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# The Study of Reaction Intermediates by Means of a Mass Spectrometer

#### Part I. Apparatus and Method

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A method for coupling a reaction chamber to a Dempster-type mass spectrometer in such a manner that short lived intermediates can reach the electron beam is described. The presence of radicals is denoted by an increase in the ion current of the corresponding mass. The sensitivity of the method depends on the difference between the appearance potential of the given ion produced by electron bombardment of either reactants or end products and the ionization potential of the free radical. It is shown experimentally that excited molecules are not present in sufficient quantity to invalidate the assumption that free radicals are responsible for the changes in ion current. The method has already extended more than tenfold the pressure range in which radicals are detectable, thus bridging the gap between mirror and spectroscopic methods so that low pressure combustion phenomena may be studied.

#### INTRODUCTION

THE investigation reported in this communication was undertaken before the war primarily to study the possibilities of a new approach to the experimental study of reaction kinetics.

The Paneth mirror method of detecting transient intermediates has yielded valuable data but is unfortunately restricted to low pressures and essentially oxygen-free reactions. Spectroscopic methods have been developed for such radicals as OH, CH, and SO, but they cannot be a complete solution so long as the spectral complexities of such simple radicals as  $CH_3$  remain unsolved. Moreover, because of the absorption by oxygen in the Schumann region, the application to combustion studies is again limited.

It was not anticipated that a mass spectrometric method would be free from difficulties of its own. Nevertheless, it was thought that the uniqueness with which, in some cases, a measure of mass is a guide to radical identity and adaptability to higher pressures and oxygen-containing atmospheres, warranted a careful survey. One additional advantage which might compensate for the complexity of the method lies in the fact that direct continuous measurements can be made of changing concentrations, thus avoiding the necessity and uncertainties of renewing mirrors or photographic plates for each parameter change. No attempt has been made in this investigation to study any one particular reaction exhaustively, since it was realized that the apparatus as originally constructed would serve to explore only semiquantitatively a limited range of applications, and that as a result of accumulating experience a more accurate and universal apparatus might be designed.

# PRINCIPLE OF THE METHOD

If a molecule, XY, is bombarded by electrons of energy, E, it will ionize and dissociate with a certain probability when  $E \ge A(X^+)$  where  $A(X^+)$ is the appearance potential for the ion  $X^+$  formed by electron bombardment of the parent molecule XY. If, however, atoms or radicals X are already present as a consequence of thermal or chemical dissociation of the parent molecule, then an energy  $E \ge I(X^+)$  will be effective in producing ions  $X^+$ , where  $I(X^+)$  is the ionization potential of the free radical or atom X. Since  $I(X^+) < A(X^+)$  by an amount which depends on the dissociation energy of the parent molecule and the kinetic energies of the separating fragments, it should be possible to select for each radical a value of the electron bombarding energy which is sufficient to ionize the radical but insufficient to ionize and dissociate the parent molecule. In this way a positive-ion current of a given mass in a mass spectrometer becomes a measure of the concentration of a given free radical.

In order to ensure that radicals produced by



FIG. 1. Low pressure quartz reactor R.1 attached to ionization chamber of mass spectrometer. Ground joint J, water-cooled jacket W, quartz double-walled tube Q, diaphragm D, ion-collimating slits  $S_1$  and  $S_2$ , pumping leads  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$ .

chemical reaction in a reactor adjacent to the ionization chamber shall reach the latter, it is necessary to provide a practically collision-free path. The ordinary means of sample extraction by capillary are clearly useless, and resort has to be made to thin diaphragms separating the reactor from the ionization chamber. With a pumping speed of about 7 l/sec. at the diaphragm, it has been found possible to maintain a pressure of ca. 100 mm in the reactor and a vacuum of ca. 10<sup>-3</sup> mm in the ionization chamber.

# APPARATUS

# **Mass Spectrometer**

In the exploratory work described here, a simple Dempster 180° type mass spectrometer was used. The radius of curvature of the ions was 3.5 cm, and the magnetic field was stabilized by batteries and ballast tubes. Entrance slits of 0.2 and 0.3 mm by 6 mm were used at various times, and these were mounted in soft iron eccentrics for vertical and lateral adjustment. The whole ionization chamber was enclosed in a

soft iron shield to minimize the effect of stray field on the low velocity electron beam. It is essential that the source of electrons be separated from the ionization chamber in order to avoid competition between radicals produced in the furnace and those produced at the hot emitter. A number of different types of electron gun were tried, but in spite of the apparent advantages of the acceleration-retardation type emploving two or more anodes, a simple platinum cone directed towards the emitter was found to be more satisfactory. For the lower paraffins an indirectly heated oxide emitter possesses the advantages of low temperature, low velocity spread, and high emission. However, such emitters rapidly become poisoned by organo-metallic compounds and higher hydrocarbons. In such cases it was necessary to use bare tungsten filaments coiled into a flat spiral and backed by a platinum cup attached to the negative end of the filament.

The ionization and collimating chambers were evacuated by two four-stage oil diffusion pumps of 25 l/sec. capacity, while the filament and analyzing chambers were evacuated by two single-stage air-cooled oil diffusion pumps (1.5 l/sec.) backed by a low vacuum diffusion pump of similar design. Octoil was used throughout, and a single Megavac exhausted the fore-vacuum manifold for all five diffusion pumps.

A Western Electric D-96475 tube in a stabilized DuBridge circuit with a Leeds and Northrup galvanometer of  $10^{-10}$  amp./mm sensitivity was used to record the ion currents. The galvanometer deflections were registered by a photo-pen recorder<sup>1</sup> to which were geared potentiometers for varying either the electron or ion accelerating potentials. These potentiometers were additional to the usual manual controls and were of value in checking sensitivity and resolving power automatically. When using the instrument for studying changes of radical concentration with temperature, all electrical parameters were maintained constant and the abscissa of the photo-pen recorder then represented a time base.

The over-all sensitivity was controlled from the main panel by solenoid switches inside an evacuated and shielded housing surrounding the

<sup>&</sup>lt;sup>1</sup> D. J. Pompeo and C. J. Penther, Rev. Sci. Inst. 13, 218 (1942).

D-96475 tube. These solenoid switches were designed with two positions of mechanical stability so that only a momentary application of current in one direction or the other was required in order to cut in or out a range of grid leak resistors from  $10^8$  to  $10^{12}$  ohms.

One of the main experimental difficulties encountered throughout was occasioned by changes in sensitivity resulting from polarizing layers in the ionization chamber. Since the all-metal construction did not lend itself to thermal outgassing, an additional filament was used in the earlier stages as a source of intense electron bombardment. It was later found that coating the inside of the ionization chamber with Aquadag gave greater reproducibility and higher sensitivity.

# The Reactor

Three main types of reactor have been used. Fow low reaction pressures (up to ca. 4 mm) it is not essential, although quite desirable, that the temperature at the place of exit of the gas sample be the same as that of the furnace. At higher pressures this condition must be met in order to approximate to the ideal of infinitely rapid expansion and freezing of the sample between the place of origin (reactor) and the place of analysis (ionization chamber).

The low pressure reactor, R.1, attached to the mass spectrometer at a ground joint, J, is illustrated in Fig. 1. The reactor consists of a water-cooled jacket, W, the inner wall of which is a stainless steel tube threaded at the lower end to receive the diaphragm holder.

The furnace consists of a double-walled quartz tube, Q, down the center of which the reactants enter. A platinum heating spiral with quartz dust insulation and a thermocouple (not shown) occupy the space between the quartz walls at the lower end. The main bulk of the reactants and products, after passing through the hot zone, are deflected upwards along the inner walls of the cooler to the exit where they are pumped away by mercury diffusion and Megavac pumps. Flow speed, pressure, and residence time are controlled by suitable valves and measuring devices. The size of the diaphragm, D, is selected so that a pressure of ca. 0.001 mm can be maintained in the ionization chamber for the required reactor pressure.

In certain investigations the quartz-tube furnace was replaced by a grid of five carbon filaments (Fig. 2) which could be lowered into a position just above the diaphragm. This type of reactor will be referred to as R.2. Temperatures were estimated by means of an optical pyrometer focused on the grid through a plane window situated on top of the reactor.

At higher pressures, such as are required for the study of unstable or reactive intermediates formed during combustion, neither R.1 nor R.2are suitable. With an effective pumping speed of ca. 7 l/sec. at the diaphragm, it has been possible to work at reaction pressures up to 140 mm using the reactor, R.3, illustrated in Fig. 3. As before, this reactor is attached to the mass spectrometer at a joint, J, and consists of a water cooler, W, which is essentially a thick copper cylinder with vertical interconnecting channels milled in the outer surface, over which a tightly fitting thin brass sleeve is fitted. The water thus follows a number of up and down

FIG. 2. Carbon filament reactor R.2. This replaces the quartz tube Q of Fig. 1. The short carbon filaments then lie immediately above the diaphragm D.



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zig-zags around the copper surface, and provides efficient cooling for the waste gas as well as for the vacuum joints. In order to minimize pumping resistance and to leave reasonable space inside the reactor for the development of chains, the reactor is itself the heating element H. The furnace was made from a solid bar of 18:8 stainless steel, accurately bored internally to  $\frac{5}{8}''$ diameter. The outer surface, except at the two ends, was then turned on a lathe until the wall thickness was approximately 20 mil and, after shaping the lower end to preserve a uniform mass of metal over any annular section of constant radial width, the furnace was heated by passing a heavy current through it. The temperature profile along the length was measured with a



FIG. 3. High pressure reactor R.3. Stainless steel furnace H, water-cooled jacket W, joints for attachment to mass spectrometer J, and to exhaust M, copper conductor C, expansion joint S, diaphragm recess D. Enlarged view of furnace bottom in insert on right.

thermocouple, and metal was removed from those parts which were at a low temperature. With this design and method of manufacture a furnace was obtained which not only preserved a uniform temperature distribution over a considerable distance up from the bottom in which the thin diaphragm was fitted, but also exposed a minimum of heated surface to the ionization chamber. At high reaction pressures the diaphragm hole is of necessity small (<1 mil), and the danger of leaks between the reactor and the ionization chamber correspondingly great. The lower end of the reactor was screwed into the water cooler and sealed with a lead wire gasket under high mechanical compression. The diaphragm, usually an 0.8-mil gold disk, was compressed between gold washers against a recessed shoulder in the bottom of the furnace. By using Bethlon A (Bethlehem Steel) for the threaded compression plug retaining the diaphragm, the tendency of the metals to seize at high temperatures (up to 1000°C) was minimized, and little trouble was encountered in changing diaphragms. The upper end of the furnace was screwed into a thick copper tube, C, which served as one lead for the transformer current, the other lead being the water cooler. Waste gas passed through eight tubular ports in the cylinderical walls near the flat bottom and passed to exhaust via the spherical ground joint and sylphon M. In order to avoid distortion of the thin-walled reactor, the upper end of the copper tube, C, was brought out through the sylphon, S, which was held in neutral equilibrium by spiral springs which counteracted the differential pressures between the outside and inside of the reactor. The furnace was therefore free to expand, and the relative motion between the ends of the sylphon, S, amplified by a dial gauge, was in fact a convenient indicator of the wall temperature.

