

THE MASS SPECTROMETRY OF FREE RADICALS

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A STUDY of the free radicals which are intermediates in many gas-phase reactions is of great importance in understanding the mechanisms of these reactions. There are at present only a few experimental methods by which the chemical nature of free radicals can be studied; of these methods optical spectroscopy has been very successful with certain radicals,¹ while microwave spectroscopy and paramagnetic resonance have as yet found little application to gaseous radicals. Mass spectrometry has been of increasing importance during the last two decades, since it affords a simple method of identifying a radical by its molecular weight. The experimental difficulties of transferring a sample from relatively high pressure reaction systems to the very low pressure mass spectrometer without losing any radicals through collisions in the gas phase or on surfaces, and of preventing the formation of radicals by surface reactions in the mass spectrometer itself, have been a severe limitation on the method.

The mass spectrometer

(a) **Instrumental.**—Mass spectrometry began in J. J. Thompson's experiments with "anode rays" or "positive rays", and in F. W. Aston's separation of gaseous ions of different masses (or rather, mass/charge ratios) by focusing beams of these ions with electrostatic and magnetic fields. The modern instrument,^{2,3} however, shows more clearly its descent from that of Nier,⁴ and it is this type which has been used to study gaseous radicals.^{5,6}

Fig. 1 shows schematically a Nier-type mass spectrometer. An electron beam (*E*), produced by a heated filament (*F*), ionizes gas molecules in a metal box (*B*), which is at a high positive potential (usually 2 kv) with respect to earth. The positive ions (*J*) are drawn through a slit in the box by a potential field formed by a stack of plates, the last of which is at earth potential; some of these plates are used as an electrostatic lens to focus the ion beam on a small slit in the last plate (*D*). Having left the source, the ions travel down a metal tube (*T*), through a magnetic field (*M*) which causes them to move in a circular path; the magnetic field is uniform and extends over a 60° or 90° sector, and acts to focus an ion beam of uniform

¹ Norrish and Thrush, *Quart. Rev.* 1956, **10**, 149.

² Dunning, *Quart. Rev.* 1955, **9**, 23.

³ Duckworth, "Mass Spectroscopy", Cambridge University Press, Cambridge, 1958.

⁴ Nier, *Rev. Sci. Instr.*, 1947, **24**, 119.

⁵ Lossing, *Ann. New York Acad. Sci.*, 1957, **67**, 499.

⁶ Beckey, *Angew. Chem.*, 1958, **70**, 327.

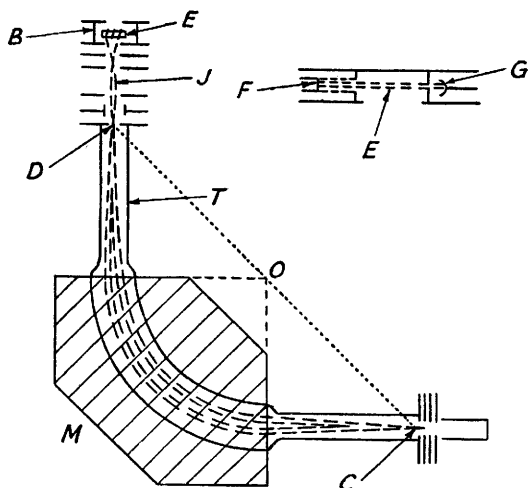


FIG. 1 *Nier-type mass spectrometer.* The N pole of the magnet (*M*) is above the paper, and the S pole below. The inset shows the electron gun at right angles to the plane of the main diagram, with the filament (*F*) and the electron collector (*G*).

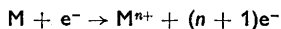
energy on a collecting slit (*C*). Ions of different mass/charge ratios require different magnetic fields to focus them on *C*. Behind the collecting slit a metal cup collects the ions, and the current so formed is amplified by an electrometer. In order to prevent ion-ion and ion-molecule collisions and also space-charge effects in the ion beam, the pressure in the instrument is kept as low as possible (usually 10^{-7} to 10^{-5} mm.) The condition for focusing is that *C*, *O*, and *D* are collinear, with $OC = OD$ (Fig. 1).

This instrument gives constant deviation, direction focusing, with the mass of a singly charged ion, in focus, related to the magnetic field (*H*) and the ion accelerating potential (*V*) by:

$$mV \propto H^2$$

A mass spectrum can be scanned with either *V* or *H* constant, the other being varied; in practice magnetic scanning is more usual.

