82. *Methylene.*

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For many years the methylene radical has been of theoretical importance owing to its postulated existence as an intermediate in the combustion and decomposition of various organic molecules. Previous attempts to show the presence of the radical directly have either failed or led to contradictory conclusions.

In the present paper an account is given of its isolation from both keten and diazomethane by thermal and photochemical methods. Its properties have been studied—it behaves as a very reactive molecule rather than a free radical—and the results obtained enable the discrepancies in the literature to be reconciled.

The first attempt to establish the existence of a stable bivalent form of carbon was described by Nef in a series of papers (*Annalen*, 1892, **270**, 267; 1894, **280**, 291; 1895, **287**, 265; 1897, **298**, 202) covering over 385 pages and describing the properties and reactions of more than 100 compounds. He concluded " that organic compounds readily undergo a primary decomposition into a stable smaller molecule and a radical containing bivalent carbon." To-day it is recognised that, although many of his premises transgress accepted views of valency and energetics, some of his conclusions are close to the truth, for example : " The exclusive production of formaldehyde when ethylene is burnt in oxygen at 400° is . . . explained on the assumption that the hydrocarbon is dissociated into methylene " (*Abstracts*, 1898, **74**, 102).

Much earlier, Marchand (*J. pr. Chem.*, 1839, **36**, 478) had obtained large quantities of methane during the decomposition of ethylene at bright red heat, and concluded that the ultimate resolution of a hydrocarbon into its elements at high temperatures cannot be regarded as the result of a single chemical change. These views were clarified by Bone and Coward (J., 1908, **93**, 1191) in an investigation of the decomposition of methane, ethane, ethylene, and acetylene between 500° and 1200°. An examination of the residues revealed the existence of intermediate stages, and the authors supposed that the primary effect, in the cases of ethane and ethylene, causes an elimination of hydrogen and the dissolution of the bond between the carbon atoms to yield residues such as $:CH_2$ and $\vdots CH$. This research was the first of a long series of investigations by Bone and his collaborators, in consequence of which he (*Trans. Faraday Soc.*, 1934, **30**, 150) reaffirmed his belief in the existence of the methylene radical.

In 1932 Kassel (*J. Amer. Chem. Soc.*, 1932, **54**, 3949) studied the decomposition of methane at 700—800°, and showed that the reaction is homogeneous and kinetically of the first order. Of the two ways in which the reaction might conceivably occur, *viz.*,

$$CH_4 = CH_3 + H - 125 \text{ kg.-cals.}$$
$$CH_4 = CH_2 + H_2 - 47 \text{ kg.-cals.}$$

he favoured the latter on the ground of a comparison of the heats of these reactions and the experimental heat of activation, and concluded that methylene is a comparatively inert substance, the energies of activation for its addition reactions with methane, hydrogen, and itself being 44, 32, and 24 kg.-cals. respectively.

Meanwhile, Schmidlin and Bergmann (*Ber.*, 1910, **43**, 2821) discovered that above 600° acetone yields not only keten but also ethylene in increasing amounts, and its presence was ascribed to the methylene radicals from keten.

The first positive evidence was adduced from photochemical experiments. Lardy (*J. Chim. physique*, 1924, **21**, 353) recorded the absorption spectrum of keten, noted its resemblance to that of acetone, and observed a series of five diffuse bands in the region corresponding to the carbonyl group, the significance of which was subsequently revealed by Norrish, Crone, and Saltmarsh (J., 1933, 1533). They measured the wave-lengths of the various bands, established that the region most responsible for the photochemical change corresponded with the absorption region of the carbonyl group, and found that the dissociation was accompanied by the formation of ethylene and carbon monoxide in the ratio of 1 : 2. These results led the authors to conclude that: (1) " The primary change is simply interpreted as a splitting of the molecule at the olefinic bond according to the equation $CH_2{:}CO + h\nu = CH_2 + CO$, the liberated CH_2 reacting further with undecomposed keten, to give ethylene and carbon monoxide: $CH_2{:}CO + CH_2 = C_2H_4 + CO$."

(2) " The energy relationships from the primary change when analysed, show that it cannot be represented purely as a rupture of the olefinic bond; they are, however, consistent with a decomposition into CH_2 and CO molecules, each containing carbon in the bivalent form." This deduction was made in order to reconcile the spectroscopic data with the known heats of formation, the minimum quantum effecting decomposition corresponding with $\lambda = 3850$ A., or 74 kg.-cals. per mol., the maximum with 2600 A. or 110 kg.-cals. per mol., neither of which is comparable with the 167 kg.-cals. necessary for the rupture of the olefinic bond in the ordinary way to yield CO and CH_2 *radicals*.

Ross and Kistiakowsky (*J. Amer. Chem. Soc.*, 1934, **56**, 112) repeated and confirmed these experiments and determined in addition the overall quantum yield of the reaction. They obtained the values 1·17, 1·03, 1·11, 1·19, 0·97, and 0·98 (mean 1·08) at 3130 A., smaller values at 3600 A., whilst at longer wave-lengths the photo-reactions became negligible. Since in the region of maximum absorption the quantum yield was close to unity, they were unable to agree with Norrish's secondary reaction, $CH_2{:}CO + CH_2 = CO + C_2H_4$, and concluded that the ethylene is produced by direct union of methylene radicals. Subsequently, Norrish and his collaborators (*ibid.*, p. 1644) attempted to justify their secondary mechanism by pointing out that the quantum yield of a primary reaction for a polyatomic molecule may be less than unity over a considerable range of frequencies, since a large part of the absorbed energy may be dissipated as heat (Auger effect) in the chromophoric carbonyl group. In this case, the quantum yield should increase towards a maximum as the magnitude of the absorbed quantum exceeds by greater amounts the energy necessary for the fission of the molecules. This would lead to an overall yield of 2 if the mechanism of Norrish and his colleagues is correct, and 1 for that proposed by Ross and Kistiakowsky. The fact that the values were less than unity at 3650 A., and somewhat exceeded it at 3130 A. was held to lend probability to the theory of the former school.

Numerous unsuccessful attempts appear to have been made to establish by direct tests the presence of methylene in the decomposition of keten. F. O. Rice and his co-workers (*ibid.*, p. 1760) made an extensive survey of the mode of preparation and properties of keten, but did not comment upon its thermal or photochemical decomposition, apart from a statement in their book (" The Aliphatic Free Radicals," Baltimore, 1935, p. 41) that keten is too stable to be used as a source of free radicals. Ross and Kistiakowsky (*loc. cit.*) mentioned that they intended to pursue the investigation of methylene, but have not reported any experimental results. Paneth and Lautsch (J., 1935, 380) effected the thermal dissociation of keten by passing a rapid stream of the gas through a heated quartz tube, but they were " unable to raise the temperature sufficiently to effect any appreciable decomposition, with the formation of free methylene," although keten is said to decompose at relatively low temperatures with the separation of carbon (Williamson, *J. Amer. Chem. Soc.*, 1934, **56**, 2212).