One of the chief difficulties with the steel furnace was the tendency of the diaphragm to become plugged. This was especially the case during a study of carbon monoxide combustion, and some evidence was obtained that this was caused by carbonyl formation and subsequent decomposition on the gold diaphragm. This difficulty was overcome by fabricating an exact thin gold replica of the inside surface of the reactor. The replica was obtained as a 0.7-mil electro-



FIG. 4. Temperature profiles of quartz reactor R.1 and steel reactor R.3 in the vicinity of the diaphragm.

deposit on a polished copper form. After burnishing the gold, the copper was dissolved in acid and the thin shell inserted, with clearances of <1 mil, into the steel furnace. Gold was chosen for its low catalytic activity in hydrocarbon decompositions.

# PERFORMANCE AND OPERATION

By means of a movable Chromel-Alumel thermocouple, the temperature gradient in the vicinity of the diaphragm was taken under operating conditions. Typical curves for R.1 and R.3 are shown in Fig. 4, with the distance in inches above the diaphragm plotted as abscissa. It is clear that the particular design of R.3 has provided a sensibly zero gradient in the immediate vicinity of the point of extraction, and equilibrium will therefore be maintained. In some models of the furnace, R.3, an additional heater was placed between the upper surface of the cone and the lower surface of the bottom. In this case either negative or positive temperature gradients could be maintained, but in general this refinement was considered unnecessary.

The procedure adopted in detecting reaction products was briefly the following. After suitable outgassing, the flow of reactants was adjusted until the pressure below the diaphragm remained constant at some pressure between  $10^{-3}$  and  $10^{-4}$  mm. Input and output flow values were adjusted to give a residence time in the hot zone of  $10^{-1}$  to  $10^{-3}$  sec. If the particular required product was also a product of the electron bombardment of one of the reactants, the electron voltage was increased until the ion appeared in sufficient strength to be focused on the final slit by adjustment of the ion accelerating field. The ion peak was then extinguished by lowering the electron voltage to the appearance potential, and the current through the furnace was increased slowly by means of a Variac in series with a low voltage transformer. The temperature was followed on a potentiometer and marked off along the time base of the photo-pen recorder. The photo-pen recorded any increase in the ion current occasioned by the formation in the reactor of the radical under investigation.

Rigid tests of the effect on the electrons and ions of the alternating magnetic field accompanying the heavy heating currents (up to 500 amp. in the case of R.3) failed to reveal any measurable influence. The complete axial symmetry of the furnace unit is instrumental in achieving this result.



FIG. 5. Ionization functions of  $CH_3^+$  with R.1 hot and cold, showing that in an ethane stream containing 0.6 percent Pb(CH<sub>3</sub>)<sub>4</sub> sufficient radicals are produced to lower the normal appearance potential approximately 3 volts. Reaction pressure *ca*. 0.2 mm.

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FIG. 6. Tracing taken from a photo-pen recording of the change of methyl radical concentration with time as the temperature of the furnace was increased. Markings along the abscissa indicate positions when the thermocouple registered integral values on a potentiometer. Time of complete record, approximately 10 min. Mixture,  $C_2H_6$  +0.6 percent Pb(CH<sub>8</sub>)<sub>4</sub> at 0.15 mm pressure.

# THE VALIDITY OF UNDERLYING ASSUMPTIONS

In Fig. 5 the low potential ionization functions corresponding to the two processes

 $C_2H_6 + \vec{e} \rightarrow CH_3^+ + CH_3 + 2e$ 

and

$$CH_3 + \vec{e} \rightarrow CH_3^+ + 2e$$
 (2)

are reproduced. These were obtained in a mixture  $C_2H_6+0.006$  Pb(CH<sub>8</sub>)<sub>4</sub> in reactor *R.1* at a reaction pressure of *ca.* 0.2 mm. With the furnace at room temperature, process (1) is the only source of CH<sub>3</sub><sup>+</sup> ions, but at 685°C, the temperature at which curve (2) was taken, there is clearly a source of CH<sub>3</sub><sup>+</sup> ions requiring a lower energy for ionization. It is reasonable to assume that this new source is the CH<sub>3</sub> radical produced by thermal dissociation of the lead tetramethyl. At still higher temperatures (*ca.* 800°C) it is unnecessary to add the lead alkyl, and a curve similar to (2) is obtained by thermal dissociation of the pure ethane.

The curves of Fig. 5 were taken considerably prior to the publication by J. A. Hipple and D. P. Stevenson<sup>2</sup> of a paper in which a study was made of the ionization potential of CH<sub>3</sub> radicals produced by thermal dissociation of lead tetramethyl at low pressure  $(10^{-5} \text{ mm})$  in the ionization chamber of a mass spectrometer. Our value of 11.3 volts for the ionization potential of CH<sub>3</sub> taken from curve (2) agrees with that found by R. G. T. Fraser and T. N. Jewitt<sup>3</sup> but is about one volt higher than that found by Hipple and Stevenson. Since we were primarily interested in the maximum electron potential which could be applied without dissociating the parent molecule electronically, the causes for the discrepancy have not been sought. The low concentration of radicals compared with the carrier gas is undoubtedly a factor in our experiments which would decrease the apparent difference between  $A(CH_3^+)$  and  $I(CH_3^+)$ .

Figure 6 is a photo-reproduction of an actual record taken of the thermal decomposition of the same mixture as used for Fig. 5, but with the electron acceleration, E, held constant just below the appearance potential, and the temperature increased manually. The temperatures marked off along the horizontal time base are those of the uncorrected furnace thermocouple. The details of this and similar curves obtained with different carrier gases will be discussed in Part II. Here it is sufficient to note that the concentration of CH<sub>3</sub> radicals apparently passes through a maximum and a minimum. The steep rise (when replotted on a linear temperature scale) after the minimum corresponds to a similar increase obtained in the absence of lead tetramethyl and is, therefore, attributable to a chemical change occurring in ethane.

The question arises as to whether the second increase in  $CH_{3}^{+}$  ions can be unequivocally attributed to an increasing concentration of methyl radicals or to some other mechanism. There are three other alternatives. Some secondary decomposition product of ethane might have a lower  $A(CH_{3}^{+})$ . One of the products, e.g.,  $C_{2}H_{4}$ , might dissociate under electron impact to give the methylene ion in sufficient abundance so that the  $C^{18}H_{2}$  isotope would account for the increase

<sup>3</sup> R. G. T. Fraser and T. N. Jewitt, Phys. Rev. **50**, 1091 (1936); Proc. Roy. Soc. **A160**, 563 (1937).

(1)

<sup>&</sup>lt;sup>2</sup> J. A. Hipple and D. P. Stevenson, Phys. Rev. 63, 121 (1943).

in mass 15. And finally there might be a sufficient concentration of vibrationally excited ethane molecules entering the ionization chamber so that the appearance potential of  $CH_{3}^{+}$  is shifted below the fixed value of E chosen for the experiment.

The first possibility can be ruled out on the grounds that the value of  $A(CH_3^+)$  is lower for ethane than for any  $C_nH_m$  hydrocarbon. The published values for methane, ethane, propane, *n*- and *i*-butane are 14.4, 14.2, 17.0, 22.5, and 20.7 volts, respectively. Actually the values for hydrocarbons higher than ethane mean very little since the "tail" of the ionization curve extends a considerable distance towards lower voltages. Nevertheless, the absolute intensity at voltages below 14.2 is quite negligible as was confirmed repeatedly in the present work.

The electronic production of  $CH_2^+$  ions from ethylene can also be ruled out at 14.2 volts, since at least 19 volts would be required and the intensity of the isotope would be only 1.1 percent even at this high potential. No  $CH_2^+$  ions were detectable in our apparatus, even at potentials where  $CH_3^+$  was giving off-scale deflections.

The third possibility, namely, that the appearance of  $CH_{3}^{+}$  ions on heating the gas is attributable to excited molecules rather than free radicals, is more difficult to disprove. From energy considerations it is natural to suppose that the rate of production of excited molecules will be greater than that of free radicals. However, it is probable that this increased rate will not be wholly represented in an increased equilibrium concentration because of the greater ease with which the vibrational energy can be dissipated. In the case of the decomposition of methane, it was possible to show that at high temperatures  $CH_3^+$  ions could be detected at electron energies below the ionization potential of methane itself. To explain such a result on the basis of vibrational energy would require the hypothesis that excited molecules when struck by a low voltage electron can only dissociate to give a  $CH_3^+$  ion. Yet any reasonable assignment of Morse curves coupled with the requirements of the Frank-Condon principle would lead one to expect that vibrational energy would lower both the ionization potential of the parent molecules (in this case methane), and the appearance potential of the  $CH_{3}^{+}$  ion. We should, therefore, expect that since under normal conditions  $CH_{4}^{+}>CH_{3}^{+}$ , no such violent change in this ratio as was actually found could take place on increasing the temperature, unless new particles such as free radicals are being formed thermally.

In the case of ethane it is not so easy to obtain such unequivocal experimental proof on account of the lower ionization potential of ethane and the large difference in mass. Nevertheless, other contributory evidence points to the same conclusion and is briefly reviewed below.

In one series of experiments, in order to study the effect of surface on radical concentration, a small, flat, movable spiral of tungsten was mounted inside the quartz tube of R.1. Keeping a constant temperature in the furnace windings, the spiral was gradually lowered towards the diaphragm. This resulted in a decrease in CH<sub>3</sub><sup>+</sup> concentration as indicated by the galvanometer deflection. With the spiral in its lowest position it was then heated by an electric current, whereupon the residual deflection disappeared almost completely. Thus the addition of energy had decreased the concentration of excited molecules or free radicals between the furnace and the diaphragm. Such a result is much more plausible on the hypothesis of a recombination of methyl radicals requiring an energy of activation than on the supposition of deactivation of excited molecules. With the spiral heated to still higher temperatures, the galvanometer deflection began to increase, indicating that the spiral was itself becoming a source of free radicals. This behavior parallels very closely the phenomena of recombination of atoms on heated surfaces studied by Roginsky and Schechter.<sup>4</sup>

Other evidence tending to confirm the radical rather than the molecular origin of the increase of  $CH_{3}^{+}$  with temperature was obtained when the temperature coefficient was found to be independent of the electron accelerating potential. If excited molecules were responsible, we might anticipate that as the electron energy was increased the thermal activation energy would decrease as lower vibrational levels became effective. This was not the case. Such a result,

<sup>&</sup>lt;sup>4</sup>S. Roginsky and A. B. Schechter, Acta Phys. Chim. U.S.S.R. 6, 401 (1937).

however, is quite consistent with the requirement that a free radical is involved in the change of methyl ion concentration with temperature.

Finally it was found that the ratio of the height of the minimum to that of the maximum, in curves similar to that depicted in Fig. 6, was independent of the electron potential (provided of course the latter did not exceed  $A(CH_3^+)$  from unexcited ethane). This result also is consistent with the view that the same species of particle is responsible for both the low and high temperature increase of  $CH_3^+$ , and since there can be little doubt as to the radical origin of the decomposition product of lead tetramethyl, it follows with considerable certainty that the high temperature decomposition of ethane into free radicals can be studied by following the low voltage production of  $CH_3^+$  ions.

