2\text{H}_4]}{[\text{cis-} + \text{trans-1,2-Dimethylcyclopropane}]} = \frac{k_2}{k_{11}\text{M}} \quad (13)$$

Hence a plot of the left-hand ratio against the reciprocal of the total pressure should yield a straight line passing through the origin. Such a plot is shown in Fig. 3. As can be seen, a good straight line results, which passes through the origin. From the slope of the graph it appears that ethylidene reacts ~ 20 times more slowly with propene than with diazoethane.

Reactions of Ethylidene with But-2-ene.—Photolyses of mixtures of diazoethane with large excesses of *cis*- and *trans*-but-2-ene yielded only traces of new products. The reaction of ethylidene with but-2-ene must be considerably slower than its reaction with propene.

Reactions of Ethylidene with Propane and Butane.—In photolyses of mixtures of diazoethane with a 20-fold excess of propane, and with a similar excess of butane, no evidence was obtained of any insertion reaction of the ethylidene. If such a reaction occurs at all it must be at least 1000 times slower than the reaction with diazoethane.

General.—The results reported in this paper show that in many respects there is a considerable difference between the reactions of ethylidene and those of methylene. Owing to the possibility of an intramolecular rearrangement in the case of ethylidene (to yield ethylene), the other reactions of ethylidene are somewhat more difficult to observe than in the case of methylene. Nevertheless it is clear that addition of ethylidene to a carbon double bond is much more specific than is the case with methylene. The large change in the relative rate of attack on propene and but-2-ene is evidence of this. Another point of dissimilarity is the absence of an insertion reaction.

It is reasonable to assume that the rate at which ethylidene rearranges to ethylene, and the rate at which this excited ethylene molecule decomposes to give acetylene, depend on the extent of the vibrational excitation of the ethylidene. The more highly vibrationally excited the ethylidene, the higher will be the ratio of acetylene to ethylene at a particular pressure. Similarly, the more highly vibrationally excited the ethylidene, the higher the ratio of ethylene to but-2-ene at a particular pressure. The presence of an excess of translational energy in ethylidene would not be expected to influence the rate of the reaction to give ethylene, but it might be expected to increase the collision efficiency of the reaction leading to but-2-ene. In the light of these considerations it is interesting to compare the present results with those of Brinton and Volman³ at 200 mm. They obtained a value of ~ 10 for $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_2]$ and also for $[\text{C}_2\text{H}_4]/[\text{C}_4\text{H}_8]$. In the present work the corresponding values at 200 mm. were 170 and 8. The major difference in the two sets of results is the relatively large amounts of acetylene observed in the earlier work. In Brinton and Volman's work the radiation responsible for the decomposition was in the range 2500—2700 Å. It the present work 4358 Å radiation was used, and hence it is reasonable to assume that the ethylidene produced in the earlier work contained considerably the more energy. This would account for the difference in the ratios of $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_2]$ in the two investigations. The ratio of $[\text{C}_2\text{H}_4]/[\text{C}_4\text{H}_8]$, which is not appreciably different in the two investigations, implies that the collision efficiency for the reaction leading to but-2-ene was higher in the earlier work. And this suggests that ethylidene produced by the shorter-wavelength radiation contains excess vibrational energy and excess kinetic energy compared with that produced by photolysis at longer wavelength. The similarity of the two ratios suggests almost an exact cancellation of the two effects.

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