We have found that keten is not easily decomposed thermally to yield free radicals, but at the temperature attained by a quartz tube heated in a good blast Bunsen burner large quantities of free methyl are liberated, and have been detected and identified by their reactions with tellurium, antimony, and lead, but detectable concentrations of methylene were never obtained. When, however, keten was exposed to light in the region of 2580—3130 A., plenty of methylene was obtained and identified by the formation of the various polymers of telluro- and seleno-formaldehydes, $(TeCH_2)_x$ and $(SeCH_2)_x$, and their addition compounds with mercuric halides. There was no diminution in the concentration of the radicals while they passed along 80 cm. of 11-mm. diameter quartz tube during 0·05 sec., in which each radical must have made 3×10^3 impacts with the walls of the tube, and 4×10^5 impacts with other molecules. This surprising result, indicating as it does that methylene has an order of persistence entirely different from that of the alkyl radicals (half-value period, 5×10^{-3} sec.), led us to examine the products of the thermal and photochemical dissociation of diazomethane, because Rice and Glasebrook (*J. Amer. Chem. Soc.*, 1934, **56**, 2381) had obtained methylene in its thermal decomposition, and, without recording data, had ascribed to it a life-period similar to that of methyl.

It has been known for some time that diazomethane vapour decomposes slowly at room temperature to yield nitrogen and a solid polymer of methylene melting at 128° (Bamberger and Tschirner, *Ber.*, 1900, **33**, 956). Steacie (*J. Physical Chem.*, 1931, **35**, 1493) established that the composition of the gaseous products at higher temperatures is approximately: N_2, 67; C_2H_4, 30; CH_4, etc., 2%, in satisfactory agreement with that calculated from the equation $2CH_2N_2 = 2N_2 + C_2H_4$. He found the reaction to be homogeneously bimolecular, independent of the presence of powdered quartz in the reaction vessel, and to have an activation energy of 36 kg.-cals. per mol. The results were held to be best explained by a mechanism involving, not free radicals, but excited molecules which reacted in direct collision, thus $CH_2N_2^* + CH_2N_2 \longrightarrow 2N_2 + C_2H_4$.

The mechanism of the photochemical decomposition was studied by Norrish and Kirkbride (J., 1933, 119). The absorption spectrum consists of a series of diffuse predissociation bands, stretching from about 4700 A. and merging into a continuum at about 4200 A. The reaction yields N_2, 91·3; CH_4, 4·2; C_2H_4, 13·1; C_3H_6, 9·4; C_2H_6, 3·0%, together with some condensable products (partly nitrogenous bases), is kinetically unimolecular, and has an overall quantum yield of 4—5 between 4360 and 3650 A. The authors argued that the primary photochemical process involves complete dissociation into methylene and nitrogen, $CH_2N_2 + h\nu \longrightarrow CH_2 + N_2$, followed by a short chain of secondary reactions consuming about four molecules of diazomethane.

The first direct evidence of the presence of methylene in the products of decomposition of diazomethane was obtained by Staudinger and Kupfer (*Ber.*, 1912, **45**, 501, 504, 508), who passed a mixture of diazomethane and carbon monoxide through a heated silica tube and identified keten amongst the effluent gases. Subsequent experimental results are very conflicting. Paneth and Lautsch (*loc. cit.*) studied many reactions in which methylene was likely to be liberated. Their experiments with keten have already been described. They next tried to prepare the radical from diazomethane by passing the gas rapidly through a quartz tube heated to 600°, using both helium and hydrogen as transport gases. For identification they chose benzoic acid and carbon: $C_6H_5{\cdot}CO_2H + CH_2 \longrightarrow C_6H_5{\cdot}CO_2CH_3$, $C + 2CH_2 \longrightarrow CH_2{:}C{:}CH_2$, but neither reagent was perceptibly affected. In another experiment, to avoid the possibility of destroying the methylene in the hot tube, decomposition was effected by an electric discharge. Although the diazomethane was quantitatively decomposed, no methylene was detected. Finally, they sought to obtain the radical from the reaction $CH_2Cl_2 + 2Na \longrightarrow 2NaCl + CH_2$, the probable occurrence of which had been demonstrated by Hartel and Polanyi (*Z. physikal. Chem.*, 1930, *B*, **11**, 97). A wide variation in experimental conditions failed to reveal anything beyond a considerable deposition of carbon. They concluded that methylene is far inferior to methyl and ethyl in stability and required more refined methods for its isolation and identification. This conclusion was in agreement with some experiments which had been previously described by Belchetz (*Trans. Faraday Soc.*, 1934, **30**, 170). A rapid stream of methane at 0·01 mm. pressure was allowed to pass over a strongly heated platinum or carbon filament and then to impinge on a cooled surface, covered with tellurium or iodine. When the distance from the filament to the cooled surface exceeded the mean free path of the molecules, the methyl radical alone was identified. When the distance was within the mean free path, the tellurium mirror was attacked to yield a minute amount of a grey white solid ($TeCH_2$?) which reacted with bromine to yield a liquid of b. p. 103—108° (methylene bromide, b. p. 98·5°). The iodine mirror gave a heavy oil, b. p. 145° (methylene iodide, b. p. 180°). The discrepancy was ascribed to the presence of chloroform used in the extraction. The impure methylene iodide was therefore shaken for 15 minutes with mercury in the presence of chloroform, and the mixture filtered. The yield of fine yellow crystals remaining after evaporation of the chloroform had m. p. 230° (CH_2I_2Hg, m. p. 230°; Sakurai, J., 1881, **39**, 485). The existence of the methylene as a highly reactive molecule thus appeared to be conclusively established, although the brief statement of the results here recorded gives no idea of the difficulties encountered during the experimental manipulation. Belchetz's apparatus is ingenious and obviates the formation of secondary products, but the yields obtained are minute, so that unequivocal identification is almost impossible. Shortly after the publication of these experiments, Rice and Glasebrook (*loc. cit.*) obtained methylene by decomposing a rapid stream of diazomethane in a silica tube at temperatures below 500°. They obtained the following important results (cf., however, Rice, *Chem. Reviews*, 1935, **17**, 60): (1) Mirrors of tellurium, selenium, antimony, and arsenic were readily removed, whereas zinc, cadmium, thallium, lead, and bismuth were not attacked. (2) With tellurium, neither dimethyl telluride nor ditelluride was condensed in a trap immersed in liquid air, but a deep red solid was deposited in the walls of the tube just beyond the tellurium; this could just be sublimed at 100° in a high vacuum (even then with some decomposition), it was stable in air, insoluble in water and the usual organic solvents, decomposed at 110° to yield tellurium, and contained C, 8·28; H, 1·33 (Calc. for CH_2Te: C, 8·40; H, 1·41%). (3) Although they published no data, the authors stated that methylene has a life period similar to that of methyl and ethyl. (4) Heated above 700°, diazomethane gave only methyl radicals.

The properties of telluroformaldehyde observed by Rice and Glasebrook were so different from those described by Belchetz that Rice and Dooley (*J. Amer. Chem. Soc.*, 1934, **56**, 2747) were led to re-investigate the thermal decomposition of methane. Unfortunately, from the point of view of precise comparison, they used a quartz tube heated by an electric furnace. They were unable to detect any methylene, but obtained a large yield of methyl radicals, and doubted the validity of Belchetz's work. Later, Belchetz and Rideal (*ibid.*, 1935, **57**, 1168) repeated their former experiments, and although reaching the same conclusion concerning the primary formation of methylene, they were unable to reproduce any of their former results. Referring to telluroformaldehyde, they merely state that " the greyish substance which was considered formerly to be such a compound . . . must have consisted of a trace of hydrogen telluride and a little tellurium," whilst the m. p. of 230° obtained for the mercury–methylene iodide compound was ascribed to coincidence, since two compounds $Hg_2CH_2I_2$ and $HgCH_2I_2$ are formed simultaneously and their separation is extremely difficult. We have found it impossible to obtain a compound of fixed melting point merely by mixing methylene iodide and mercury, and in agreement with Sakurai (*loc. cit.*) observed that the compounds take, not 15 minutes, but days to form, are insoluble in chloroform, and can be separated by fractionation only in methylene iodide. From the second paper, two facts emerge: methylene could be identified by conversion into formaldehyde, followed by the Schryver–Rimini test; and the existence was confirmed of the red solid polymeric telluroformaldehyde of Rice and Glasebrook, which was obtained in one experiment with tellurium mirrors. Furthermore, the necessity for collecting the methylene radical within the mean-free-path distance of its formation was established.