There remains one other feature which might invalidate results obtained at higher pressures using R.3. As the reaction pressure is increased, it is necessary to reduce the size of the aperture in the diaphragm separating the reactor from the ionization chamber. The diaphragm, however, is at the same temperature as the reactor, and its underside is exposed to the gas in the ionization chamber. Since all investigators are apparently agreed that the detection of free radicals by the mirror method becomes increasingly difficult as the reaction pressure rises above a few mm Hg, it might at first sight seem surprising that the mass-spectrometric method has already extended the pressure range tenfold without approaching any insuperable difficulties. Using reactor R.1, in which the diaphragm is essentially at room temperature, the upper useful limit of pressure was ca. 15 mm, whereas with reactor R.3 radicals have been detected at 120 mm.

In order to examine the implication of this result more closely, let us take the two primary reaction mechanisms which have been proposed for the formation of methyl radicals from ethane:

$$2C_2H_6 = 2CH_3 + C_2H_6 \tag{3}$$

and

$$C_2H_6 = 2CH_3.$$
 (4)

The main mechanism for the removal of methyl radicals will be

$$CH_3 + C_2H_6 \rightarrow C_2H_5 + CH_4, \tag{5}$$

so that the equilibrium concentration of methyl radicals in the reactor will be,

$$[CH_3]_1 = k_1/k_3 \cdot C_2H_6$$

in the first case and

$$[CH_3]_2 = k_2/k_3$$
 in the second,

where  $k_1$ ,  $k_2$ , and  $k_3$  are the rate constants for reactions (3), (4), and (5), respectively. If now we have a series of diaphragms,  $d_1, d_2, \dots d_n$ , such that reaction pressures  $p_1, p_2, \dots p_n$  above the diaphragm will give a constant pressure p' (ca.  $10^{-3}$  mm) in the ionization chamber below, and if the primary production of methyl radicals proceeds according to a bimolecular mechanism, the partial pressure of the radicals in the ionization chamber will be

$$p_R = \frac{k_1}{k_3} \cdot \left[ C_2 H_6 \right] \cdot \frac{p'}{p_n} = \frac{k_1}{k_3} \cdot p'$$

i.e., independent of the reaction pressure. If, however, the primary production is unimolecular the partial pressure of the radicals will be

$$p_R = \frac{k_2}{k_3} \cdot \frac{p'}{p_n}$$

and will decrease as the reaction pressure is increased to accommodate smaller diaphragms.

Hence it only will be possible to detect free radicals over a wide range of pressures if the order of the producing mechanism is the same as or greater than that of the radical removing mechanism.

Since, however, the radical partial pressure in the ionization chamber depends on the ratio  $k_1/k_3$ , which in turn depends exponentially on the difference between the activation energies  $E_1$ and  $E_3$  of the two reactions (where  $E_1 \gg E_3$ ), it is clear that the radical concentration will decrease rapidly with increasing pressure if the radicals have to pass through a long length of cooler gas as in the mirror technique.

Thus our finding that methyl radicals could be readily detected at high pressures would indicate a bimolecular mechanism for their production and an absence of an appreciable cool zone in reactor R.3, provided we eliminate any possible additional source of radicals such as the hot

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surface of the diaphragm exposed to the ionization chamber.

This source of uncertainty in the interpretation was removed by comparing the concentration of methyl ions under identical conditions, except that in the one case a pressure of  $10^{-3}$  mm was maintained in the usual way by ethane at a high pressure effusing into the ionization chamber through the reactor diaphragm, whereas in the second case a pressure of 10<sup>-3</sup> mm was maintained in both the reactor and the ionization chamber by means of an auxiliary leak to the latter. Even when the pressure was increased to 3.10<sup>-3</sup> mm there was no deflection attributable to CH<sub>3</sub> radicals in the second case. Thus there can be no doubt that the radicals observed in the first case were actually coming from inside of the furnace and not from the heated underside of the diaphragm.

# LIMITATIONS OF THE METHOD

As a result of the control experiments summarized above, the validity and usefulness of the method were considered well established. Before proceeding to a more detailed discussion of the application of the method to specific examples, certain limitations will be briefly discussed.

#### Sensitivity

It is not possible to give any one figure which will represent the lower limit of concentration which can be detected. Apart from the usual reciprocal relationship between resolving power and slit-width, there is the important factor that the upper limit of allowable electron energy is the appearance potential of the particular radical ion formed by electron bombardment of either the parent molecule or one of the reaction products—whichever is the lower. For example, a study of Table I, in which data have been collected on the products of electron dissociation of ethane, ethylene, and methane from the measurements of Hipple,<sup>5</sup> Kusch, Hustrulid, Tate,6 L. G. Smith,7 and others, reveals considerable differences between the probable de-

tectability of different products. Of the end products of the thermal decomposition of ethane, both hydrogen and methane are detectable in quantities far smaller than ordinarily required in chemical analysis. Ethylene, because of its great abundance in the electron spectrum of ethane, and the relatively small difference (1.3  $\pm 0.6$  volts) between the appearance and ionization potentials, is less detectable-though relatively easily detectable compared with the low concentration radicals. Preliminary calculations indicated that methyl and methylene radicals with potential differences of  $4.2 \pm 0.3$ and  $4.3 \pm 1.0$  volts, respectively, should be detectable in concentrations down to ca. 0.001 percent or even lower with an improved design of mass spectrometer.

The ethyl radical deserves mention on account of its predicted abundance in the decomposition of ethane and because it serves to illustrate the caution required in this type of analysis. The difference between the appearance and ionization potentials being  $4.2 \pm 0.2$  volts, its detectability might be expected to be moderately high. However, much larger amounts of ethylene will accompany the formation of ethyl at moderate pressures and contact times, so that we have to reckon with the ethylene isotope of mass 29 which will also be present to the extent of 2.2 percent of the ethylene formed. Since the ionization potential of ethylene is  $10.8 \pm 0.5$ , this potential, and not the appearance potential  $12.9\pm0.2$ , must be used when searching for the ethyl radical. This naturally decreases very materially the sensitivity in this particular case.

TABLE I.

Ionization potential	Appearance potential from C2H6	Appearance potential from C <sub>2</sub> H <sub>4</sub>
11.6±0.1	11.6±0.1	
$8.7 \pm 0.2$	$12.9 \pm 0.2$	
$10.8 \pm 0.5$	$12.1 \pm 0.1$	$10.8 \pm 0.5$
9.9	$15.2 \pm 0.3$	$14.1 \pm 0.1$
$11.2 \pm 0.1$	$15.0 \pm 0.3$	$13.4 \pm 0.2$
11.3	$27.0 \pm 1.0$	$19.2 \pm 1.0$
	$31.5 \pm 1.0$	$26.4 \pm 1.0$
$13.1 \pm 0.4$		_
10.0	$14.2 \pm 0.3$	
11.9	$16.2 \pm 1.0$	$19.2 \pm 0.3$
11.1	$24.5 \pm 1.0$	$22.9 \pm 0.5$
(11.3)	$30.4 \pm 1.5$	$24.6 \pm 0.5$
15.4	$28.0 \pm 1.5$	$22.4 \pm 1.5$
13.5	$20.8 \pm 1.0$	$26.2 \pm 1.5$
	Ionization potential $11.6 \pm 0.1$ $8.7 \pm 0.2$ $10.8 \pm 0.5$ $9.9$ $11.2 \pm 0.1$ $11.3$ $13.1 \pm 0.4$ $10.0$ $11.9$ $11.1$ $(11.3)$ $15.4$ $13.5$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

<sup>&</sup>lt;sup>6</sup> J. A. Hipple, Jr., Phys. Rev. **53**, 530 (1938); J. A. Hipple, Jr. and D. P. Stevenson, Phys. Rev. **63**, 121 (1943); D. P. Stevenson, J. Am. Chem. Soc. **65**, 209 (1943). <sup>6</sup> P. Kusch, A. Hustrulid, and J. T. Tate, Phys. Rev. **52**, 843 (1027).

<sup>843 (1937)</sup> 

<sup>&</sup>lt;sup>7</sup> L. G. Smith, Phys. Rev. 51, 263 (1937).

# Calibration

Theoretically, if we know the potential at which the measurements are made and the probability of ionization, it would be possible to estimate the absolute concentration of the radicals. Ionization probabilities at low potentials are mostly unknown, however, and are naturally sensitive to such factors as electron energy spread and space charge in the ionization chamber. Calibration for the permanent end products of a reaction is carried out in the conventional manner by comparing ion deflections of a given product, when the latter is produced thermally, and by addition of a known amount to the gas stream.

In order to calibrate for a transient radical there is no such golden rule, in fact no rule at all in most cases. In the case of methyl radicals, by working at low pressures and with neutral carrier gases containing small known amounts of lead tetramethyl, curves similar to Fig. 5 (except that the deflection reaches a plateau instead of passing through a maximum and minimum) may be used to indicate the maximum deflection corresponding to total decomposition of the lead tetramethyl. Similar techniques, in which are used diazomethane for CH<sub>2</sub>, lead tetraethyl for C<sub>2</sub>H<sub>5</sub>, and Bonhoeffer and Reichardt's<sup>8</sup> steam equilibria data for OH, might be applicable but have not been tried in the present work. For the allyl and vinyl radicals there is at present no such known approach.

#### DISCUSSION

During the course of the experiments reported above and in the two communications which follow, it became increasingly clear that considerable improvements in performance could be expected by making use of the Nier-type mass spectrometer employing a 90° magnetic path. In this way the ion source is sufficiently far from the pole pieces to allow a more effective location of the pump with respect to the diaphragm through which the radicals are issuing.

This feature, which is of relatively little importance at low reaction pressures where the aperture in the diaphragm is comparatively large, may be decisive in the detection of certain radicals at higher pressures.

For a pumping speed of S liters per sec. in the ionization chamber, the diameter of the aperture, D, required to maintain a differential pressure ratio  $p:10^{-3}$  mm, where p is the reaction and  $10^{-3}$  the ionization pressure, will be given approximately by

$$D = \left(\frac{4S}{\pi} \cdot \frac{10^{-3}}{12p}\right)^{\frac{1}{2}} \text{ cm.}$$
 (6)

Substituting S = 7 l/sec. and p = 100 mm, we get  $D = 2.7 \cdot 10^{-3}$  cm or  $27\mu$ .

Now the average number of collisions (n) made by each molecule on the walls of a short channel of length L and diameter D can be shown to be approximately 4L/D during the time of transfusion. Hence radicals or atoms which are sensitive to a single wall collision at high temperature will be removed almost completely from the sample when 4L/D > 1.

If we adopt as a criterion of "free" passage through the aperture the condition that

# $n \ge 0.8$ ,

which will allow at least 20 percent of the radicals to transpire without suffering a wall collision, then with  $L=10\mu$ , which probably represents a practicable lower limit of diaphragm thickness, the diameter, D, must be at least  $50\mu$ , and the pumping speed (from Eq. 4) must be approximately 25 l/sec. for a reaction pressure of 100 mm.

This seeming diversion into the realm of future development of the method was deemed necessary to illustrate the care with which a negative result must be treated. There is evidence that the lower hydrocarbon radicals are fairly stable towards surface collision at moderate temperatures. Atoms such as H, O, and the radical OH are probably less stable (W. V. Smith<sup>9</sup>), and although theoretically it might be possible to select specific materials such as Ta for H atoms or W for O atoms to minimize recombination, the more general approach of high pumping speed would appear preferable.

In concluding this section it is a privilege to record my deep appreciation of those who at

<sup>9</sup>W. V. Smith, J. Chem. Phys. 11, 110 (1943).

