TABLE III

COMPARISON OF ACTIVITY COEFFICIENTS OF ALKALI NITRATES

F = f. pt. data in Landolt–Börnstein. S = data of Scatchard and Prentiss. R = present results.

m	F	S	R
	$LiNO_3$		
0.1	0.794	0.800	0.785
.2	.753	.763	.748
.3	.736	.748	.734
	$NaNO_3$		
0.1	0.754	0.770	0.755
.2	.704	.712	.699
.3	..	.680	.661
.5	.624	.634	.613
.7	..	.598	.581
1.0	.553	.555	.546
	KNO_3		
0.1	0.724	0.730	0.730
.2	.653	.658	.656
.3	..	.609	.605
.4	.543	.544	.540
.5	..	.497	.492
.6	.449	.443	.439

TABLE IV

AVERAGE MOLAL HEAT OF DILUTION OF ALKALI ACETATE SOLUTIONS, IN CAL. PER MOLE OF SALT

m	0.2	0.3	0.5	0.7	1.0
$LiC_2H_3O_2$	116	221	364	505	744
$NaC_2H_3O_2$	125	155	92	120	134
$KC_2H_3O_2$	48	149	185	334	424

dilution decreases in the order Li > K > Na, resembling in this respect the alkali hydroxides.

The osmotic coefficients of these nine salts at 1 *M* concentration are as follows

	Li		Na		K
NO_3	0.977	←	0.836	←	0.744
$C_7H_7SO_3$	.889	←	.833	←	.786
$C_2H_3O_2$	.944	→	.985	→	.995

I wish to tender my thanks to Dr. H. S. Harned for his encouragement and his advice in the compilation of this and the preceding paper.

Summary

1. Measurements of the concentrations of aqueous solutions of alkali nitrates, acetates and *p*-toluenesulfonates isopiestic with solutions of known strength of potassium chloride at 25° have been made.

2. From these the activity coefficients of the salts have been computed. The values of this quantity derived from these measurements agree with the activity coefficients computed from freezing point measurements in the case of the nitrates. In the case of solutions of the other salts, direct comparison with freezing point data could not be made. However, from the freezing point data and the vapor pressure data at 25°, the relative partial molal heat content of the acetates has been estimated.

AUCKLAND, NEW ZEALAND RECEIVED MARCH 21, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF COLLOID SCIENCE, THE UNIVERSITY]

The Primary Decomposition of Hydrocarbon Vapors on Carbon Filaments

BY LEONARD BELCHETZ[1] AND ERIC K. RIDEAL

It is now certain that radicals are involved in the cracking as well as in the combustion of hydrocarbon vapors, but the nature of those produced in the primary decomposition cannot be regarded as firmly established. Neither is it known whether the products vary when the decomposition is effected at different hot catalytic surfaces. This communication deals with the decomposition of methane and ethane on carbon filaments.

In a preliminary note[2] experimental evidence was advanced in support of the views that of the two most probable reactions in the decomposition of methane at a hot platinum surface

$$\text{(a)}\quad CH_4 + M \longrightarrow CH_3 + H + M$$
$$\text{(b)}\quad CH_4 + M \longrightarrow CH_2 + H_2 + M$$

the second reaction occurs exclusively.[3]

In the case of ethane, it is generally considered that ethylene and hydrogen are primary products. Rice,[4] however, has suggested that a break of a C–C bond first occurs with the production of methyl radicals, which are able to initiate chains.

The very careful work of Travers and Hockin[5]

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[1] Emmanuel College External Research Scholar and H. B. Webb Gift Research Scholar (South Africa).

[2] Leonard Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

[3] From the theoretical considerations of Lennard-Jones [*ibid.*, **30**, 70 (1934)] Mullikan [*J. Chem. Phys.*, **1**, 500 (1933)] and Van Vleck [*ibid.*, **2**, 20 (1934)], this also appears to be the case for the homogeneous decomposition. For an alternative view, see Rice [*Trans. Faraday Soc.*, **30**, 152 (1934)] and Rice and Dooley [THIS JOURNAL, **56**, 2747 (1934)].

[4] Rice, THIS JOURNAL, **53**, 1959 (1931); **55**, 3035 (1933).