(b) *Uses.*—The probability of occurrence of the process



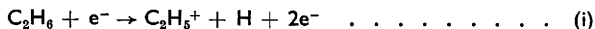
is proportional to the electron beam intensity, the pressure of *M* and the ionization cross section of *M*; the last is zero for an electron beam whose energy is less than the *n*th ionization potential (I_n) of *M*, and it increases with the excess of electron energy for a beam of greater energy than I_n . The probability of forming M^{2+} is always much less than the probability of forming M^+ , and only singly charged ions need be considered here.

The use of a mass spectrometer for qualitative and quantitative analysis is based on the fact that, other parameters being kept constant, the presence

of an ion beam M^+ is diagnostic for the presence of M , and the relative intensities of different ion beams from a mixture are proportional to the products of the ionization cross sections and the pressures of the parent molecules. One major complication must be considered here; this is that a polyatomic molecule gives not only parent ions formed by abstraction of an electron, but also fragment ions formed by processes of the type:



where A and B may be polyatomic. Thus ethane gives ions $C_2H_6^+$, $C_2H_5^+$, $C_2H_4^+$, CH_3^+ , etc. The energy required for the process



is the dissociation energy of the C_2H_5-H bond plus the ionization potential of the C_2H_5 radical, *i.e.*, $D(C_2H_5-H) + I(C_2H_5)$, which is greater than the energy $I(C_2H_6)$ for the process



so that at low electron energies (*ca.* 15v) the parent peak (ii) predominates, but the spectrum is very dependent on electron energy. As the electron energy is increased, the spectrum changes, process (i) becoming more important, and at high energy (50—70 v) the parent peak is quite small, and the relative heights of the peaks will be much less dependent on the energy of the electrons. Quantitative analytical applications require that the spectrum, or "cracking pattern", obtained from a pure compound, at the appropriate electron energy, be known accurately; analysis of a mixture is then a question of solving several simultaneous linear equations. If the cracking pattern of some of the components is not known, or cannot be determined, a complete quantitative analysis is not possible.

The electron energy at which an ion current first appears is called the appearance potential (A) for the ion in question; it is equal to the ionization potential (for a parent ion), or the fragment ionization potential plus the energy of the bond broken in fragmentation plus any kinetic energy of fragments; a plot of ion current against electron energy should, therefore,

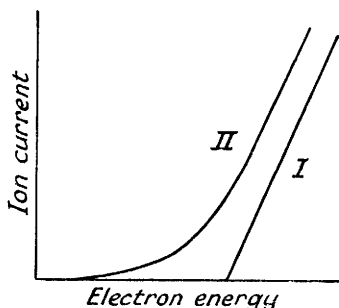


FIG. 2 Ionisation efficiency curves: I, monoenergetic electrons; II, electrons with Boltzmann energy distribution.

enable one to determine these quantities. For constant energy electrons the curve is shown at I in Fig. 2; but the electrons are obtained from a heated filament, and, therefore, they have a Boltzmann distribution of energy centred on the measured electron energy. Electrons at the high-energy end of the Boltzmann distribution will cause ionization when the measured electron energy is below the appearance potential, and the curve obtained is, therefore, like II in Fig. 2. Various empirical methods have been used for obtaining the appearance potential from such curves. These include extrapolation of the more or less linear, upper, part of the curve to the energy axis,⁷ estimation of the "initial upward break" of the curve from the energy axis,⁸ application of a tangent of "critical slope" to the plot of log (ion current) against electron energy,⁹ and extrapolation of the energy differences between the curve in question and that for a standard gas to zero ion current.¹⁰ The obvious differences between these methods are largely removed in practice by measuring appearance potentials relative to that of a standard gas (*e.g.*, argon) whose spectroscopic ionization potential is accurately known; this is necessary also because irreproducible effects due to contact potentials in the electron gun, and field penetration in the ionization chamber, make the measured electron energy different from the true one.

Three experimental methods exist for minimising the effect of the Boltzmann distribution of energy in the electron beam¹¹ or for minimising the distribution itself;¹² these methods suffer from the disadvantage that the overall sensitivity of the instrument is much reduced, and it has not yet been possible to apply them to the study of free radicals.