<sup>&</sup>lt;sup>8</sup> K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie A139, 75 (1928).

various times have contributed to the development of the method—Professors N. N. Semenov and V. N. Kondratjew in whose laboratories the groundwork was laid, E. Luttrop, N. S. Heikes, and the Fanger Research Laboratories for constructional ideas and skill, and Dr. O. Beeck for his steady interest during all phases of the work.

# Part II. The Thermal Decomposition of Some Lower Hydrocarbons

The method described in Part I has been applied in a preliminary survey of certain intermediates occurring during the decomposition of methane, ethane, propane, propylene, butanes, butylenes, oxygen, and nitric oxide with and without admixtures of lead tetramethyl, and in dimethyl ether and diazomethane. Methylene appeared in the last named case but not in the low pressure decomposition of methane. Methyl radicals both at high and low pressures were detectable and reasons are given for the belief that the primary decomposition of ethane is bimolecular. The interaction of methyl with ethane and propylene has been followed up to 1000°C, and, in the case

The results which form the subject of this communication were obtained during an investigation of the range of application of the method described in Part I. The original objective had been to extend if possible the range of pressures at which radicals can be detected so that combustion phenomena could be studied more directly. The choice of hydrocarbon decompositions was dictated by their comparative simplicity and the desirability of having a basis of comparison between the mirror and mass spectrometric methods. Although results obtained with several hydrocarbons are reported, this should not be taken as meaning that such hydrocarbons have as yet been studied exhaustively by the new method. It was considered expedient at this stage of development to survey a broad field semiquantitatively.

The following abbreviations will be used:

R.1-quartz furnace with cool diaphragm,

R.2-carbon filaments above the cool diaphragm,

- *R.3*—steel furnace with uniform temperature distribution in the neighborhood of the diaphragm,
  - *E*—electron accelerating potential.

#### METHANE

Using a freshly blown and outgassed quartz furnace no CH<sub>3</sub> radicals could be detected in pure methane in the pressure range 0.01 to 0.3 mm, up to temperatures of 1100°C. After heating the tube to *ca.* 950°C in a stream of of propylene, the allyl radical was detectable but not vinyl. The interaction between methyl and various carrier gases falls qualitatively in the following series of descending order,  $C_8H_8$ , NO,  $C_2H_8$ ,  $C_2H_4$ ,  $H_2$ ,  $O_2$ , and He. CH<sub>3</sub>O from methyl ether is apparently more reactive or unstable than methyl. The rate constant of decomposing Pb(CH<sub>3</sub>)<sub>4</sub> is found to be  $k = 1.5 \cdot 10^{10} \exp(-28,000/RT)$ . Hydrogen atoms and ethyl radicals have been found in certain instances, but further refinements in technique will be required before these and heavier radicals can be studied systematically.

ethane or natural gas at *ca*. 1-mm pressure for one hour, it was found that methyl radicals could readily be detected in pure methane and that the surface activity then persisted even after such treatments as outgassing, heating in air, or washing in nitric acid.

The growth of  $CH_{3}^{+}$  with temperature at a reaction pressure of 0.014 mm is illustrated in Fig. 1. In spite of the non-uniform temperature profile of R.1 (see Part I, Fig. 4) a reasonable estimate of the temperature coefficient at this pressure can be made from the  $\log CH_{3} \sim 1/T$  replot given in Fig. 2. From the slope of the line



FIG. 1. Growth of  $CH_3^+$  with temperature in methane. Reaction pressure, 0.014 mm. Concentration of  $CH_3$  in arbitrary units.



FIG. 2. Temperature coefficient of methyl concentration in methane. Reaction pressure, 0.014 mm.

we get a value of ca. 46 kcal. for the activation energy. At 0.014-mm pressure, the mean free path is of the same order as the diameter of the reactor (3 mm) and very much greater than the diameter of the pores of the surface structure, created presumably during activation. In such cases, as Zeldowich<sup>1</sup> has shown, a lowering of the activation energy by a factor of two may be expected at high temperatures.

Repeated efforts to detect  $CH_2$  radicals and H atoms with the quartz reactor failed. In both cases the mass-spectrometric conditions are quite favorable. Thus Smith<sup>2</sup> gives for the appearance and ionization potentials of  $CH_2$ ,  $15.7\pm0.5$  and  $\leq 12.0$  volts, respectively, and in the case of hydrogen atoms we have the corresponding values of 18.0 and 13.5 volts. In the latter case the value of the appearance potential in hydrogen is taken rather than the value in methane (22.7  $\pm 0.5$  volts), since molecular hydrogen was detectable in the decomposition products.

In practice, the sensitivity for methylene detection is even greater than for methyl radicals on account of the much lower yield of  $CH_2^+$  from electron bombardment of methane. In order to check the possibility of detecting free methylene, experiments were conducted in which helium, purified by passage over active charcoal in liquid nitrogen, was passed over a 3 percent solution of diazomethane in diethyl ether contained in a low temperature trap. The helium pressure in R.1 was varied from 0.1 to 0.01 mm. With the trap at  $-110^{\circ}$ C there was no evidence of CH<sub>2</sub>, but on increasing the temperature to  $-90^{\circ}$ C, deflections as high as 50 cm could be obtained at *ca*. 500°C. The deflection was still increasing at 900°C, indicating that at these low pressures, and residence times of the order  $10^{-3}$  second, decomposition was not complete. On decreasing the pumping speed the deflections increased rapidly, indicating that reaction products were not appreciably diminishing the methylene concentration.

These qualitative results proved conclusively that the absence of methylene radicals in the low pressure decomposition of methane could not be attributed to a failure of the method of detection.

Belchetz and Rideal<sup>3</sup> have published evidence that the methylene radical can be detected in methane by interaction with a cooled iodine mirror, provided the place of origin of the radicals is within the mean free path of the detecting surface. The yields were very small and only after some four hours had sufficient methylene iodide accumulated for analysis. Methyl radicals made their appearance when the distance between the hot carbon filament and the iodine was increased from 3 mm to 1 cm, which at 0.1-mm pressure is greater than the mean free path. F. O. Rice<sup>4</sup> has repeated part of this work using tellurium mirrors and found no evidence of  $CH_2$ . Methyl radicals were detectable at separations greater than the mean free path as in Belchetz and Rideal's experiments. Pearson, Purcell, and Saigh<sup>5</sup> conclude from the behavior of CH<sub>2</sub>, produced thermally from diazomethane and photo-chemically from ketene in various carrier gases, that the results of Belchetz and Rideal are more plausible.

Since the only direct evidence of  $CH_2$  radicals from methane has been obtained when using platinum or carbon filaments as the source of heat, a similar source was constructed using

<sup>&</sup>lt;sup>1</sup> Ya. B. Zeldowich, J. Phys. Chem. U.S.S.R. **13**, 163 (1939). <sup>2</sup> L. G. Smith, Phys. Rev. **51**, 263 (1937).

<sup>&</sup>lt;sup>3</sup> L. Belchetz and E. K. Rideal, J. Am. Chem. Soc. 57, 1168 (1935).

<sup>&</sup>lt;sup>4</sup> F. O. Rice, J. Am. Chem. Soc. 61, 213 (1939).

<sup>&</sup>lt;sup>8</sup> T. G. Pearson, R. H. Purcell, and G. S. Saigh, J. Chem. Soc. 409 (1938).

several short parallel carbon filaments embedded in Aquadag between nickel foil, and this gridlike heater was placed at a distance of 3 mm above the diaphragm of the water cooler. The aperture in the diaphragm was 1.5 mm so as to give ample opportunity for any CH2 radicals to escape unhindered into the ionization chamber below. With temperatures up to 1200°C and pressures down to 10-3 mm no CH2 radicals could be detected although CH<sub>3</sub> radicals were abundant. At these low pressures it would appear probable that the methyl radicals are primary and not caused by reaction of methylene and methane. It is difficult to reconcile our results with those of Belchetz and Rideal unless different surface conditions prevailed on the carbon filaments. The fact that Belchetz and Rideal had to renew the iodine surface at frequent intervals in order to obtain measurable quantities of product is possibly of significance since in our experiments, especially with metal filaments, transient phenomena on reheating the filaments were a common feature. Thus, allowing the cool filament to rest for a few minutes in the stream of gas always produced an anomalous distribution of products when the filament was reheated. No attempt was made in this preliminary survey to study these changes systematically, but enough evidence was accumulated to indicate that, with suitable modifications, the mass spectrometric method might be adapted to provide a sensitive means of investigating certain phases of surface reactions, in particular those occurring on single crystals of preferred orientation where the amount of material is usually too small for chemical methods.

At high pressures, up to 100 mm, methyl radicals were readily detectable in methane using R.3, but for reasons given later the yield was not studied quantitatively.

# ETHANE AND PROPYLENE

In an attempt to obtain a more quantitative estimate of the number of methyl radicals entering the ionization chamber, small concentrations of tetramethyl lead (TML) were carried in a stream of pure helium into R.1. A typical decomposition curve showing the growth of CH<sub>3</sub> radicals as a function of temperature is shown in Fig. 3. Provided the reactor was clean, the helium pure, and the pressure low, the curve flattened off at a temperature of ca. 700°C depending on the contact time. The general rule in carrying out these calibrations was to keep the TML concentration below 1 percent of the carrier gas so that other decomposition products  $(CH_4, C_2H_4, and C_2H_6 were identified)$  would not interfere appreciably with the transport of the methyl radicals to the ionization chamber. In practice it was found convenient to saturate the carrier gas at low pressures and temperatures  $(ca. -70^{\circ}C)$  so that the gas line could be rapidly pumped out without evaporating large quantities of TML. Since the vapor pressure of TML at  $-70^{\circ}$ C was not accurately known, a master calibration with a saturator at 0°C and helium at atmospheric pressure was also made. Since a number of approximations have to be made in applying the results of such calibrations in the present apparatus, we can rely only on obtaining the right order of concentration, and in the following it will be assumed that where a concentration x of TML has been totally decomposed, the galvanometer deflection is that produced by a corresponding concentration of methyl radicals.

From curves of the type shown in Fig. 3 we can obtain a value for the heat of activation and the unimolecular frequency factor for the decomposition of TML. Thus the concentration of



FIG. 3. Growth of methyl concentration with temperature in He+0.006 Pb(CH<sub>3</sub>)<sub>4</sub> mixture. Reaction pressure, 0.4 mm. Quartz reactor R.1.



FIG. 4. Temperature coefficient of methyl concentration in a decomposing stream of He+0.006 Pb(CH<sub>2</sub>)<sub>4</sub>. Reaction pressure 0.4 mm. Quartz reactor R.1.

radicals in an unreacting atmosphere will be z where

$$z = \alpha(x_0 - x). \tag{1}$$

Here x and  $x_0$  are the instantaneous and zerotime concentrations of TML, and  $\alpha$  is a constant of the order of unity. We also have

$$-dx/dt = k_1 x, \qquad (2)$$

where  $k_1$  is the velocity constant for TML decomposition. Thus after integration and substitution we have

$$z = \alpha x_0 (1 - \exp(-k_1 t_0)), \qquad (3)$$

where  $t_0$  is the reaction time. Since, by assumption, the maximum value of the radical concentration  $z_m$  is given by

$$z_m = \alpha x_0$$

we obtain finally

$$\ln(z_m - z)/z_m = -k_1 t_0.$$
 (4)

In Fig. 4 the plot of  $\log k_1$  against  $10^4/4.57T$  is given. From this, and similar curves for slightly different values of  $t_0$ , a mean expression for  $k_1$  was obtained in the form

$$k_1 = 1.5 \cdot 10^{10} \exp(-28200/RT).$$

The only value of E found in the literature is that of Romm<sup>6</sup> who, in the course of induced

polymerization experiments, obtained a value of 23.5 kcal. Leermakers<sup>7</sup> obtained 36.9 kcal. for the decomposition of tetraethyl lead.