[5] Travers and Hockin, *Proc. Roy. Soc.* (London), **A126**, 1 (1932).

and Travers and Pearce[6] indicates that the decomposition of pure ethane is partly heterogeneous, for unless reaction tubes were filled with hydrogen and heated overnight at 600°, irreproducible results invariably were obtained. Even then the results were reproducible for one particular reaction vessel only, but became generally so, however, if equilibrium mixtures of ethane, ethylene and hydrogen were used to start with. To interpret these effects, Travers and Pearce suggest that ethylene is first produced; it is then activated and can initiate chains. The formation of a condensate from ethylene, which is a bimolecular reaction, is explained on the assumption of the formation of activated ethylene.

Any proposed reaction mechanism must be capable of accounting for the formation of methane as a secondary product. Rice[4] considers it to be formed as the result of interaction of methyl radicals and ethane, as follows

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$

Travers and Pearce, on the other hand, show quite definitely that ethylene is the parent substance of this product, and find that the rate of formation of methane is accurately expressed by the equation

$$d[CH_4]/dt = K_{\text{methane}}\,[C_2H_4]\{[C_2H_6] + [CH_4] + [H_2]\}$$

Ethylene is thought to be activated by collision with ethane, methane and hydrogen, active ethylene then reacting with hydrogen in two stages as follows

$$C_2H_4^1 + H_2 \longrightarrow CH_4 + CH_2$$
$$CH_2 + H_2 \longrightarrow CH_4$$

Experimental

In the ordinary hot tube method any radicals formed undergo a number of collisions before striking the acceptor, such as a tellurium mirror. If the radicals are reactive with no or small energies of activation the products caught will be chiefly secondary products; to obviate this as far as possible two different types of apparatus were employed, Fig. 1 and Fig. 2.

In each apparatus the gas streamed through at a high velocity (*ca.* 100 cm./sec.) and at a pressure of 0.1 mm. In 1 the radicals formed at the hot filament f were caught on the cooled glass surface (G) which was distant 3.0 mm. (*ca.* a mean free path at the usual filament temperatures) from the filament. On the glass surface mirrors could be deposited. Volatile products formed during the run were collected in the liquid air trap H and redistilled out of contact with air into H′. After the run the mirror could be examined and, if volatile, distilled with any products into H and fractionated into H′. In the second apparatus the products were collected in liquid air traps as in 1 at the end of the flow tube, the flat face of the reaction bulb being covered with a mirror internally and cooled externally by cold water. It is clear that apparatus 2 approximates more closely to the conditions existing in a hot tube apparatus than the first one and as we shall note the nature of the reaction products differed in an unmistakable manner with the form of apparatus employed, a definite indication that secondary products are formed with surprising ease.

A second point is worthy of note, *viz.*, that the products obtained differed with the nature of the mirror. In addition to tellurium, iodine was employed as a mirror for the reason that if compounds of the type CH_2I_2 are formed these are much more stable than compounds of the type CH_2Te; for telluroformaldehyde unless rapidly removed from the presence of the other reaction products can like formaldehyde readily undergo further reaction and reduction to dimethyl ditelluride and presumably also to dimethyl telluride.

Results with Platinum Filaments.—The two apparatus were first tested with platinum filaments and tellurium mirrors. It was found that with filament temperatures up to 1400°, as determined by an optical pyrometer, only hydrogen telluride could be frozen out at the end of the tube, no trace of any condensable compound of tellurium with organic radicals being observed. It is clear that these remained behind on the tellurium. Utilizing the first apparatus and an iodine mirror the previous work was confirmed in that at temperatures between 1100 and 1400° on a platinum filament molecular hydrogen and methylene were the products of decomposition and above 1200° atomic hydrogen in addition could be identified. At temperatures up to 1400° with a tellurium mirror no formation of either dimethyl telluride or dimethyl ditelluride was observed. The grayish substance which was considered formerly to be such a compound was not formed on adequate cooling of the mirror and must have consisted of a trace of hydrogen telluride and a little tellurium. With iodine mirrors on the other hand the formation of methylene iodide was confirmed both by conversion of the product collected on the iodine mirror to formaldehyde and testing by the Schryver–Rimini method (see later).

Results with Carbon Filaments.—Owing to the greater range of temperature over which carbon filaments can be used, they are far superior to platinum for the study of the primary decomposition, and the method has been extended to their use.