We have examined the photochemical and thermal dissociation of diazomethane streaming at a low pressure and high velocity through a silica tube. Free methylene has been identified in both processes by conversion into telluroformaldehyde. Its life period in the presence of excess of diazomethane but in the absence of a carrier gas was found to be $5{\cdot}0 \times 10^{-3}$ sec. when produced thermally, and $6{\cdot}4 \times 10^{-3}$ sec. when produced photochemically, values which are held to be identical within the limits imposed by unavoidable experimental differences. Methylene thus appears to have three different half-value periods: in methane it is of the order of the time taken to traverse the mean free path, say 10^{-7} sec., in diazomethane it is similar to that of an alkyl radical, 5×10^{-3} sec., and in keten it is too long to be measured by the ordinary methods.

The experiments recorded in the later pages of this paper are concerned with the resolution of these paradoxes. It is demonstrated that free methylene is to be regarded rather as a highly reactive molecule than a free radical in the sense that methyl is. Its persistence is therefore entirely a function of its environment. We are thus forced to the conclusion that the carbon in methylene is essentially bivalent (^3P), as postulated by Nef, Kassel, Mecke (*Trans. Faraday Soc.*, 1934, **30**, 211), and Lennard-Jones (*ibid.*, p. 70), and especially emphasised by Norrish and his colleagues (see p. 410). These conclusions cover the whole of our experimental results, and serve to account for all the pertinent data recorded by other workers, which are discussed in detail later.

EXPERIMENTAL.

Preparation of Keten.—After a careful examination of the methods available for the preparation of keten (Hurd, *J. Amer. Chem. Soc.*, 1923, **45**, 515, 3095; Ott, Schröter, and Packendorff, *J. pr. Chem.*, 1931, **130**, 170; Staudinger and Kubinsky, *Ber.*, 1909, **42**, 4213; Staudinger and Klever, *Ber.*, 1908, **41**, 594; Hurd and Tallyn, *J. Amer. Chem. Soc.*, 1925, **47**, 1427), we chose the pyrolysis of acetone on a vanadium pentoxide catalyst according to Berl and Kullmann (*Ber.*, 1932, **65**, 1114). After the system had been filled with nitrogen, acetone was vaporised in a flask immersed in boiling water, and carried through the furnace packed with pumice, which had been previously soaked in 5% ammonium vanadate solution and ignited. Excess of acetone was removed from the effluent gases in the water condenser, and in a glass spiral cooled to −70°, and the keten frozen out in a number of traps immersed in liquid air. At the completion of the run, the more volatile fractions were distilled slowly into one trap in a stream of nitrogen. The trap was sealed off, and immediately connected by a ground joint *A* to the purification train (Fig. 1), wherein the products were submitted to a rigorous fractional distillation.

After a prolonged investigation of the best experimental conditions (furnace at 700°, acetone vaporised at the rate of 20 c.c./min.), we obtained a yield of 3% of purified keten (calculated on the total acetone passing through the furnace). Higher yields under other conditions were invariably accompanied by larger amounts of impurity from which the keten could not be separated. Even under the best conditions, our final purified product held 3·8% of unsaturated hydrocarbons (bromine-water test) which we could not eliminate in spite of many attempts, for we were emulating Rice (*J. Amer. Chem. Soc.*, 1934, **56**, 1760, 2132, 2268) who had obtained 100% keten by the use of a vacuum fractionating column. The vapour pressures of a typical sample are recorded below, since no figures, except the b. p. −41°, are given in the literature.

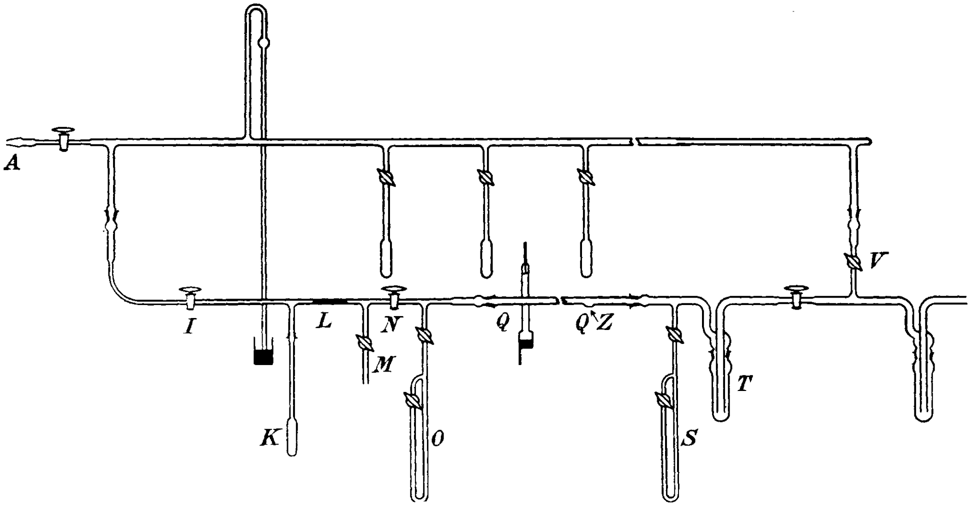
Temp. ...	−71·0°	−72·0°	−75·5°	−90·0°	−91·0°	−92·0°	−93·0°	−94·0°	−94·5°	−120°
Press., cm. Hg	14·8	14·6	13·1	3·1	3·1	2·7	2·5	2·5	2·3	0·4

This keten was used in our experiments, since we did not anticipate difficulties from the presence of the unsaturated hydrocarbons.

The apparatus used in studying the products of dissociation is shown in Fig. 1. The purification train between *I* and *V* in the upper part of the diagram formed a part of the system to enable the keten to be redistilled during a series of experiments without being exposed to the air.

The purified keten, stored in K, was admitted to the quartz tube Q by the tap N at a pressure controlled by the capillary L and the temperature of a bath surrounding K, and measured with the butyl phthalate manometers O and S. The keten was dissociated either thermally or photochemically in the quartz tube, passed over metallic mirrors formed from the metal contained in the reservoir Z, and the unchanged keten and reaction products condensed out in T, which was immersed in liquid air. Pure hydrogen, to assist in the fashioning of the metal mirrors, was available through M.

FIG. 1.



Production and Identification of Methylene.—The experimental procedure was essentially the same as that described in previous communications from this laboratory (J., 1934, 1718; 1935, 1151; 1936, 253, 1777; 1937, 567). It was soon found that the products from keten would not remove cold tellurium mirrors, owing no doubt to the deposition of a thin deposit of polymer on the surface of the metal, an effect previously observed (Pearson and Purcell, J., 1935, 1151) in connection with the photo-dissociation of acetaldehyde. We therefore wound a few turns of No. 36 nichrome wire (2 mm. between the threads) round the tubes, and by means of a rheostat kept the temperature at 70—80°. The mirrors were then rapidly attacked by keten irradiated with the light from a cold or a hot mercury arc. To prove that the attack was due solely to the decomposition product, the following tests were made : (1) the mirror was heated in a vacuum for 30 mins., but no thinning was noticeable; (ii) keten was then passed over the heated mirror for long periods, but no removal resulted. That heating was essential was shown by passing keten for 5 secs. over a fresh, cold mirror, which was then heated, and the keten irradiated, but the mirror remained quite unaffected. All these experiments were repeated several times with fresh mirrors.