The behavior of the radical concentration as a function of temperature was quite different from that illustrated in Fig. 3 when a reactive gas was used as the carrier. A preliminary note<sup>8</sup> on this has already been published in which curves obtained at *ca*. 0.1-mm pressure were reproduced. More reliable data have been obtained for the carrier gases ethane and propylene at higher pressures. The curves, each point on which is the mean of three experimental readings, are reproduced in Fig. 5.

The marked maxima and minima may be explained in the following manner. As the temperature is increased the TML commences to decompose. Simultaneously, some of the radicals are removed by the reaction

# $CH_3 + RH \rightarrow CH_4 + R.$

Since the activation energy of this reaction is less than that for TML decomposition, there can be no maximum unless and until appreciable quantities of the TML are decomposed in the first sections of the furnace. These sections being further removed from the diaphragm afford greater time for the removal reaction to "filter out" the radicals. Thus at certain pressures, temperatures, and contact times the removal mechanism will overtake production, and this will continue until a new source of radicals, namely, the carrier gas itself, causes production to overtake removal.

We can set up the equation for such a mechanism in the following way. Assuming unimolecular decomposition and bimolecular removal, the instantaneous rate of production of radicals z will be

$$dz/dt = k_1 x + k_2 y - k_3 z y, (5)$$

where x and y are the instantaneous concentrations of TML and the carrier, respectively. Provided  $x_0$ , the initial concentration of TML, is small compared with y, we may regard the latter as constant. Then, since

$$x = x_0 \exp(-k_1 t), \tag{6}$$

<sup>7</sup> J. A. Leermakers, J. Am. Chem. Soc. **55**, 4508 (1933). <sup>8</sup> G. C. Eltenton, J. Chem. Phys. **10**, 403 (1942). we get by substitution and integration

$$z = \frac{k_1 x_0}{(k_3 y - k_1)} \left[ \exp(-k_1 t_0) - \exp(-k_3 y t_0) \right] + \frac{k_2}{k_3} \left[ 1 - \exp(-k_3 y t_0) \right].$$
(7)

In this equation  $x_0$ ,  $t_0$ , and y are experimentally determinable, while  $k_1$  has already been found for a neutral carrier gas. Thus it is simple, though somewhat laborious, to substitute probable values of  $k_3$  in the first term on the righthand side of Eq. (7) until the low temperature rise and the maximum are fitted to the experimental curve. A similar procedure with the second term establishes the minimum and the high temperature rise. Unfortunately for this section of the discussion the experimental results were not taken with sufficient refinement to justify placing much weight on numerical values obtained by this procedure. Uncertainties in the temperature distribution and contact time were not eliminated at this stage of development as interest lay in the endeavor to devise techniques for much higher pressures where the removal of CH<sub>3</sub> by the carrier is so rapid that the maximumminimum character of the curve is obliterated. Such curve-fitting as was attempted with the present inadequate data showed clearly the great sensitivity of the positions of the maxima and minima to the frequency factors. For example, using 9.0 kcal. for  $E_3$  in the case of TML in  $C_2H_6$ , a frequency factor as low as 5.10<sup>7</sup> had to be used and the results with propylene suggest that its greater efficiency as a remover of CH<sub>3</sub> may be attributable in this temperature range to a higher frequency factor rather than the lower activation energy of 3.1 kcal. as found by Smith and Taylor.<sup>9</sup> It should be noted in passing that Eq. (7) does not take into account the removal of CH<sub>3</sub> by lead liberated in the reaction and deposited in the cooler sections of the reactor, and evidence was subsequently obtained that a more accurate picture might have been obtained had oxygen been used instead of helium in deriving the constants of TML decomposition.

Before leaving the subject of the maximumminimum type curves depicted in Fig. 5 we may

briefly summarize the results obtained with other carrier gases. In argon the behavior, as was to be expected, was similar to that in He. In ethylene and hydrogen there was considerably less removal of CH<sub>3</sub> and less production of CH<sub>4</sub> than in  $C_2H_6$ . In oxygen there was, contrary to expectation, less removal than in C<sub>2</sub>H<sub>6</sub>. An O<sub>2</sub>-TML curve plotted on the same scale as that used for  $C_2H_6$  and  $C_3H_6$  is included in Fig. 5. Methyl radicals are, therefore, rather stable towards oxygen, a conclusion which is supported by measurements of methyl radicals in methaneoxygen flames (see following communication). That some reaction is taking place is made evident not only by the appearance of a maximum but also by the appearance of significant amounts of mass 30. This was ascribed to formaldehyde rather than to ethane since only insignificant amounts were formed when nitrogen was substituted for oxygen.

In nitrogen there was significantly less de-



FIG. 5. Production of methyl in mixtures of 0.6 percent Pb(CH<sub>3</sub>)<sub>4</sub> in oxygen  $[0, \text{ ethane } 0, \text{ and propylene } \times.$  Quartz reactor *R*.1. Pressure *ca*. 1.1 mm.

<sup>&</sup>lt;sup>9</sup> H. S. Taylor and J. O. Smith, Jr., J. Chem. Phys. 8, 543 (1940).

velopment of methyl than in oxygen. This, at first sight, anomalous result is probably an indication of the influence of atomic and deposited lead in reducing radical yields. With oxygen as a carrier it seems plausible to assume that the lead is poisoned and its radical removal efficiency decreased.

When nitric oxide was mixed with ethane in the proportions 1:2 and used as a carrier, there was a scarcely noticeable increase in the rate of removal, indicating that, although a chain breaker, its affinity for methyl does not greatly exceed that of ethane. When using pure nitric oxide as a carrier, the radical concentration was drastically reduced but there was evidence that this was partly a surface effect since, on returning to an ethane stream, several runs had to be made before the normal ethane curve was obtained.

On account of polarizing layers built up on the electrode surfaces when the three butylenes were decomposed, a strict comparison could not



FIG. 6. Production of methane, hydrogen, and methyl in decomposing ethane with and without addition of Pb(CH<sub>3</sub>)<sub>4</sub>. Large symbols—with approximately 0.1 percent TML added. Small symbols—pure ethane. Quartz reactor R.1. Pressure 19 mm.

be made with these carrier gases. There were indications that iso-butylene removed methyl more effectively than  $\beta$ -butylene and that the activation energy for methyl production in isowas less than in  $\beta$ -butylene. It is probable that with the improved geometry which could be achieved with a 90° magnetic path less trouble would be encountered, since the molecular beam can be directed parallel with, rather than perpendicular to the plane of the first ion-collecting slit.

# THE EFFECT OF PRESSURE ON THE MAXIMUM-MINIMUM CURVES

The effect of pressure on the shape of the methyl curve can best be explained in terms of what for want of a better expression we shall call the appearance temperature. This is the temperature at which a positive deflection due to ionization of a product appears. Provided the sensitivity of detection remains constant, the appearance temperature is an indication of the partial pressure of the product in the ionization chamber and above the exit from the reactor. By increasing the pressure in the reactor we automatically increase the pressure in the ionization chamber, and we should, therefore, expect the appearance temperature to decrease for both unimolecular and bimolecular processes. However, if as is more desirable though also more laborious, the pressure in the ionization chamber is maintained constant by adjusting the size of the diaphragm, then the appearance temperature will depend on the relative partial pressures of reactant and product, the latter being small. Hence the appearance temperature will increase for a unimolecular production mechanism and should remain sensibly constant for a bimolecular mechanism.

Although we were not primarily interested in this aspect it became clear that over the pressure interval 0.1 to ca. 4 mm a bimolecular process in the decomposition of ethane was becoming increasingly dominant over the surface reaction previously mentioned. Above 7 mm the appearance temperature when using R.1 increased rapidly, but this can be accounted for by the efficiency of the cool zone between the furnace and the diaphragm in removing radicals much faster than they are produced. In Fig. 6, curves obtained in  $C_2H_6$  with and without addition of approximately 0.1 percent TML are reproduced for the products CH<sub>4</sub>, CH<sub>3</sub>, and H<sub>2</sub>. It is clear that the CH<sub>3</sub> radicals produced from the TML have been almost completely filtered out and have been replaced by methane. The addition of the TML has also increased the production of hydrogen. The curves for  $CH_4$  and  $H_2$  obtained without TML can be replotted for estimating the activation energies; these replots are shown in Fig. 7. From the slopes we obtain:  $E(CH_4)$ =91 kcal. and  $E(H_2) = 77$  kcal.—values which appear slightly high although the latter agrees with that found by Kuchler and Theile<sup>10</sup> and used by Rice and Herzfeld.<sup>11</sup> In a static system we should expect  $E(CH_4)$  to equal the activation energy for the primary rupture of ethane into two methyl radicals provided the stationary state, represented by

$$dCH_3/dt = dz/dt = k_2y - k_3zy = 0,$$

has been reached. Actually, however, at low pressures and contact times of the order 0.001 second, the stationary state is not reached and we have

whence

4

$$z = k_2/k_3 \cdot (1 - \exp(-k_3 y t)),$$

$$dCH_4/dt = du/dt = k_2 y(1-\alpha),$$

where  $\alpha = \exp(-k_3yt)$  and the "activation energy" obtained from the temperature coefficient will be

where

$$\beta = \left[ \alpha (1 + k_3 yt) - 1 \right] / \left[ k_3 yt + \alpha - 1 \right].$$

 $d\ln u/d(1/T) = -E_2/R + \beta E_3/R,$ 

 $\beta$  is negative and approaches  $-1/k_3yt$  as yt becomes large. Since in general  $E_2 \gg E_3$ , the errors become negligible at pressures above 10 mm, but they may be as high as 6 kcal. at 1 mm.

Convincing evidence that the rise in the appearance temperature with increasing pressure is ascribable to the filtering action of the cool zone rather than to a unimolecular primary rupture was obtained when using R.3 where the cool zone is eliminated. Although this reactor was primarily designed for combustion studies and does not have the proper dimensions for



FIG. 7. Temperature coefficient replot of hydrogen and methane production in pure ethane. Quartz reactor R.1. Pressure 19 mm.

establishing temperature equality throughout a given cross section at the streaming velocities required, nevertheless the sample, being drawn from the center, will, if anything, be at a lower temperature than that registered by a thermocouple situated off-axis. Hence any errors will tend to increase the appearance temperature. Actually the appearance temperature at 30 mm is considerably lower than that obtained at 18 mm in R.1, and is not sensibly different from values obtained at still higher pressures-up to 110 mm. Although it might be premature at this stage of development to place complete confidence in these semiquantitative results, the evidence is considerable that the primary rupture of ethane is bimolecular, as proposed by Kuchler and Theile, when the pressure is sufficiently high to escape contributions from the unimolecular surface reaction.