At 1745° for example some 21% of the methane passing through the reaction vessel underwent decomposition. With the filaments employed for investigating the reaction products on iodine and tellurium decomposition to the extent of about 10% occurred. When the radicals were formed in the first apparatus and allowed to fall on a deposit of iodine cooled to −65° as previously described, the latter was immediately attacked, but the reaction slowed down as the iodine became coated with a product which proved to be methylene iodide. For this reason the iodine surface was frequently renewed. At the end of a four hour run the cooling mixture was removed and the iodine and products pumped over into the detachable

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(6) Travers and Pearce, *J. Chem. Soc. Ind.*, **53**, 321T (1934).

liquid-air trap H (Fig. 1). Attempts to separate the oil from excess iodine by diffusion into the cooled tube H′ were not very successful. The impure methylene iodide was therefore dissolved in a little chloroform, shaken up with a small drop of mercury to remove the excess iodine as mercurous iodide and the solution filtered into a small tube. The chloroform was evaporated off in a water-bath, and the oil heated to 180° in a sealed tube with 0.5 cc. of distilled water and a little lead oxide. When hydrolysis was complete, the aqueous solution was filtered into a solution containing 2 cc. of 1% phenylhydrazine hydrochloride and 1 cc. of 5% potassium ferricyanide. On the addition of 5 cc. of concentrated hydrochloric acid, a magenta color appeared immediately (the Schryver–Rimini test for formaldehyde). Blank tests were performed on the water, chloroform and methyl iodide. Only after standing for several hours did the treated solutions show any color.

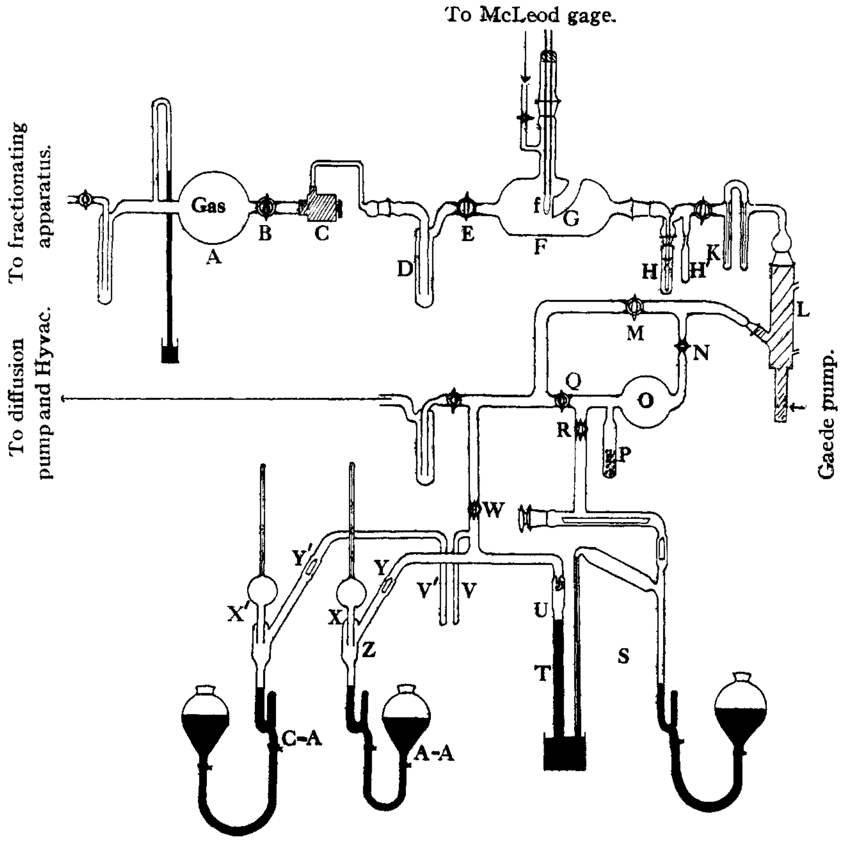

Fig. 1.