The identification of the radical proved as troublesome as usual, and experimental difficulties were aggravated by the conflicting opinions concerning methylene telluride (telluroformaldehyde). The red modification could not be produced in the ready manner described by Rice and Glasebrook (*loc. cit.*). Keten was distilled back and forth many times, and although large mirrors were being constantly removed, no trace of red solid was deposited anywhere in the quartz tube. A little trough was therefore built round the tube just behind the mirror and filled with solid carbon dioxide. After eight runs of keten, equivalent to 3 hours' irradiation, the bath was removed. The interior of the quartz tube was coated with a layer of deep orange, fluorescent solid, which was evidently Rice's red modification : it could be distilled in a high vacuum at 100° with slight decomposition, was insoluble in water, alcohol, and ether, and had the unpleasant odour subsequently found to be associated with all modifications of telluroformaldehyde. The layer of telluroformaldehyde could be formed anywhere in the quartz tube by cooling with carbon dioxide snow. On cooling the tube for only 15 mins., no solid could be observed, but as the photodissociation was continued, it gradually accumulated at the place where the bath had been. Thus it seems that the formation of the polymer required " seeding."

In addition to the red compound, a solid had formed in the liquid-air trap, colourless at −70°, and turning pale grey-green at room temperature. It had the penetrating organometallic odour typical of telluroformaldehyde, quite distinct from dimethyl telluride and hydrogen telluride; it was readily soluble in acetone, chloroform, and ether, and darkened on exposure to air. The acetone or chloroform solutions rapidly decolourised iodine solutions, with the formation of methylene iodide. Attempts were first made to identify the methylene iodide in the manner used by Belchetz, *viz.*, by the addition of mercury. Belchetz claimed to have obtained the compound CH_2I_2Hg, m. p. 230°. Our repeated efforts failed to isolate it. We tried in vain to synthesise it from authentic methylene iodide, but obtained substances with various m. p.'s, all well below 230°. Finally, Sakurai's paper was consulted, and it was found that, in agreement with our observations, the reaction takes days for completion, yields two compounds, CH_2I_2Hg and $CH_2I_2Hg_2$, which are insoluble in all the usual solvents, and can only be separated in methylene iodide.

We therefore identified the methylene iodide by converting it into formaldehyde, and tested for the latter by means of the Schryver–Rimini reaction. The necessary runs were made, and in the absence of air, iodine and chloroform were introduced by distillation. The trap was removed, the products allowed to react, and the excess of iodine removed by shaking with pure mercury. The yellow mercurous iodide and excess of mercury were filtered off, the clear solution evaporated on the water-bath, the residue moistened with chloroform, poured into a micro-Carius tube, and the chloroform again removed by evaporation. A little lead oxide and 0·5 c.c. of water were added, the tube was sealed, and heated in the furnace to 180° for about an hour. After cooling, the contents were filtered into a test-tube containing 2 c.c. of 1% aqueous phenylhydrazine hydrochloride and 1 c.c. of 5% potassium ferricyanide. On addition of 5 c.c. of concentrated hydrochloric acid an intense violet colour at once appeared, showing the presence of formaldehyde. The extreme sensitivity of this reaction led us to make two careful blank experiments. (i) In the first, chloroform and iodine were frozen in the trap T together with a little keten, the mixture warmed to room temperature, and an excess of iodine added, followed, in due course, by a drop of mercury; after shaking to remove the iodine, the filtered solution was evaporated to a small bulk in the water-bath, transferred to a micro-Carius tube, evaporated to dryness, treated with lead oxide and water, and heated. (ii) A second Carius tube was prepared in the same way, the keten being omitted. In neither experiment was a coloration obtained even after several hours' standing.

One further observation must be mentioned: the amounts of red and grey telluroformaldehyde taken together were obviously insufficient to account for the whole of the tellurium removed by the radicals, and it was found that on preserving the residual keten for a few days in liquid air, it left a substantial white deposit on evaporation, which did not redissolve readily in keten. It was similar in appearance, odour, and solubility to the white modification already described, but was contaminated with a considerable amount of polymerised keten, as indicated by a micro-carbon and -hydrogen analysis which gave values agreeing with the formula $TeCH_2,12\frac{1}{2}CH_2{:}CO$.

It is evident, therefore, that telluroformaldehyde is first generated as a gas, which undergoes the familiar aldehydic condensations to a white form and a red form, the latter, in view of its solubility, being the higher polymer. We were unable to detect methyl radicals in any of these experiments.

Inability to synthesise an authentic specimen of telluroformaldehyde led us to examine the selenium analogue, a polymeric form of which had been described by Vanino and Schinner (*J. pr. Chem.*, 1915, **91**, 116) as white columnar crystals, m. p. 215°, turning light green on exposure to sunlight (see also Brandt and Valkenburgh, *Proc. Indiana Acad. Sci.*, 1929, **39**, 165). We prepared it in good yield by passing hydrogen selenide at the rate of 2 bubbles per second for 1½ hours into a mixture of 40% formaldehyde (10 c.c.) and concentrated hydrochloric acid (30 c.c.). The white precipitate of selenoformaldehyde was filtered off, washed with much water, and recrystallised from a large volume of alcohol. It was deposited in very pale yellow needles, which became pale green on exposure to light. It had a garlic odour similar to that of telluroformaldehyde but somewhat less repulsive, and dissolved, on prolonged boiling in ether, acetone, and chloroform. Under the microscope, long polarising needles and clusters of small opaque granules were observed. The clusters melted at 66°, and began to distil away at 140°, whereas isolated needles melted between 200° and 220°. A crystallised sample one week old still showed the two modifications. After 3 weeks, however, there was no sign of melting at 66°, and complete melting at 206°. Selenoformaldehyde, therefore, separates in a metastable form, m. p. 66°, which slowly reverts to the stable modification, m. p. 205—215°.

Solutions of selenoformaldehyde in acetone react to give insoluble compounds with solutions of certain salts: mercuric chloride gives a pale yellow precipitate, which begins to char at 190°, and is completely black by 230°. Mercuric bromide and iodide respectively give yellow and bright yellow precipitates which behave in a similar fashion. These compounds are more insoluble than the corresponding dimethyltelluride mercuric iodides, and on slow crystallisation form clusters of needles similar to the lactosazones. Silver nitrate gives a yellowish-brown, and palladous chloride a greenish-brown precipitate, but lead nitrate, 2 : 4-dinitrophenylhydrazine, semicarbazide, and picric acid are without action.

Since keten was to be present in our actual experiments, we used it as a solvent for some synthetic crystalline selenoformaldehyde which consisted almost wholly of the columnar crystals having the higher m. p. To allow time for any polymerisation processes, the solution was kept at −70° for some hours. The keten was removed by distillation, and a sample of the residue examined on the heating block under the microscope. The selenoformaldehyde now consisted of a mixture of polarising columnar crystals and opaque granular clusters. The granules began to melt at 60°, and finished melting at 68°, whilst the polarising needles melted at about 190°. Evidently, keten assists the formation of the lower-melting modification.