#### **OTHER RADICALS**

 $C_{2}H_{b}$ —Reference to Table I of Part I in this series shows that although the difference between the ionization potential of  $C_{2}H_{b}$  and the appearance potential from  $C_{2}H_{b}$  is approximately 8.7 -12.9 = -4.2 volts, which should afford sufficient freedom in selecting a potential such that  $\Delta_{0}C_{2}H_{b}^{+}\ll\Delta C_{2}H_{b}^{+}$ , where  $\Delta_{0}$  and  $\Delta$  are the electronically and thermally produced contributions, respectively, nevertheless the ethyl radical

 <sup>&</sup>lt;sup>10</sup> L. Kuchler and H. Theile, Zeits. f. physik. Chemie
 B42, 359 (1939).
 <sup>10</sup> F. O. Rice and K. F. Herzfeld, J. Chem. Phys. 7, 671 (1939).



FIG. 8. Growth of the ethyl radical in a decomposing stream of  $C_2H_6+0.006$  percent Pb(CH<sub>3</sub>)<sub>4</sub>. Pressure 0.03 mm. Approximately one-third of the height of the curve is attributable to the C<sup>13</sup>C<sup>12</sup>H<sub>4</sub> isotope.

has proved to be one of the most difficult to detect with certainty. The difficulty is occasioned by the fact that the ionization potential of  $C_2H_4$ is only about two volts higher than that of  $C_2H_5$ so that in reactions where  $C_2H_4$  appears as an end product its isotope of mass 29 also appears in quantities comparable with, and usually greater than the anticipated concentration of free ethyl. With the present apparatus, limited as it is in resolving power and homogeneity of the electron beam, all the  $\Delta C_2 H_5$  observed at high pressures can be accounted for as  $\Delta C^{12}C^{13}H_4$ . At pressures below ca. 1 mm we found that the  $\Delta 29$  was some threefold greater than could be expected from the isotope of ethylene, and hence the major contribution was ascribed to free ethyl. A curve of  $\Delta C_2 H_5$  in a  $C_2 H_6 + TML$  mixture is reproduced in Fig. 8.

 $C_{3}H_{5}$ —This radical may be anticipated as a result of the capture of H by methyl radicals in propylene. Figure 9 shows that it can be detected at temperatures where the removal mechanism is well underway.

 $C_2H_3$ —Since propylene has been shown to yield CH<sub>3</sub> at high temperatures, we might expect the simultaneous appearance of the residual vinyl radical. In spite of favorable conditions for its detection none was found. We must conclude that the vinyl radical is particularly reactive and its life time much shorter than that of methyl. Testimony as to its reactivity is afforded by the growth of the C<sub>2</sub>H<sub>4</sub> curve (Fig. 9) which is clearly associated with the temperature range where methyl production is considerable. It is possible that the vinyl radical is surface reactive and that redesign of the apparatus to reduce the residence time in the detecting system would reveal measurable concentrations.

 $CH_2$ —Although the potential relations for this radical render its detection relatively easy, it was only detected in the decomposition of diazomethane. Its concentration in the detector was estimated for other gases to be at least 100-fold less than that of the methyl radicals.

**CH**—Hopes were entertained that this might be detectable when decomposing acetylene. Although positive results were obtained, there was considerable discordance, indicating that the condition of the surface of the carbon filaments used for decomposing the acetylene might be a determining factor.

H-Atomic hydrogen was remarkable by its absence at both high and low pressures. Since its concentration in ethane according to the Rice mechanism should be independent of the ethane pressure, its absence at high pressures may be a natural consequence of the diminishing ratio of atomic hydrogen to ethane in the effluent. At low pressures it is probable that its rapid recombination on surfaces operates against detection in the present apparatus. By the use of tungsten or carbon filaments at ca.  $10^{-2}$  mm and 1000°C, atomic hydrogen was detectable in city (natural) gas but not in ethane or methane. Here again, the influence of impurities and surface condition was noted but not investigated. It is to be hoped that using the known noncatalytic properties of tantalum in the design of critical parts the detection of H atoms will be feasible. Calculations of its probable concentration in the ethane decomposition indicated that its measurement is only a matter of refined technique.

#### OTHER GASES

As a guide to future and more detailed investigation propane and n- and iso-butane were run through the apparatus. The detectability of methyl radicals increases with carbon number on account of lower activation energies and increasing appearance potentials, which effectively increases the available sensitivity within limits imposed by secondary methane formation. The reverse, however, is true when we attempt the detection of the heavier radicals. Not only must we contend with lower stability and smaller concentrations but the usable potential differences are considerably reduced. Higher resolving power, sensitivity, and electron-beam homogeneity will be required if quantitative results in this field are contemplated.

An oxygenated compound, dimethyl ether, gave no trouble. Methyl radicals were abundant but a search for the residuum, CH<sub>3</sub>O, yielded negative results. Large quantities of HCHO were found, together with CH<sub>4</sub>, CH<sub>3</sub>OH, CHO, and  $H_2$ . Since it might appear at first sight that the absence of CH<sub>3</sub>O is connected with its rapid conversion to CHO and H<sub>2</sub>, a test was made to discover whether electron bombardment of the main product HCHO would reproduce the quantities of CHO<sup>+</sup> actually found. A comparison of the ratios of HCHO+/CHO+ from formaldehyde vapor in a stream of argon with the corresponding ratio from decomposing methyl ether indicated that, within the rather large experimental error, the bulk of the CHO+ was of electronic rather than thermal origin-a result which illustrates the caution with which the appearance of a given mass from a reaction must be interpreted.

# DISCUSSION AND CONCLUSIONS

Since this investigation was primarily directed towards finding the limitations of and possible improvements in a new method of approach to the measurement of short-lived intermediates, a detailed discussion of each gas or radical surveyed would be premature. Certain conclusions, however, seem sufficiently well established to be summarized as follows. The method is more sensitive, rapid, and universal than the mirror or spectroscopic methods. The detection of higher radicals of greater instability awaits further refinement. Under favorable conditions the lower limit of detection is at present *ca*. 0.0005 percent. Methylene does not appear in these concentrations except in the case of the decomposition of diazomethane. The reaction between methyl radicals and oxygen is considerably slower than might be expected on the basis of the value  $E \ge 3$  kcal. deduced by Bates and Spence<sup>12</sup>—a value which may be drastically

increased if we take Jones'13 value of 12 kcal. for the reaction between methyl and iodine, which would entail a value of  $E \ge 15$  kcal. for the oxygen-methyl reaction. It seems probable, however, that the slowness of the reaction should be attributed to a high steric factor rather than a high activation energy. Bates and Spence concluded that a steric factor of  $10^{-4}$  was required. The concentration of methyl radicals from decomposing ethane both at low and high pressures, is higher than can be accounted for without introducing a considerable steric factor into the rate of removal. At low pressures surface catalysis may be partially responsible, but it was found in our experiments at high pressures, using R.3, that the introduction of additional surface near the orifice reduced rather than increased the total yield. Until a modified type R.3furnace with lower Reynold's number is used, a discussion of the relative roles of activation energy and steric factor must be postponed.



FIG. 9. Appearance of the allyl radical and ethylene during the decomposition of  $C_{3}H_{6}+0.006$  percent Pb(CH<sub>3</sub>)<sub>4</sub> in a quartz reactor at 0.1-mm pressure.

<sup>13</sup> J. L. Jones, J. Am. Chem. Soc. 61, 3284 (1939).

<sup>&</sup>lt;sup>12</sup> J. R. Bates and R. Spence, Trans. Faraday Soc. 27, 468 (1931); J. Am. Chem. Soc. 53, 1689 (1931).

The main difficulty encountered with the present apparatus at higher pressures lies in the interpretation of a negative result—the absence of a probable radical such as  $C_2H_3$ . Absence may be attributable to high volume reactivity or to

# Part III. Low Pressure Flames

The method described in Part I has been applied in a preliminary survey of intermediates formed during the combustion of methane, propane, and carbon monoxide at pressures ranging from 30 mm to 140 mm. The object of the investigation was to obtain data for the improvement of the method rather than to study exhaustively any particular reaction. By following the intensity changes of intermediates formed in mechanically-oscillating and pulsating-flow flames, the intermediates may be assigned to zones or phases of the oscillating or pulsating cycle. Pending more detailed study the following intermediates ap-

#### INTRODUCTION

**I** T is probably not an exaggeration to say that there is no chemical field in which the necessity of introducing the concept of material chains is more apparent, and the experimental detection of the carriers less certain, than in the



FIG. 1. Internal modifications of steel reactor R.3 for flame studies. Gas components A and B enter as shown, and the flame extends from the side hole O, across the diaphragm D. The distance OD can be varied by oscillating the tube T in a vertical direction, lateral movement being prevented by the spring guide H. A retractable Pt-Ir coil S, moving in guides G, serves to ignite the mixture. rapid removal on the walls of the extractor diaphragm. As pointed out in Part I, this difficulty may be largely eliminated by the use of higher pumping speeds and wider diaphragms in future models.

# parently exist in detectable quantities, HO<sub>2</sub>, CH<sub>3</sub>O, CH<sub>2</sub>O, CH<sub>0</sub>O, C<sub>2</sub>H<sub>2</sub>, and CH<sub>3</sub>. Only doubtful traces of OH were detected, and the low concentration is attributed to the rapidity of surface removal. The temperature coefficients of CH<sub>2</sub>O and CHO are strongly negative, of HO<sub>2</sub> slightly negative, and of CH<sub>3</sub> strongly positive. The CH<sub>3</sub> radical is definitely a chemical intermediate and not attributable to thermal decomposition of methane. The production of an intermediate of mass 16 in a propane-oxygen flame is discussed, but as yet it has not been possible to distinguish between CH<sub>4</sub> and atomic oxygen as the source of this mass.

field of combustion. Since one of the original objectives of our research had been to develop a method of studying intermediates at moderately high pressures, even the limited successes achieved with the present instrument in the field of hydrocarbon decomposition encouraged us to attempt a preliminary survey of the more complex phenomena anticipated in flames. It must be emphasized that the results are suggestive rather than conclusive, since we were primarily interested in discovering the defects and range of application rather than in solving any particular problem. For reasons outlined in Part I of this series, it was recognized that several improvements could be effected by a complete rebuilding of the apparatus. The results reported below have lent precision to our knowledge of the means whereby such improvements can be made effective.

#### APPARATUS

The apparatus was essentially the same as that described in Part I. Copper tubes for preventing flash-back, and traps for removing condensible combustion products were incorporated. In order to prevent condensation in the water cooler, the latter was maintained at *ca.* 35°C by a circulatory system. Reactor R.3 was used throughout. In Fig. 1 the internal modifications are illustrated. Since premixing of the combustibles was found to be undesirable, the gases were introduced separately so that with flames burning at pressures between 80 mm and 150 mm one component, (A), entered down the narrow stainless steel or quartz tube, T, and met the other component, (B), at a small side hole, O, and the flame was directed across the gold diaphragm, D. A movable platinum-iridium heating spiral, S, could be lowered towards O for ignition, after which it was retracted from the flame zone. In one series of experiments the tube T was moved up and down by an external lever mechanism actuated by a synchronous motor which, by gearing, provided one complete oscillation of the flame in 2.5 minutes. The springy steel guide, H, maintained the tube T in position relative to the axis of the furnace. As before, the furnace walls, F, and the diaphragm could be heated by passage of heavy a.c. currents.