In other experiments, the methylene iodide was converted into the addition compounds[7] $HgCH_2I_2$ and $Hg_2CH_2I_2$.[7] The iodine and oil were dissolved in 0.5 cc. of ether and shaken up for a long period with a drop of mercury. Excess mercurous iodide which keeps the mercury in a finely divided condition is necessary for the success of the reaction. The ether was boiled off, the residue leached out with a solution of potassium iodide to remove iodides of mercury, and washed by decantation with water, alcohol and ether. The mercury was then run off. This method was preferred to that previously employed owing to the slight solubility of the products in chloroform and to the danger of contamination by mercurous iodide. It was found, however, that with the small quantities of substance available we were unable to prepare a pure specimen of one or the other of the mercury addition compounds, since the only suitable solvent for effecting a separation is methylene iodide itself. We therefore employed the formaldehyde test described above to the exclusion of the one given here.

No evidence whatever of the formation of methyl iodide or iodoform was obtained. Since the former only freezes at −65° any formed during the course of the experiment should have collected in the liquid air trap with the hydrogen iodide. Prolonged pumping with the cooling tube maintained at a temperature of −45° failed to reveal any product in the liquid air trap except a trace of iodine. When, however, the filament was moved back 1 cm. from the mirror the yield of methylene iodide became negligible while a liquid in quantities too small to be identified with certainty but which appeared to be methyl iodide, collected in the trap.

Experiments with Water Cooled to −80°.—The possibility of the formation of methyl alcohol by the action of methylene with water frozen onto the cooling tube G (Fig. 1) was next investigated. Instead of reacting with the water, the radicals combined with one another on the cold surface with the production of ethylene which then proceeded to dissolve

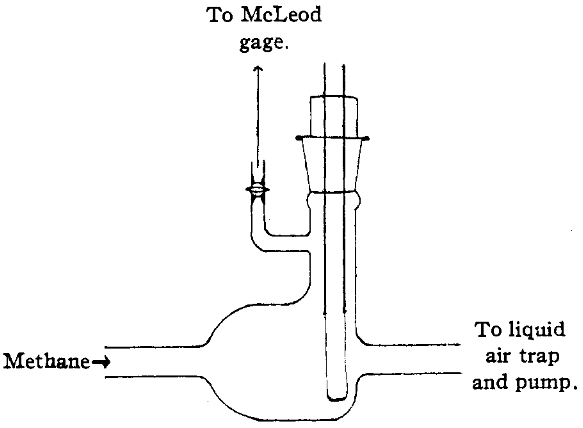

Fig. 2.

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(7) Sakurai, *J. Chem. Soc.*, **39**, 485 (1881).

in the water. The solution smelled strongly of the gas and decolorized bromine water instantaneously.

The formation of ethylene was further confirmed by allowing the radicals to combine on the glass surface G cooled to −80° and condensing the product in pure bromine diffused over to and frozen in H. At the end of four hours, dry air was admitted into the apparatus, the detachable liquid air trap H removed and immediately closed with a stopper, and the ethylene and bromine allowed to react. After excess bromine had been allowed to escape, about 0.03 cc. of an almost colorless oil remained, the boiling point of which was determined as 132° (b. p. of ethylene bromide, 131.5°).

Experiments with Tellurium

The first few experiments with tellurium were performed with the apparatus in Fig. 2. Mirrors were deposited on the flat face of the reaction vessel and the position of the filament adjusted to within 3 mm. of the tellurium. Efficient cooling was effected by enveloping the reaction vessel in cotton wool which was kept wet by a rapid stream of cold water. In this manner the passage of tellurium to the liquid air trap was entirely prevented.

Appreciable quantities of dimethyl ditelluride (f. p. −20°), dimethyl telluride (b. p. 80°) and a relatively small quantity of hydrogen telluride were obtained. When these were diffused into the side tube H′, the product condensed in separate layers, respectively orange, pale yellow and white. The properties of the orange product corresponded exactly to those described by Rice and Glasebrook.[8] On standing, it changed first into a yellow, and finally into a gray solid, which could be converted to tellurium by gentle heating. We were unable to determine the boiling point of the orange liquid by the micro method, however, for between 90 and 120° it polymerized in the capillary to a red solid which decomposed at 195° to a gray substance corresponding to the one obtained from the oil on long standing. The temperatures at which these changes occurred depended entirely on the length of time the oil had been standing. In addition, the relative amounts of dimethyl telluride increased in quantity as the filament was placed at increasing distances from the tellurium.