Selenium mirrors, even cold ones, were readily removed by the radicals from photolysed keten, but were not attacked by keten in the absence of light. The products of reaction collected only in the liquid-air trap, and could not be subsequently removed by distillation, so polymerisation was rapid and complete. After removal of the keten by distillation, the trap contained a pale greenish-yellow viscid solid, identical in odour with selenoformaldehyde. It was sparingly soluble in boiling alcohol, and from the solution, granular crystals were obtained by cooling. On heating, the edges of most of the crystals began to soften at 62°. At 66° these were completely melted. A residue of tiny polarising crystals remained which began to melt at 202° and were completely molten at 210°. This behaviour, identical with that of synthetic selenoformaldehyde which had been recrystallised from keten, was verified in a mixed m. p. determination.

From these observations it is clear that selenoformaldehyde, like telluroformaldehyde, exists first as a gas and polymerises to the two solid forms, m. p.'s 62—68° and 205—215°. The keten does not appear to act entirely as a solvent, for selenoformaldehyde crystallised from it no longer yields a precipitate with mercuric iodide.

The rate of decay of methylene was measured by observing the times of removal of warm standard tellurium mirrors situated at various distances from the irradiated zone in the quartz tube. Our first measurements served to show that we were dealing with a fragment of exceptionally long life. The quartz tube was 35 cm. long, and in this the time of removal of the mirrors was independent of their position in the tube. A fresh quartz tube 1 m. long was therefore built into the system, and despite the increased length, we could observe no decay. The results are recorded below:

Distance of mirror from lamp, cm.	5·0	30·7	53·5	81·5
Time of removal of mirror, secs.	133	132	143	128

The streaming velocity, 811 cm./sec., was determined by weighing in potassium hydroxide solution the amount of keten which passed through the tube in a measured time.

Average diameter of quartz tube = 1·1 cm. Pressure in first manometer = 0·153 cm. Hg. Average pressure gradient = 0·000912 cm. Hg. Therefore, time taken to traverse 81 cm., calculated from Herzfeld's equation (Paneth and Lautsch, *Ber.*, 1931, **64**, 2702), is 0·05 sec.

Thus, in 0·05 sec. the concentration of methylene had not perceptibly diminished.

For the purposes of discussion (see below), it is desirable to estimate the amount of keten dissociated. This may be obtained from the data recorded for diazomethane, which was found to be 59% dissociated when it took 45 secs. to remove a standard mirror at the furnace mouth.

Velocity of stream of diazomethane = 0·00722 g./min.

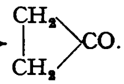
$$\therefore \text{ Yield of } CH_2 \text{ radicals in 45 secs.} = 0{\cdot}00722 \times \frac{45}{60} \times \frac{59}{100} \times \frac{14}{42} = 0{\cdot}00106 \text{ g.}$$

Now, the average time of removal of the standard mirrors with keten = 134 secs.

∴ Yield of CH_2 in 134 secs. = 0·00106 g. = 0·000076 g.-mol. Total amount of keten passing in 134 secs. = 3·020 × 134/1095 = 0·370 g. = 0·0088 g. mol.

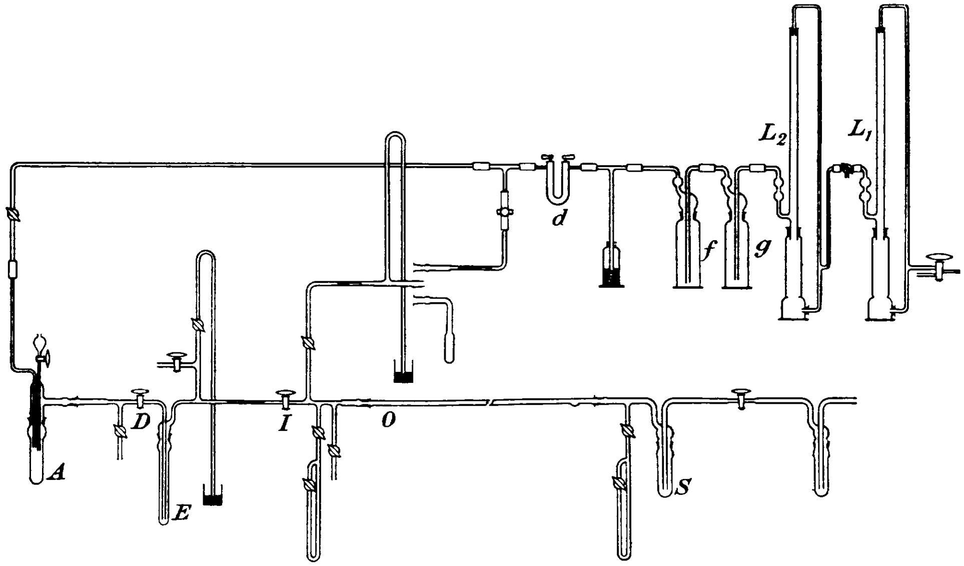
∴ Degree of dissociation = (0·000076 ÷ 0·0088) × 100 = 0·86%.

This estimate is almost certainly too high, for it assumes that all the diazomethane dissociated into free radicals; nevertheless, it is a safe value on which to base the later discussion.

The possibility arose that the long life of the molecule was due to the formation of a loose compound easily dissociated in contact with metallic mirrors, *e.g.*, $CH_2 + CH_2{:}CO \longrightarrow$  $\left.\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\right>CO$.
This compound exists only in solution, and any attempt to remove it results in a viscous polymer (Lipp, Buchkremer, and Seeles, *Annalen*, 1932, **499**, 1). It does, however, form a crystalline semicarbazone. Repeated attempts to prepare such a derivative from the fractionated products of the photolysis of keten were unsuccessful.

We were thus faced with the anomaly of a methylene radical short-lived in methane and diazomethane, and completely stable in keten. We therefore decided to investigate the radical obtained from diazomethane. The diazomethane was prepared by gradually adding nitrosomethylurethane (1 vol.) to a cold 6% solution of sodium in ethylene glycol (2 vols.) (Meerwein and Burneleit, *Ber.*, 1928, **61**, 1840), and since it had to be handled in the complete absence of air, the apparatus used in Fig. 2 was constructed. The preparation was effected in the vessel *A*, provided with a tap-funnel and delivery tube for admitting pure dry nitrogen, in which the diazomethane was carried forward to the vessel *E*, containing purified, dry butyl phthalate or ether, cooled until viscous in a bath of carbon dioxide snow. After all the diazomethane had collected in *E*, the nitrogen was removed by closing *D* and evacuating through *I*, the last traces being eliminated together with any volatile impurities by successively warming, cooling, and evacuating the vessel.

FIG. 2.



The nitrogen, since it was also to be used as a transport gas for free radicals, was carefully freed from oxygen in the towers L_1 and L_2 containing concentrated aqueous ammonia and spirals of copper gauze, and was washed with dilute sulphuric acid in *g*, syrupy phosphoric acid in *f*, and dried over phosphoric oxide in *d*.

The thermal decomposition of diazomethane was first investigated. Decomposition was effected by an electric furnace, 15 cm. long, surrounding the quartz tube close to *O*. The temperatures were read on a millivoltmeter connected with a platinum–platinum-iridium thermocouple calibrated against a platinum-resistance thermometer. Plentiful yields of active fragments were obtained from a stream of diazomethane vapour at 2 mm. pressure with or without ether as a carrier gas, but above 400°, decomposition was accompanied by the deposition of carbon within the heated zone, and with rising temperature, the yield of radicals began to diminish. This deposition of carbon was not recorded by Rice and Glasebrook (*loc. cit.*), but it accords with their observation that at higher temperatures methylene gives place to methyl; and accounts for the deposition of carbon in Williamson's experiments (*loc. cit.*).