In view of the large change of initial pressure accompanying combustion, a device for automatically restoring the pressure during combustion to its pre-combustion value was installed. This has already been described1 and consists essentially of a pneumatic Wheatstone bridge. The variable resistances in the two gas lines are motor driven Fowler-type valves. The reversible Telechron motors are in circuit with relays operated from two double contacts, one pair in a mercury-filled U-tube, which plays the role of the galvanometer in the electrical analog, and the other pair in a manometer which registers and controls the pressure in the reactor. It was possible in this way to restore the pressure automatically, by increasing the flows of the two components, while maintaining a constant component ratio at any predetermined value. It was also possible to maintain a regular pulsating regime by proper choice of the pneumatic analogs of capacity, resistance, and inductance.

#### METHOD

Theoretically, every positive ion of low mass occurring in the flame spectrum should be regarded as an electron dissociation fragment of some heavier chemical product unless by calibration with the higher mass it can be proved that the electron velocity is too low to produce the



FIG. 2. Schematic representation of reaction zones in a horizontal flame pulsating across the sampling diaphragm. If the latter moves from x to y, corresponding to an elongation of the flame, the intensities of the zonal products ABCDE entering the ionization chamber will pass through maxima A', B', C', D', and E'. As the flame contracts the pattern will be repeated, and the maxima on an unfolding time scale will appear at D'', E'', B'', and A''.

observed yield of lower mass ions. This is a possible but laborious and, at the present stage, unjustifiable procedure. Moreover, it can be avoided in certain instances by using either a pulsating or an oscillating flame.

To simplify the discussion let us suppose that the flame issuing from the side hole in the tube, T, is composed of reaction zones and that in the various zones there will be a different distribution of products. Thus the concentration of any given product will vary with distance from the tube T. Actually these zones will be conical or spherical, but for simplicity they may be represented schematically as in Fig. 2, where A, B, C, D, and E are zones in which the concentrations of the products A, B, C, D, and E are a maximum. It is then obvious that if the diaphragm of the reactor under the flame were to be moved from position X to position Y, the intensity of the products effusing through the diaphragm would pass through maxima corresponding to A', B', C', D', and E' and that as the diaphragm returned from Y to X to complete the cycle, the maxima would be reproduced a second time so that on a continuously unfolding time scale these second maxima would appear in the positions D'', C'', B'', and A''. It is clear that simple maxima will occur only when the zones lie out-

<sup>&</sup>lt;sup>1</sup> N. Heikes, Ind. Eng. Chem. 15, 133 (1943).

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FIG. 3. Variation of formaldehyde ion as flame pulsates across the diaphragm. The three cycles shown indicate by the twin maxima an intermediate zone. Time of one cycle=2.5 minutes. Mixture, two parts  $O_2$  burning in one part CH<sub>4</sub>. Traced from original photo-pen record. Pressure 67 mm.

side the limits of the movement of X. In all other cases, such as B, C, and D, the maxima will be double and the relative depths of the two minima will be a function of the symmetry of the zone with respect to the positions Xand Y. The phases of the various products are directly related to their position in the flame, and it follows that if the intensities of B and C, for example, are not coincident in phase then the ion  $B^+$  cannot be either the isotope or the electron-dissociation fragment of the product C. Thus by using a pulsating or oscillating flame with a fixed diaphragm, which is approximately equivalent to using a moving diaphragm with a stationary flame, we not only avoid certain difficulties in interpreting the true origin of a given ion but are also able to say something concerning the chemical sequence occurring in the flame itself.

Restricted as the present instrument is by the geometry of the 180° magnetic field, it was not feasible to move the flame horizontally across the diaphragm. Mechanical oscillations were only possible in a vertical direction. In an auxiliary apparatus it was found visually that with suitable flow speeds and flame size the plane of the diaphragm would in effect penetrate from the outer to the inner mantle of the flame. Both the amplitude and mean position could be altered. In most cases an amplitude of 3 mm was suitable.

With the pulsating flame the pulsations, induced by changes in flow speed instead of mechanical motion, are mainly in a horizontal direction, but the simplicity of the interpretation on the basis of Fig. 2 is to a certain extent obscured by the fact that some change in regime occurs simultaneously as a result of greater combustion, higher temperature, etc. The fact that the flow pulsations were less than 5 percent of the total flow inclines us, however, to the belief that the large changes in ion currents actually observed and the significant phase differences are mainly attributable to the physical motion of concentration zones across the diaphragm rather than to concentration changes in stationary zones.

#### RESULTS

In order to study the performance of the present instrument and project improvements, methane, propane, and moist carbon monoxide flames were briefly investigated. A preliminary run using the quartz reactor R.1 (see Part I of this series) showed that a mixture of methane and oxygen would not burn in the narrow (3-mm) tube but that the production of CH<sub>3</sub> radicals at the cracking temperature was certainly not reduced but, if anything, enhanced by the presence of oxygen. This confirmed the result already obtained when using oxygen-TML mixtures (Part II, Fig. 5).

A tracing taken from part of an actual record of the variation of formaldehyde ions in a pulsating oxygen-in-methane flame is shown in Fig. 3. We note that the intensity passes through two maxima per cycle, indicating that the concentration is a maximum in a zone situated between the inner and outer cones, as illustrated schematically in Fig. 2 at B', B'' or at D', D''. In order to illustrate the marked phase differences among the masses 28 to 32, Fig. 4 has been constructed in which the intensities are arbitrarily equalized, and the pressure and flow variations occurring in the cycle are related to the trace made by a solenoid-operated pen. The solenoid of the latter was coupled to the automatic flow regulator mentioned previously. It will be noted that pressure and flow velocity are not in perfect phase, which may account for certain minor discrepancies in the position of the main minimum. It was found that the phase separation of the maxima was a function of the average flow. This is to be expected since an increase in average flow will tend to shift zone D towards zone C (Fig. 2) and thus increase the separation of the maxima.

In this way it was found that greater differences between the patterns of two nearly identical curves (for example CHO and CO in Fig. 4) could be induced.

From the particular set of patterns illustrated in Fig. 4, it is clear that CH<sub>3</sub>O, CH<sub>2</sub>O, and CHO are formed in different parts of the flame or under different chemical conditions. If we accept as a working hypothesis the moving-zone postulate, it can be deduced from Fig. 4 that since oxygen is richest in the inner parts of the flame the chemical sequence from the jet to the tip of the flame will be O<sub>2</sub>-CH<sub>3</sub>O-CH<sub>2</sub>O-CHO-CO. Certain reservations have to be made, however, and further study is required. The reservations may be stated briefly as follows.

Firstly, it is possible that methyl alcohol is one of the first products. Detection is rendered difficult by the identity of its mass with that of  $O_2$ , the comparatively small electron energy difference between the two ionization potentials (ca. 12.2 - 10.8 = 1.4 volts) and the large ratio of oxygen to methyl alcohol concentration. With greater electron-beam homogeneity it might be possible to obtain indications of CH<sub>3</sub>OH and thence to determine whether any of its electrondissociation fragments are contributing to the patterns of the other observed ions such as CH<sub>3</sub>O<sup>+</sup>. A more definite approach would be to use deuteromethane for this particular control, so as to obtain a mass separation of four units between deuteromethyl alcohol and oxygen.

Secondly, it is possible that CHO is the C<sup>13</sup>O isotope of CO since the latter is present in great abundance. This possibility was ruled out by measuring the ratio of  $M^{+}_{28}/M^{+}_{29}$ . It was then found that the isotope would only account for approximately one-sixth of the observed  $M^+_{29}$ . Moreover, it was possible to obtain a greater phase differentiation between CO and CHO by increasing the average flow. The phase pattern of CHO then approached that of CH<sub>2</sub>O but was sufficiently different from the latter to rule out the possibility that the observed CHO<sup>+</sup> was entirely an electron dissociation product of CH<sub>2</sub>O or a combination of this with the C<sup>13</sup>O isotope. We, therefore, feel reasonably confident that CHO has been detected and could in future work be an object of special study.

The remaining results will be summarized

under the heading of the product or intermediate concerned.

 $O_3$  and  $CO_3$ —These were not detected in appreciable quantities in any of the three flames (methane, propane, and carbon monoxide). The instrument was not suitable in its present form for masses above 45.

 $CO_2$ —The only interesting feature of  $CO_2$  production is the erratic trace which this product gives as compared with CO. All possible instrumental causes of this unsteadiness were eliminated without effect on the erratic behavior. It was concluded that small particles of carbon were oxidized *in toto*, giving rise to bursts of  $CO_2$ . If this explanation is correct, it may be deduced that solid carbon under the prevailing conditions is oxidized to  $CO_2$  in one step since the carbon monoxide curves were quite smooth.

 $H_2O_2$ —Very few observations were made on this product. In an oxygen-methane oscillating flame the M.34 peak was in phase with the oxygen M.32 and its magnitude equal to that which would be expected for the O<sup>16</sup>O<sup>18</sup> isotope. Under these conditions, therefore,  $H_2O_2$  does



FIG. 4. Summarized phase curves for intermediates measured with a pulsating oxygen-in-methane flame. The amplitudes have been equalized to facilitate recognition of the phase relationships. The solid block marks at the base represent signals transmitted from the flow controller to a solenoid-operated pen giving phase reference points. The flow and pressure lines represent the variation of these parameters during the cycle.

not appear as a major intermediate and cannot be responsible for the oscillations of M.33 (q.v. under HO<sub>2</sub>).

 $HO_2$ —In view of the considerable importance of this radical in some theories of oxidation, it was of interest to attempt detection with the present apparatus. Detection is rendered difficult on account of the proximity of the very much larger mass 32 of oxygen and by the contribution of the O<sup>17</sup>O<sup>16</sup> isotope of mass 33 identical with that of HO<sub>2</sub>. However, both these interferences must decrease when the mixture is ignited owing to the consumption of oxygen, and, hence, if any increase is found it must be attributed to a new product. By setting the electron voltage just below the ionization potential of oxygen a quite definite increase in the positive ion current of mass 33 was observed after ignition of a propane in oxygen flame. The phase was nearly but not quite identical with that of the oxygen, and apparently differed from that of the CH<sub>3</sub>O previously mentioned. Since methyl alcohol may contribute to the formation of masses 33 and 31, it is possible that the deflection, or a part of it, observed for mass 33 may have to be attributed to the isotope of methyl alcohol. At present the evidence from the phase differences appears to exclude the possibility that methyl alcohol can be responsible for both CH<sub>3</sub>O and HO<sub>2</sub>.

In an oxygen-in-methane oscillating flame a much larger phase difference was obtained between M.32 and M.33.

It was noticeable that with both the propaneoxygen and oxygen-methane flames the application of additional heat to the reactor surrounding the self-sustaining flames (pressure ca. 70 mm) decreased slightly the intensity of the M.33peak. This negative temperature coefficient is of some interest and will be referred to in discussing the production of methyl radicals.

**M.32-M.28**—The probable reality of intermediates in this mass range has already been discussed above. Formaldehyde exhibited a very marked negative temperature coefficient.

 $C_2H_2$ —In an oscillating propane-oxygen flame M.26 was readily identified as a product formed when the flame was closest to the diaphragm. The intensity dropped to zero as the flame moved upward from which we may conclude that either

the  $C_2H_2$  formed in the inner mantle is totally consumed in passing through the flame front and into the oxygen-rich outer mantle, or that the production of  $C_2H_2$  takes place only when the inner mantle plays over the metal surface.

 $C_2H$  and  $C_2$ —Since these masses were in phase with the production of  $C_2H_2$ , and the magnitude of the deflections were not inconsistent with an electron-dissociation origin, we are not as yet in a position to identify these products with a chemical process.