It is clear that when conditions are favorable for catching the primary products and rendering them chemically relatively unreactive, *e. g.*, as CH_2I_2, they are found to consist of methylene and hydrogen, but if secondary reactions can take place methyl radicals are readily obtained as is the case with tellurium in the apparatus II. If a tellurium mirror be employed in apparatus I and the organotellurium complex be given every opportunity of escaping into the liquid air-cooled chamber H, *i. e.*, by keeping the tellurium mirror warm and thus shortening the life of the organotellurium complex on the mirror where it is subject to further reduction, it was considered possible that one might obtain evidence for a methylene tellurium complex. The mirror was maintained at 100° with boiling water and the filament heated to 1750°. A yellow solid collected high up in the detachable tube of the trap H and hydrogen telluride lower down with a mere trace of the methyl tellurides. At 1850° a larger quantity of the yellow solid was obtained and identifiable quantities of the two methyl tellurides. The yellow solid was found to be insoluble in chloroform and to decompose to tellurium at about 150°.

Since Rice and Glasebrook[9] found that the polymer could not be removed except when warmed to 100° *in vacuo*, and then only with difficulty, our product must have left the mirror as the monomer, $TeCH_2$, and polymerized in the trap to the compound $(TeCH_2)_n$, or by analogy to trioxymethylene, $(TeCH_2)_3$. In view of the fact that the partial pressure of the product, $TeCH_2$, in these experiments is of the order of 10^{-3} mm. and methane is present also as a carrier gas, the probability of polymerization in the gas phase is small.

These experiments indicate that methyl radicals are very readily produced in the flow experiments but are essentially secondary products. Apart from the readiness with which methylene takes up atomic hydrogen, telluroformaldehyde is liable to be reduced by atomic or even possibly hot molecular hydrogen.

Analysis of the Gaseous Products.—An analysis of the products of decomposition on a carbon filament at 1745° gave the following data: CH_4, 59.0%; H_2, 21.0%; C_2H_6, 17.0%; C_2H_4, 2.7%. It was further found that the volume of the sample collected in an hour was 38.4 cc. at N. T. P. compared with 38.0 cc. of pure methane passed through the apparatus.

It is interesting to compare these values with those obtained by Storch[10] at practically identical temperatures by a static method in a carbon filament lamp immersed in liquid nitrogen.

Duration of experiment, min.	CH_4	H_2	C_2H_6	C_2H_4
14	73.4	11.1	13.8	1.8
17	62.6	13.6	20.3	3.4
28	55.0	16.4	25.0	3.5

It is evident that the rate of decomposition of methane cannot be followed by "the rate of change of pressure method" usually adopted. If the primary reactions are

$$CH_4 \longrightarrow CH_2 + H_2$$
$$CH_2 + CH_4 \longrightarrow C_2H_6$$

no change in volume should occur, hydrogen and ethane should be present in equal quantities but small amounts of ethylene should always be produced by the reaction

$$2CH_2 + M \longrightarrow C_2H_4 + M$$

In the experiments of Storch, secondary reactions involving the accumulating hydrogen

$$CH_2 + H + M \longrightarrow CH_3$$
$$2CH_3 \longrightarrow C_2H_6$$

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[8] Rice and Glasebrook, THIS JOURNAL, 56, 2381 (1934).

[9] Rice and Glasebrook, *ibid.*, 55, 4329 (1933).

[10] Storch *ibid.*, 54, 4188 (1932).

take place as decomposition proceeds, the concentration of ethane thus increasing at the expense of the hydrogen. If the primary reaction consisted of

$$CH_4 \longrightarrow CH_3 + H$$

Storch's analytical figures are not so readily intelligible.

Determination of the Energy of Activation

The Decomposition of Methane on Carbon.—The method employed (Fig. 1) consisted in pumping the methane rapidly over the hot filament and collecting the gaseous products in the fore-vacuum side of the apparatus, from which they were transferred to the analyzing apparatus. The hydrocarbons, methane, ethane and a small quantity of ethylene, were frozen out in liquid nitrogen and by comparison of the residual pressure with the vapor pressure of pure methane at liquid nitrogen temperatures, the partial pressure of hydrogen was obtained. It was found possible to estimate accurately less than 1% of hydrogen. For percentages greater than 5%, it was found more expedient to evaporate the liquid nitrogen, so reducing the vapor pressure of methane to a negligible value.