The fragments, in the absence of a carrier gas, were identified by their reaction with elementary tellurium. A little red telluroformaldehyde was deposited behind the tellurium where

Rice and Glasebrook had obtained a plentiful yield, but as with the seleno- and the telluroformaldehyde from keten, polymerisation could be accelerated by surrounding the tube beyond the mirror with a bath of solid carbon dioxide. On removing the bath, we observed (*a*) an orange-yellow liquid which partly distilled, leaving a residue of orange-red solid, (*b*) a white deposit which, as the tube gradually reached the room temperature, partly melted to a colourless liquid, and ultimately volatilised. The behaviour was strikingly similar to that observed during the formation of polymers from ordinary aldehydes.

The diazomethane was then carefully distilled from the other products which had collected in the trap *S*, and the residue was preserved overnight in a bath of solid carbon dioxide. A few tiny droplets, some orange-coloured, some colourless, remained in the trap. They had a strong odour of telluroformaldehyde with a background of nitrogenous bases, but no methyl or hydrogen telluride was perceptible. With a solution of mercuric iodide in acetone, canary-yellow granules were immediately deposited. On heating, they turned red, and then decomposed leaving only a black residue at 300°, a behaviour so closely similar to that of selenoformaldehyde mercuric iodide that we felt confident in assuming that we were dealing with the tellurium analogue.

It is clear, therefore, that telluroformaldehyde, whether prepared in keten or diazomethane, is first formed as a gas and has at least two other polymers. In our experiments, the red one, deposited just behind the mirror, accounted for only a small part of the total yield, and in an endeavour to confirm Rice and Glasebrook's findings that it is the sole product, their experimental conditions were followed as closely as possible by using ether as a carrier gas, and adjusting the furnace temperature to 450°. Although large tellurium mirrors were rapidly consumed, we again obtained only a fraction of the telluroformaldehyde as the red polymer.

The products from the photodecomposition were next investigated. In accordance with the arguments of Norrish and Kirkbride (J., 1933, 119), we found that the hot mercury arc, rich in radiations about 3130 A., yielded scarcely any radicals, whilst a cold arc with its maximum intensity at 2580 A. gave plentiful yields comparable with those obtained by using the furnace. The products of the reaction with tellurium were as numerous; but a greatly improved yield of the fluorescent orange-red solid was deposited behind the mirror; again, however, it was not the sole product. Methyl radicals were not detected in either the photo- or the thermo-chemical decompositions of diazomethane at lower temperatures.

The life period of the radicals was measured in the usual way by using tellurium mirrors. The radicals were prepared thermally from a sample of diazomethane kept in butyl phthalate, *i.e.*, in the absence of a carrier gas. In view of the experimental difficulties, we could not obtain a direct estimate of the streaming velocity, and assumed that it was the same as that of pure ether, which we could measure. The following data were obtained:

Temp. of furnace	400°
Initial pressure	0·8 cm. of butyl phthalate.
Final pressure	0·4 cm. ,, ,,
Distance of furnace from end of tube	72 cm.
Distance between manometers	164·5 cm.
Diameter of tube	1·1 cm.
Weight of ether passing through tube per min.	0·161, 0·156, 0·163, mean 0·160 g.
∴ Streaming velocity	1180 cm./sec.

The values for the times of removal of the mirrors are recorded in Table I, and prove that the radicals react according to a sensibly unimolecular law, and have a half-value period of $5\cdot0 \times 10^{-3}$ sec.

TABLE I.

Distance from furnace mouth, d cm.	14·3	6·2	27·3	21·6	18·4	25·4	10·6
Time of removal, t secs.*	40	21	127	75	65	92	29
Time, τ sec., taken to traverse d cm.*	0·0093	0·0041	0·0172	0·0136	0·0119	0·0161	0·0068

* The symbols d, t, and τ in subsequent tables have the same significance as in this table.

The experiments were repeated with the cold mercury arc in place of the furnace. The following two values sufficed to show the similar behaviour of the radicals, which have the half-value period $6\cdot4 \times 10^{-3}$ sec.

d, cm.	11·5	39·5
t, secs.	32	194
τ, sec.	0·0073	0·0241

These data establish beyond doubt a profound difference in the behaviour of methylene prepared from and in the presence of keten and diazomethane severally. The unlikely suggestion that methylene may exist in two forms was discounted on two grounds: the half-value periods of the radical produced thermally and photochemically were identical, and the conversion from the ${}^5S$ into the ${}^3P$ state or *vice versa* should occur, as in the case of carbon monoxide, instantaneously, so that only one form, the more stable, would ever be detected in ordinary chemical manipulations. The different half-value periods must therefore be attributed to the presence of keten in the one case and diazomethane in the other. If methylene is intrinsically as reactive as methyl, then the apparent stability in keten is to be ascribed either (*a*) to the formation of an addition compound, which has already been disposed of as unlikely (see below), or (*b*) to the poisoning of the walls of the quartz tube by keten, so that the surface no longer functions as a catalyst for the formation of ethylene ($2CH_2 \longrightarrow C_2H_4$). We disposed of this possibility by passing keten through the tube prior to each of a series of measurements of a half value period in diazomethane. The half value was not perceptibly altered. As an additional confirmation, and to establish if possible our contention that the stabilisation in keten was not due to the formation of an addition compound, we examined the effect of passing keten and diazomethane simultaneously through the furnace heated to such a temperature that only the latter was dissociated.

The keten container was immersed in a bath of solid carbon dioxide and ether so that a constant vapour pressure could be maintained. After the formation of the standard mirror, the keten stop-cock was opened slowly until the desired pressure was attained (we had previously ascertained the inactivity of the keten at the temperature of the furnace). When conditions became stable, the diazomethane stop-cock was opened until a second rise of 2 mm. was registered in the manometer limbs. Times of disappearance of mirrors were obtained for partial pressures of 2 mm. and 10 mm. of keten, the value for diazomethane being kept at 2 mm. No direct measurements were obtained for the streaming velocities at these pressures. The figures given below were extrapolated from values observed for pure ether.

Total pressure, mm. of butyl phthalate	4	10
Streaming velocity, cm./sec.	730	2000
Pressure gradient, mm. of butyl phthalate	0·00122	0·00364

Table II.

Partial pressure of keten, 2 *mm.*

d, cm.	11·8	13·0	40·7	41·3
t, secs.	80	95	384	346
τ, sec.	0·0123	0·0135	0·0399	0·0407

Half-value period = 13·4 × 10^{-3} sec.

Partial pressure of keten, 10 *mm.*

d, cm.	11·8	40·5	41·5
t, secs.	94	106	112
τ, sec.	0·0045	0·0145	0·0149

Half-value period = 50 × 10^{-3} sec.

The results show that the half-value period was considerably extended by the addition of keten, and it now remained to be discovered whether this effect was due to dilution, and could be just as well achieved by the use of inert substances such as ether and nitrogen.

The diazomethane was collected in ether which had been previously dried over sodium. After each series of measurements the concentration of diazomethane was decreased either by pumping out at −80° or by diluting a portion of the solution with ether. The initial pressure was kept throughout at 8 mm. of butyl phthalate. The results are in Table III.

The half-value periods obtained from these results are, respectively, 9, 11, 17, and 30 × 10^{-3} sec. There is a definite increase in the life period with increase in the ratio ether/diazomethane.

The passage of nitrogen through the apparatus was found to be slow, owing to the fact that the gas does not condense in the liquid-air trap. The difference in pressure between the two manometers was accordingly small, and cathetometers had to be used to observe the liquid levels. A graph was constructed from a number of readings so that the relation between the two pressures could be obtained. To obtain the rate of passage of the gas, nitrogen was stored in a Bunte gas burette, and the volumes passing over in given times at various initial pressures were measured. A graph was constructed showing the relation between pressure and c.c. at *N.T.P.*

TABLE III.