OH-In view of the considerable success of the spectrographic method in measuring the concentration of OH radicals in flames, several attempts were made to use this radical as a basis of comparison between the spectrographic and mass-spectrographic methods. It would appear from our preliminary results that whereas the hydroxyl radical is particularly suitable for spectrographic investigation it is particularly difficult to identify in the mass spectrometer. The reasons for this conclusion are not without interest for the future development of the massspectrometric method, and, therefore, a more detailed discussion of the problem seems justified. The primary condition, namely, a large energy difference between the appearance potential of OH+ from H<sub>2</sub>O and the ionization potential of free OH is satisfactorily fulfilled since  $A(OH^+)$ = 18.9 v and I(OH) = 13.8 v. However, very large quantities of H<sub>2</sub>O are formed during the combustion and the ionization potential of  $H_2O$ is  $I(H_2O^+) = 12.7$ . Thus if we select an electron energy slightly less than 18.9 v the  $H_2O^+$  peak will be strongly developed when the mixture is burning, and unless the resolving power is high there will be sufficient spreading of the M.18peak into the M.17 to mask the very small increase anticipated in the latter. In addition it has been found (see next section) that some product of mass 16 is formed under certain conditions and the isotope of this mass may be another factor contributing to the growth of M.17. Hence, although large increases in M.17have been recorded, we have not yet had at our disposal sufficient resolving power to overcome the difficulty of interpreting uniquely the origin of these increases, accompanied as they are by enormously greater increases in a neighboring mass. Unfortunately, the additional degree of freedom provided by the pulsating or oscillating flame did not in this case assist in defining the origin of the M.17 increase. Both M.17 and M.18 were in phase, and it was noticed that the amplitude of the variation was small compared with the mean deflection. This was tentatively interpreted as indicating that the concentration of water vapor in the ionization chamber was buffered by absorption and desorption on the Aquadagged walls.

In an effort to overcome the effect of the large increase in M.18 when a hydrocarbon mixture is burnt, a moist mixture of carbon monoxide and oxygen was run through the apparatus and ignited. Kondratjew<sup>2</sup> has shown that at pressures of *ca.* 35 mm approximately one percent of the water vapor is converted by chemical rather than thermal action into OH radicals. Since in this case there is no increase in M.18 as a result of combustion, there should be no difficulty in measuring and interpreting the appearance of this comparatively large increase in M.17.

At low pressures (35-50 mm) the flame of a stoichiometric mixture of CO and O<sub>2</sub> is not self-sustaining, and the reaction vessel has to be raised above 600°C. The flame is then so diffuse that it resembles a luminous glow, filling a major portion of the reactor, and the technique of oscillating or pulsating the "flame" has no meaning. It was, therefore, necessary to compare the deflections of OH<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> with the reactor hot and cold. This introduces the possibility that water driven off the reactor surfaces may contribute to the deflection, but this can be almost entirely eliminated by outgassing, using the behavior of H<sub>2</sub>O<sup>+</sup> as a control on the efficiency of the latter process.

By use of the stainless steel reactor with a gold diaphragm, some indication of OH radicals was obtained. However, the results were highly irreproducible owing to the very rapid plugging up of the orifice in the gold diaphragm. Since carbonyl formation on the steel and decomposition on the gold was suspected as a cause of the blocking of the orifice, the entire inner surface of the reactor was lined with a snugly fitting thin gold shell. This eliminated the blocking of the diaphragm, but also eliminated all but a doubtful trace of the hydroxyl radicals entering the ionization chamber. Although data on combustion in gold vessels is not available in the literature, it is known that silver has a particularly strong depressing action. In an auxiliary vessel in which a quartz reactor was partially lined with gold foil, it was noticed that the mixture burnt in the unlined section even when the latter was cooler than the section lined with gold. It was, therefore, concluded that the gold liner was acting as an efficient differential pump for the removal of certain chain carriers, and that although a flame was undoubtedly burning in the gold-lined steel reactor, the concentration of OH radicals at the walls might be much less than in the center.

Finally a thin quartz liner was fabricated by grinding and etching. This was inserted inside the gold liner and the mixture introduced through a quartz tube. Thus the only exposed metal surface was that of the small gold diaphragm and the  $\frac{1}{32}$ -inch deep walls of the well in which it was held. Even under these conditions the concentration of OH radicals entering the ionization chamber was less than one-tenth of that observed by Kondratjew.

Our essentially negative results with the hydroxyl radical do not constitute a refutation of the positive results obtained by the spectrographic method. In the latter, the light beam passes through a considerable length of gas where the reaction is homogeneous and where the influence of surface is at a minimum. In the mass spectrographic method, on the contrary, the sample is extracted through an orifice which, in the present apparatus, is too narrow to allow collision-free passage for an appreciable fraction of the radicals. As indicated in Part I, this limitation can be reduced in future models, and it should be possible, by varying the ratio of the length and diameter of the orifice, to throw light on the relative sensitivities of various radicals to surface destruction. At present we may conclude that the hydroxyl radical is highly destructable at a gold surface, and in this capacity resembles atomic hydrogen. Recently Smith<sup>3</sup> has shown, by an independent method, that the efficiency of the recombination of hydroxyl radicals on a Pyrex surface at 900°K is of the order  $10^{-1}$ .

<sup>3</sup> W. V. Smith, J. Chem. Phys. 11, 110 (1943).

<sup>&</sup>lt;sup>2</sup>V. N. Kondratjew, J. Phys. Chem. U.S.S.R. 14, 1 (1940).



FIG. 5. The production of methyl radicals in an oxygenin-methane oscillating flame. Curve 1.  $CH_4^+$  at 9.25 ev (uncorrected). At A, heat was applied to the furnace and the greater combustion reduces the second maximum without shifting phase. Curve 2.  $CH_3^+$  at 10.0 ev. Furnace unheated. Curve 3.  $CH_3^+$  at 7.75 ev. Furnace heated. The triangular reference line at the base represents the varying height of the flame above the gold diaphragm.

**M.16**—It was found that in a propane-oxygen flame considerable amounts of M.16 could be detected at electron energies below the appearance potential of O+ from the electron dissociation of either O<sub>2</sub>(20.5 v), CO(24 v), CO<sub>2</sub>(19.6 v), or  $H_2O(18.5 v)$ . The only chemical products which could give rise to this mass are atomic oxygen and methane. Since, however, the ionization potentials of these products are 13.6 and  $13.1\pm0.4$  volts, respectively, it is clear that the difference is too small to serve as basis for identification. An attempt was therefore made to utilize the electron affinity of oxygen atoms. Pure electron attachment is notoriously inefficient on account of the energy which must be dissipated. At the pressure ruling in the ionization chamber, triple collisions are so rare that we can only rely on radiation to carry off the excess energy (2.2 v) during the time of passage of the electron through the sphere of attraction of the oxygen atom. Thus the probability of attachment will increase as the velocity of the colliding electron decreases. At higher electron energies, negative atomic oxygen ions will make their appearance as a result of dissociation of an oxygen-containing molecule, the remainder of the molecule carrying off the excess energy either kinetically or, at still higher voltages, by formation of a positive ion. These two processes are more probable than that of pure radiative attachment and may be used as a guide in setting the focusing fields and checking the sensitivity.

A number of attempts were made to detect the presence of atomic oxygen, but the results were negative. It was evident from the negative ion curves obtained at electron energies from 5 v to 35 v, with and without ignition of the mixture, that a much more efficient electron gun than was available in the present apparatus would be required. We are, therefore, as yet unable to distinguish between methane and atomic oxygen as the source of the very definite appearance of M.16 in the combustion products of a propane-oxygen flame.

 $CH_3$ —In view of the relative stability of methyl radicals towards surface collision and oxygen, it was hoped that this radical would be detectable in the oxygen-methane flame. With flame pressures varying from 75 mm to 140 mm the amounts of CH<sub>3</sub><sup>+</sup> recorded were those to be anticipated from electron dissociation of the incompletely burnt methane. Moreover, both  $CH_4^+$  and  $CH_3^+$  were in phase. However, when additional heat was applied to the reactor a very striking change occurred. Not only were methyl ions detectable at electron energies below even the ionization potential of methane, but the phase of these ions in an oscillating flame indicated that their place of origin lay between the oxygen-rich and methane-rich zones. Thus the possibility that the increased methyl ion current was due to thermal decomposition of the methane was convincingly eliminated. In Fig. 5 tracings of short sections taken from much longer experimental curves have been superimposed to illustrate the phase change. Curve 1 is for methane ions with an unheated flame. At the instant marked A the furnace temperature was raised, and, since the heat capacity is small, practically the full effect of the increased temperature is developed in the next cycle which shows a decreased intensity. Evidently combustion is more complete in the heated furnace. Curve 2 shows the trace for the M.15 ion with a cold furnace. Both the magnitude and phase of this trace indicate that the major component is attributable to electron dissociation of the methane rather than to ionization of free methyl. At

the end of this trace the temperature was again raised, whereupon the M.15 ion gave off-scale deflections. The electron energy was therefore reduced by 2.25 volts and curve 3 obtained. A check of the M.16 ion at the reduced voltage gave no measurable deflection; hence we may be certain that no electron-dissociation fragment was contributing to curve 3. It is clear from the phase relationships of curves 1 and 3 that the methyl radical is most abundant in a zone between the oxygen-rich and methane-rich zones.

With the propane-oxygen flame there was no evidence of  $CH_3$  production.

In a formal sense both these results might be attributed to direct interaction of the hydrocarbon and oxygen which would yield:

and

$$CH_4 + O_2 \rightarrow CH_3 + HO_2$$

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$$C_3H_8+O_2\rightarrow C_3H_7+HO_2$$
.

The temperature coefficient of HO<sub>2</sub> formation, however, was slightly negative as compared with the high positive value qualitatively observed in the case of CH<sub>3</sub> formation, and although this might be attributed to greater instability of HO<sub>2</sub> at the higher temperatures, there would seem to be no valid reason at present for abandoning the Lewis and von Elbe scheme whereby methyl radicals are formed as a result of:

 $OH+CH_4\rightarrow CH_3+H_2O$  followed by

Here also we have to invoke a considerable thermal instability of formaldehyde, since this intermediate was found, as indicated above, to possess a large negative temperature coefficient. Since, however, formaldehyde is assumed to react according to the equation.

# $HCHO + O_2 \rightarrow HCOO + OH$ ,

a more rapid production of OH would result, and some of these would contribute to the methyl formation.

## CONCLUSIONS

It is evident to the author that the results summarized above should not be used as a basis for speculation regarding chemical processes occurring in combustion. However it is to be anticipated that by the utilization of recent advances in mass-spectrometric technique, the employment of wider diaphragms, deutero compounds, and negative ions in certain instances, and more systematic calibrations, a considerable body of otherwise unobtainable material may be accumulated. How far this will confirm or modify our present ideas on combustion is a question for the future. Some of the apparent disadvantages in the present apparatus, such as the destruction of surface-sensitive radicals in the diaphragm, may eventually turn out to be assets and assist in elucidating the important though still obscure role of surface reaction. Undoubtedly the spectroscopic method, in the few instances where it is applicable, is as yet simpler and more reliable than the mass-spectrometric method. The latter, however, is capable of considerable development and should provide a useful means of studying the behavior of intermediates which offer little opportunity for study by any other method.