The success of this method of analysis naturally depends on the employment of a gas of a very high degree of purity. After removal of unsaturated hydrocarbons with bromine water and fuming sulfuric acid, oxygen with alkaline pyrogallol, four fractionations yielded methane of over 99.9% purity, as determined by the partial pressure of uncondensable gas when a known quantity of methane was frozen in rapidly evaporating liquid nitrogen.

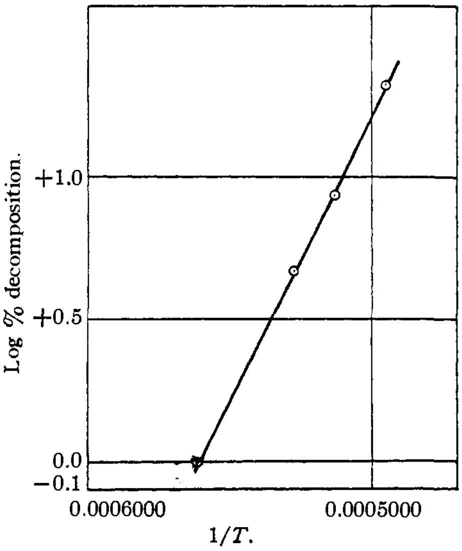


Fig. 3.—Decomposition of methane on carbon; E = 95,000 cal.

The reaction vessel F was replaced by an ordinary carbon filament lamp, the filament of which was 18 cm. long and 0.25 mm. in diameter.

To obtain constant rate of pumping, the fore-pressure of the Gaede pump, L (Type B), employed had to be maintained below a value of 4 mm. For this reason, a two liter bulb O and a charcoal trap P, the latter kept immersed in liquid nitrogen during the course of an experiment, were included in the fore-vacuum side of the apparatus to absorb the products as they came out.

With all taps except B open, the traps D and K cooled in liquid air, the charcoal in P heated by a furnace to 400°, the apparatus is evacuated to 10^{-5} mm. pressure. Taps N, Q and W are closed, the filament degassed, tap B opened, and the pressure of methane flowing through the apparatus adjusted to 0.1 mm. pressure by means of the needle valve C. The charcoal trap is then immersed in liquid air, the filament heated electrically to the required temperature as measured by a micropyrometer, tap M closed and N opened.

At the conclusion of a run, usually of an hour's duration, tap N is closed, the liquid air removed from P, and the gaseous products pumped out by means of the Toepler pump S into the analyzing apparatus, A-A. This consists of a graduated tube T connected through a small splash-head to the McLeod gage X, modified according to the diagram. The total volume of A-A from a mark Z to the first graduation U on T, as well as the volume of the bulb from the cut-off to the sealed end of the graduated capillary, is known. A similar apparatus, C-A, containing pure methane is placed adjacent to A-A so that the two liquid air traps V and V′ lie alongside each other. Ground-glass valves, Y,Y′, prevent the entry of mercury into the main apparatus when the mercury reservoirs are raised in making a measurement of the pressure.

The total volume of gas accumulated in an hour's run is measured by raising the mercury to Z and noting the reading on T. Its pressure is also observed. Both V and V′ are then immersed in the same Dewar of liquid nitrogen and the methane frozen out, a process requiring at least three hours before constancy is attained. From the difference in pressures as measured by A-A and C-A, the partial pressure of hydrogen in A-A is obtained. The volume of gas in A-A is also observed, whence the percentage of hydrogen in the total volume of gas can be calculated.

TABLE I

Temp., °K.	1780	1893	1943	2018
Percentage H_2	0.98	4.62	8.98	21.0

The logarithms of the percentage of hydrogen plotted against $1/T$ are shown in Fig. 3, from which curve an energy of activation of 95 kcal. is obtained. The value obtained by an identical method on a platinum filament at *ca.* 1400° was 59 kcal.

The Energy of Activation for the Decomposition of Ethane on Carbon.—The above method was also used in these experiments. The ethane was prepared by the reduction of ethyl iodide with a Zn–Cu couple, washed with bromine water, fuming sulfuric acid and alkaline pyrogallol and fractionated four times. A gas of 99.99% purity was obtained. The results are given in Table II. The plot of the logarithm of the percentage decomposition

TABLE II

Temp., °K.	1753	1813	1893	2003
H_2 in product, %	0.98	2.18	6.66	22.8
Decomposition, %	1.00	2.23	7.14	29.5

against $1/T$ is shown in Fig. 4, from which an energy of activation of 94.6 kcal. is obtained.