Temperature of furnace, 440°.

d, cm.	6·3	6·5	38·3	39·7
t, secs.	17	18	72	89
τ, sec.	0·0041	0·0043	0·0236	0·0243

Temperature of furnace, 430°.

(Relative concentration of CH_2N_2 had been reduced by pumping out at 1 cm. of butyl phthalate for 20 mins.).

d, cm.	12·2	37·4	38·3
t, secs.	23	56	66
τ, sec.	0·0079	0·0231	0·0236

Temperature of furnace, 430°.

(Diazomethane concentration reduced by dilution with 1½ times the volume of ether present.)

d, cm.	13·8	13·8	38·5	41·1
t, secs.	43	38	74	89
τ, sec.	0·0089	0·0089	0·0234	0·0251

Temperature of furnace, 420°.

(Carried out after further dilution with 2 vols. of ether.)

d, cm.	12·5	13·3	41·5	41·9	40·8
t, secs.	139	168	210	220	249
τ, sec.	0·0080	0·0087	0·0252	0·0255	0·0249

A mixture of nitrogen at 2 mm. of butyl phthalate and diazomethane at the same pressure was then passed through the furnace at 420°, and times of disappearance of tellurium mirrors observed. To calculate the streaming velocity, it was assumed that the conditions of flow were those in pure nitrogen.

Manometer readings : 4 mm. and 3·8 mm. of butyl phthalate. Volume of N_2 passing at 4 mm. = 0·35 c.c./min. Streaming velocity $= \frac{0\cdot35}{60} \times \frac{76}{0\cdot4} \times 13\cdot6 \times \frac{1}{3\cdot14(0\cdot55)^2} = 15\cdot8$ cm./sec. Pressure gradient $= (0\cdot4 - 0\cdot38)/164\cdot5 = 0\cdot000122$.

TABLE IV.

d, cm.	6·3	7·5 *	12·8	13·5
t, secs.	47	35	139	140
τ, sec.	0·387	0·460	0·785	0·828

Half-value period = 230×10^{-3} sec.

* Pressure of CH_2N_2 slightly over 2 mm.

These results show that there is no reason to discriminate between the effect of ether, nitrogen, and keten in prolonging the life of methylene. They function as pure diluents, which retard the diffusion of the molecules to the walls of the vessel, where they may also compete for the available adsorptive surface. The short life period in pure diazomethane must therefore be ascribed to a reaction between methylene and diazomethane. This conclusion was tested by investigating how the rate of disappearance of the radicals varied with the initial methylene concentration.

Pure diazomethane was passed through the furnace at an initial pressure of 2 mm. of butyl phthalate, and life-period measurements were made for the series of temperatures listed below. Again, the streaming velocity of ether at 2 mm. was taken as equivalent to that of diazomethane.

0·191 G. of ether was collected in the trap in 15 mins. Pressure gradient = 0·00122 cm. of butyl phthalate/cm. The streaming velocity is, therefore, 375 cm./sec.

The values in Table V are shown in Fig. 3, where the lowest straight line *A* represents the values for 392°, the pronounced curves *B* and *C* those for 422° and 495°, and the flatter line *D* the values at 525°. At 595° the initial concentration of radicals begins to diminish, and the values have been omitted from the figure to avoid confusion, as they merely confirm the general trend of the results for higher temperatures to become linear.

Before interpreting these data, it was desirable to know how the quantity of diazomethane decomposed varied with the temperature. A quantity of diazomethane at 2 mm. (butyl phthalate) was passed through the furnace at various temperatures for a measured time. The

TABLE V.

Furnace temperature, 392°.

d, cm. ...	3·2	7·7	11·5	14·7	14·8	24·9	27·2	36·7	39·0
t, secs. ...	57	82	103	157	218	295	295	570	582
τ, sec. ...	0·0049	0·0110	0·0162	0·0198	0·0201	0·0321	0·0354	0·0435	0·0461

Half-value period = 12×10^{-3} sec.

Furnace temperature, 422°.

d, cm. ...	4·2	4·0	7·2	8·1	8·5	13·5	17·8	18·2	34·2	34·4
t, secs. ...	14	10	38	46	45	87	122	127	363	368
τ, sec. ...	0·0064	0·0059	0·0106	0·0117	0·0122	0·0187	0·0237	0·0248	0·0422	0·0427

Furnace temperature, 495°.

d, cm. ...	5·0	5·5	8·0	13·5	14·7	23·5	35·2	37·2
t, secs. ...	10	13	21	48	55	171	309	298
τ, sec. ...	0·0073	0·0080	0·0114	0·0187	0·0198	0·0307	0·0430	0·0449

Furnace temperature, 525°.

d, cm. ...	4·7	5·5	7·7	9·2	19·0	19·6	36·5
t, secs. ...	8	6	15	16	90	69	352
τ, sec. ...	0·0065	0·0080	0·0110	0·0131	0·0251	0·0264	0·0439

Furnace temperature, 595°.

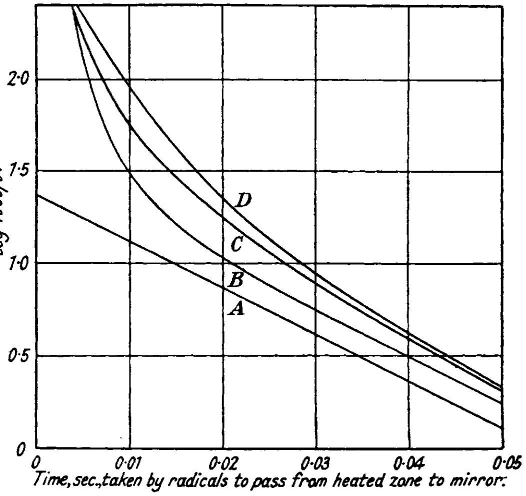
d, cm. ...	4·3	5·5	10·4	18·7	32·2
t, secs. ...	13	6	25	84	388
τ, sec. ...	0·0063	0·0080	0·0145	0·0247	0·0402

gas was collected in the trap into which had been frozen a small amount of ether. On being warmed slightly, the ether melted and dissolved the condensate. The trap was opened, and the contents quickly poured into a colorimeter. The intensity of the colour was compared with that of a solution of potassium chromate. By comparing the relative concentrations at various temperatures with that at room temperature, an estimate of the percentage decomposition was obtained:

Decomposition at 400° 67%
„ „ 495° 77%

Since the percentage decomposition is so high, appreciable quantities of nitrogen are formed, so it is necessary to introduce a correction for (*a*) the increased pressure and (*b*) the diminished streaming velocity. The furnace was brought to 495° until stable conditions of flow were obtained. The furnace was then suddenly cooled in a rapid air stream. The pressure decreased by 20%. This means that at room temperature we were running an excess of 20% of diazomethane. This correction brings the above values to 59 and 71% at 400° and 495° respectively. These values show that the 100-fold increase in methylene observed between 392° and 422° in Fig. 3 is not accompanied by a corresponding increase in the amount of diazomethane dissociated.

FIG. 3.



A *curve for* 392°; B *for* 422°; C *for* 495°; D *for* 525°.

The interpretation of the graphs in Fig. 3 can now be attempted. If the methylene disappears in a bimolecular reactions with diazomethane, these curves should be expressed by the general law

$$-\mathrm{d}x/\mathrm{d}t = K[a - (x_0 - x)] = K(B + x)$$

where x = concentration of the methylene at time t, x_0 and a are the initial concentrations of methylene and diazomethane respectively (*i.e.*, at $t = 0$), and $B = a - x_0$. Integrating between the limits x_0 and x, we have

$$[\log_e x(B + x_0)/x_0(B + x)]/B = Kt$$

When a is large compared with x_0, this reduces to $(\log_e x/a)/a = K't$, and the values follow the unimolecular law, *i.e.*, the straight line A at 392°. When a is comparable with x, the plot of $\log_e x$ against t must yield curves such as B and C; and the flatter curve D is due, once more, to the diminution in x_0. The conclusion must therefore be drawn that the decay of methylene is due to a reaction with diazomethane, which, from the experiments in the presence of diluent gases, probably occurs on the surface of the quartz tube.

There is no reason, therefore, to regard methylene as anything other than a reactive molecule. In particular it does not possess that property which discriminates a free radical from other molecules, *viz.*, that of combining readily with itself to yield a stable dimeric form. Thus, in our experiments with keten, each molecule suffered no less than 3×10^3 collisions with the wall of the tube and 4×10^5 collisions with other molecules in passing along the quartz tube without signs of reaction.

It was finally decided to measure the activation energy of the reaction responsible for production of free radicals from diazomethane by observing how the yield of radicals (at the furnace mouth) varied with the temperature. The experiments were made with ether as a carrier gas to avoid as far as possible differences in streaming rate due to the different proportions of nitrogen produced from diazomethane at different temperatures. The results are recorded in Table VI.

TABLE VI.

Temperature, 387° (660° K.).

d, cm.	13·7	14·4	37·9
t, secs.	130	140	256
τ, sec.	0·0088	0·0094	0·0232

Temperature, 430° (703° K.).

d, cm.	13·8	13·8	38·5	41·1
t, secs.	38	43	74	89
τ, sec.	0·0089	0·0089	0·0234	0·0251

Temperature, 525° (798° K.).

d, cm.	7·2	10·2	11·6	22·5	24·5	30·3	32·5	35·0	38·6	43·0	43·5	44·0
t, secs.	10	13	16	32	38	63	80	81	81	97	110	113
τ, sec.	0·0047	0·0066	0·0074	0·0142	0·0154	0·0190	0·0200	0·0217	0·0235	0·0261	0·0263	0·0267

The extrapolated values of log $1000/t$ at the mouth of the furnace (distance 8·0 cm.) are recorded below, and give as the apparent activation energy, determined graphically, 22 kg.-cals.

Temp., K.	660°	703°	798°
log $1000/t$	1·05	1·57	2·20

An interesting feature of these experiments is that a unimolecular law is followed by the radicals in the experiments at the higher temperatures. If the conclusions previously discussed, concerning the mode of disappearance, are correct, the unimolecular decomposition would only occur if the quantity of diazomethane decomposed in these experiments were small. It was found that even at 430° only 9% of the diazomethane had been dissociated. It thus appears that the ether prevents the propagation of some chain process responsible for the large dissociation (*ca.* 60%) in the pure gas.

SUMMARY AND CONCLUSIONS.

Methylene has been prepared by the thermal dissociation of diazomethane, and by the photodissociation of diazomethane and keten, and has been detected by its reactions with tellurium and selenium, whereby telluro- and seleno-formaldehydes are formed. They are first produced as vapours, which subsequently polymerise to give in each case at least two solids. Tellurium gives the characteristic orange-red form previously described by Rice; and a greyish-white form which has some resemblance to that claimed by Belchetz, but subsequently regarded as a mixture of hydrogen telluride and tellurium. We cannot agree with Rice that the sole reaction product of methylene and tellurium consists of the red telluroformaldehyde, and his criticism of Belchetz's work on this ground, and in the belief that telluroformaldehyde could not have passed from the mirror to the liquid-air trap, can no longer be upheld.

It has been found that, whereas methylene has a half-value period of 5×10^{-3} sec. in the presence of diazomethane (Table I), there is no measurable decay in the presence of keten even in 50×10^{-3} sec. The half-value period in diazomethane can be extended by dilution with keten (Table II), an effect which is due neither to the poisoning of the walls of the tube by the keten, with the consequent suppression of the association process $2CH_2 \longrightarrow C_2H_4$, nor to the formation of a loose complex of methylene and keten, but to an ordinary dilution effect which can be equally well realised with ether (Table III) or nitrogen (Table IV). In the presence of the latter, the half-value period has been increased to 230×10^{-3} sec., and this has been ascribed to the suppression of a wall reaction, which suppression may be very efficient in a tube under conditions of stream-line flow.

The short life period in diazomethane is due to a bimolecular reaction between diazomethane and methylene, revealed in a study of the kinetics of the decay of methylene in various initial concentrations of diazomethane either alone (Table V), or diluted with ether (Tables III and VI).

These results give a good reason for the difference in quantum yields obtained for keten (Ross and Kistiakowsky) and diazomethane (Norrish and Kirkbride). We have shown that reactions between methylene and keten must be very slow, so that the methylene first formed is probably removed by association. In our opinion this view accords better with Ross and Kistiakowsky's interpretation than with that of Norrish and Kirkbride because (*a*) each methylene survived 4×10^5 collisions with keten in our quartz tube, and (*b*) we do not think that the quantum yields observed by Ross and Kistiakowsky, which have a mean value of 1·08, can be safely assumed to exceed unity in view of the errors inherent in such measurements. In the case of diazomethane, the reaction with methylene is so rapid that the quantum yield must be 2 even in the absence of secondary reactions. That such secondary reactions are probable may be seen from the influence of ether in inhibiting reaction chains in the furnace, so that a quantum yield of 4—5 is not surprising, and confirms the findings of Kirkbride and Norrish.

The controversy between Belchetz and Rideal, on the one hand, and Rice and his colleagues on the other, appears to have been provoked by a misapprehension which the present experiments dispel. Although there is no reason to suspect a rapid reaction between methylene and methane at room temperature, for Kassel suggests an energy increment of 44 kg.-cals. for the reaction, and we find no reaction between methylene and ether, yet above 800°, as in the furnace used by Rice or with the activated methane molecules doubtless present in Belchetz's gases as they left the filament, a reaction must be possible, and would account for the inability of Rice *et al.* to detect methylenes at all, and of Belchetz to obtain them when his detector mirrors were situated at distances greater than the mean free path from the heated filament. The preparation of methylene from diazomethane below 400° is not surprising. Above 500° it would be, but for the occurrence of the chain reaction in the furnace which more than compensates for the tendency of the radicals to dissociate and to interact with other species until the temperature exceeds 600°, when only methyls are detectable (Rice and Glasebrook, *loc. cit.*).

The possibility that methylene is a primary product of the dissociation of methane, in agreement with the postulates and experiments of Nef, Bone and Coward, and Kassel, is thus once more open, and if this present justification of Belchetz and Rideal's work be valid, the occurrence of methylene must be held to be at least more likely than that of methyl.

The failure of Paneth and Lautsch (*loc. cit.*) to detect methylene in the thermal or electrical dissociation of diazomethane, and possibly in the reaction between methylene chloride and sodium vapour, must be ascribed to their choice of carbon and benzoic acid as detectors, for there is nothing to lead us to suspect that a rapid reaction should occur between either of them and methylene.

The whole of our experimental results accord with the view (see p. 413) that in methylene the carbon is essentially bivalent; the molecule has none of those properties which one would naturally associate with the highly unsaturated, and therefore reactive, species $>CH_2$.

The authors wish to thank Messrs. Imperial Chemical Industries, Ltd., for a grant with which some of the apparatus was bought.

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