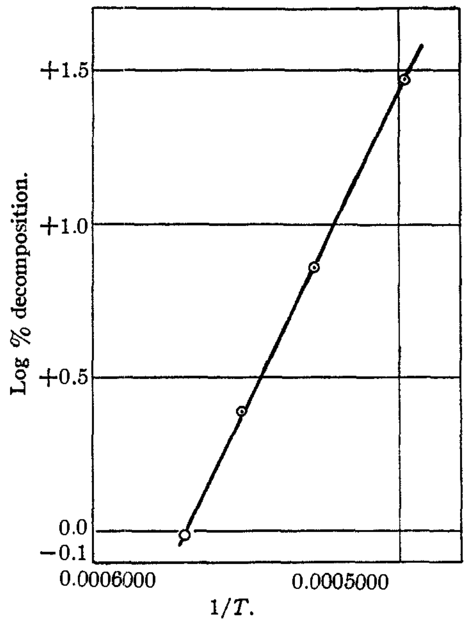


Fig. 4.—Decomposition of ethane on carbon; $E = 94{,}000$ cal.

Identification of the Products of Reaction of Ethane

Experiments with Iodine. (a) The Use of Cooled Iodine Mirrors.—Between temperatures of 1450 and 1800° except for the production of hydrogen iodide, no reaction of any sort ensued between the products of decomposition and the iodine, although the temperature of the latter was raised to −40°. A very careful search for methyl iodide failed to reveal any of the product. On the other hand, if ethylidene radicals were being produced, their conversion to ethylene or combination to butylene on the cold surface may have been responsible for our failure to find them.

(b) Experiments with Iodine Vapor.—Ethane, purified as far as possible from mercury vapor by the trap A (Fig. 5) cooled to −80°, enters the reaction vessel at a pressure of 0.1 mm. and after coming in contact with the filament B meets a stream of iodine vapor (partial pressure 0.1 mm.) issuing from the capillary tube D. By means of liquid air in the bulb E, it was expected to increase the streaming velocity of the gas and at the same time keep iodine vapor from the filament.

The upper part of the filament was situated 4 cm. from E, and the position of the exit of D varied in different experiments from 0.5 cm. from the filament to 0.5 cm. from E. We found it impossible, however, to prevent back diffusion of some of the iodine, a small quantity always finding its way to the trap A, even with the tube D very close to the liquid air.

In the complete absence of iodine, ethane is decomposed under the conditions of our experiments, without production of carbon. Decomposition of the gas in the presence of iodine, however, gave rise to a fairly large quantity of carbon which deposited on the walls of the reaction vessel and on the cooling vessel in particular. The only liquid product obtainable was ethyl iodide (b. p. 79°) separated from excess iodine by diffusion into a small cooled tube. Very large quantities of hydrogen iodide were also formed.

The formation of ethyl iodide may have occurred as the result of reaction between hot iodine and ethane, or possibly by the addition of hydrogen iodide to ethylidene or ethylene. That the substitution reaction was mainly responsible for this product was proved by increasing the partial pressure of the iodine tenfold relative to that of the ethane, so ensuring some collisions between iodine and any radicals present. This, however, did not result in the formation of any ethylidene iodide, nor was any ethylene iodide formed.

The products were examined for traces of ethylidene iodide by shaking the products plus excess iodine in a small sealed tube with 1 cc. of water, a little lead oxide, and two drops of mercury, the latter to remove excess iodine as mercurous iodide. The tube and contents were heated for fifteen minutes at 200°, any ethylidene iodide being in this manner converted to acetaldehyde. After cooling, the tube was opened and the solution filtered. The addition of a drop of fresh sodium nitroprusside solution and a drop of piperidine (Cohen, "Theoretical Organic Chemistry," p. 140) should have revealed the presence of acetaldehyde by the development of a blue color. All the tests we performed on our products proved negative, although the nitroprusside–piperidine reaction is sensitive to 1 part in 100,000 of acetaldehyde.

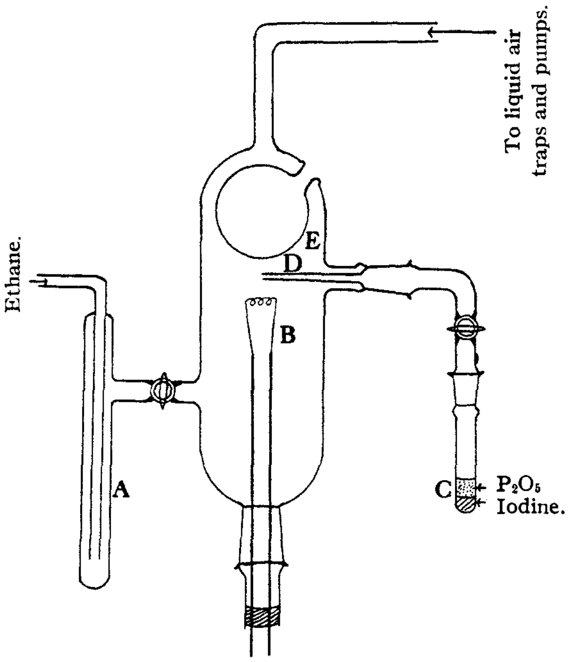


Fig. 5.

Experiments with Tellurium.—The only product obtained in these experiments was hydrogen telluride. Even at 1800° no dimethyl telluride or dimethyl ditelluride could be detected. The presence of ethylene in the effluent gases, however, could be demonstrated readily by condensing the product in pure bromine diffused over to and frozen in H.

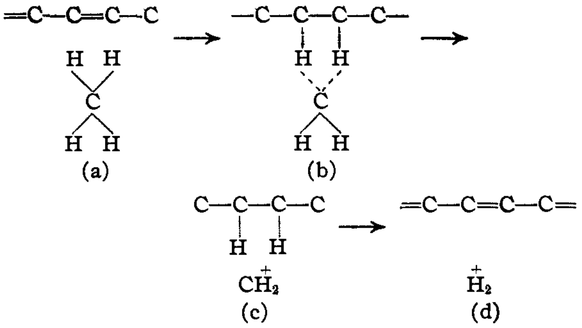
Discussion

The correspondence of the energy of activation for the decomposition of ethane with that of methane suggests that the same process is involved. One obvious possibility is that the reaction consists in the removal of both atoms of hydrogen as a molecule from the same carbon atom with the production in the case of ethane of an ethylidene radical, a process first proposed by Kassel.[11] If this be the mechanism the ethylidene radical must undergo tautomeric conversion to ethylene immediately after formation. It appears more likely that ethylene must be the primary product.

The energy of activation for the homogeneous decomposition of ethane to ethylene and hydrogen has been found by Marek and McCluer[12] to be 73,000 cal., in good agreement with the value obtained indirectly by Pease and Durgan[13] from the energy of activation and heat of reaction for the hydrogenation of ethylene. It is clear, therefore, that some process on the carbon surface, which is independent of any change occurring in the hydrocarbon molecule itself, must be determining the rate of reaction. This view finds confirmation from some results (to be published later) which we have obtained for propane and butane.

The course of the reaction may be represented diagrammatically as shown herewith.

It is as yet uncertain which step governs the velocity of the reaction and is responsible for the observed energy of activation.



In conclusion, we wish to thank Professor Bone very sincerely for his gift of pure methane. One of us (L. B.) is indebted to the University of South Africa and Emmanuel College, Cambridge, for scholarships.

Summary

1. Qualitative experiments are described showing that the primary decomposition of methane on carbon and platinum filaments takes place to methylene and hydrogen.

2. Methylene radicals when condensing on a cooled surface readily react with one another to form ethylene. Telluroformaldehyde is readily reduced to dimethyl telluride and dimethyl ditelluride.

3. The energy of activation for the decomposition of methane on carbon is 95 kcal./mole.

4. The energy of activation for the decomposition of ethane to ethylene on carbon is 94.6 kcal./mole.

5. No evidence for the formation of methyl or ethylidene radicals was obtained.

CAMBRIDGE, ENGLAND

RECEIVED MARCH 25, 1935

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[11] Kassel, *Chem. Rev.*, **10**, 11 (1932).

[12] Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931).

[13] Pease and Durgan, THIS JOURNAL, **50**, 2715 (1928).