Application to free radicals

(a) **Principles of the Method.**—The appearance potential of the ion CH_3^+ from CH_4 is equal to the dissociation energy of the $\text{CH}_3\text{-H}$ bond plus the ionization potential of the CH_3 radical formed plus the kinetic energy of the fragments, *i.e.*,

$$A(\text{CH}_4 \rightarrow \text{CH}_3^+) = D(\text{CH}_3\text{-H}) + I(\text{CH}_3) + \text{kinetic energy}$$

An empirical rule by Stevenson¹³ states that the kinetic energy is zero if the ionization potential of the non-ionized fragment is greater than that of the ionized fragment, which is usually the case: $I(\text{H}) > I(\text{CH}_3)$. The appearance potential of the ion CH_3^+ from CH_3 is simply the ionization potential of the radical

$$A(\text{CH}_3 \rightarrow \text{CH}_3^+) = I(\text{CH}_3)$$

⁷ Mariner and Bleakney, *Phys. Rev.* 1947, **72**, 807.

⁸ Smith, *Phys. Rev.* 1937, **51**, 263.

⁹ Honig, *J. Chem. Phys.*, 1948, **16**, 105.

¹⁰ McDowell and Warren, *Discuss. Faraday Soc.*, 1951, **10**, 53.

¹¹ Morrison, *J. Chem. Phys.*, 1954, **22**, 1219.

¹² Fox, Hickam, Grove, Kjeldaa, *Rev. Sci. Instr.*, 1955, **26**, 1101; Hutchison, *J. Chem. Phys.*, 1956, **24**, 628.

¹³ Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35

which is clearly less than $A(\text{CH}_4 \rightarrow \text{CH}_3^+)$. If the electron energy (E) were such that $A(\text{CH}_3 \rightarrow \text{CH}_3^+) < E < A(\text{CH}_4 \rightarrow \text{CH}_3^+)$, the ion beam CH_3^+ would only be formed from methyl radicals; an ion beam with mass 15 is then evidence for the presence of methyl radicals in the gas sample. At high electron energy, however, there will be a peak at mass 15 due to methane (and other molecules containing a methyl group); detection of the radicals in the sample is, therefore, most conveniently done at low electron energies. Unfortunately, the rapid change of cracking patterns with electron energy, and the relatively low ionization efficiency, at low energies makes it necessary to use beams of high-energy electrons for measurement of concentrations, even for radicals.

The utility of the mass spectrometer in observing free radicals is due to several factors: (i) the method is more specific than Paneth and Hofeditz's mirror,¹⁴ the catalytic probe,¹⁵ or Wrede-gauge¹⁶ methods, since it is diagnostic for molecular weight; (ii) mass spectrometry is less selective than optical spectroscopy,¹ for this is dependent on the radical's having a considerable absorption in a suitable energy range; for example the HO_2 radical has not yet been detected spectroscopically, although its detection was one of the early triumphs of the mass-spectrometric method;¹⁷ (iii) although the ion source must operate at very low pressures, it is possible to sample through a pinhole leak (see below) from much higher pressures, and thus bridge the gap between the low pressures necessary for Paneth techniques and the rather high pressures desirable in spectroscopy; (iv) continuous records of concentration changes can be obtained by focusing on one peak; (v) the mass spectrometer can be used as a fast scanning instrument to record rapid changes in concentration of several substances at once; (vi) the presence of oxygen in the mixture, which makes the mirror technique impossible, and often renders spectroscopic techniques difficult owing to Schumann absorption, is no disadvantage to the mass spectrometer.

(b) **Experimental Difficulties.**—(i) *Sampling.* The essential nature of free radicals, *viz.*, their reactivity, especially their tendency to recombine or react on surfaces, makes it difficult to transfer radicals from the gas system under investigation into the electron beam of the mass spectrometer. The gas system in which the radicals are produced, *e.g.*, a homogeneous gas reaction, is often at too high a pressure for direct coupling to the ion source, and some form of sampling leak is required. A common type of leak used in simple analytical mass spectrometry is a sintered disc; this is of no use in free-radical studies, as it presents to the gas a large surface area, thus giving radicals a high chance of recombining. The ideal form of leak is a single pinhole in a very thin diaphragm, so that molecules may pass straight through without collision with the walls of the leak

¹⁴ Paneth and Hofeditz, *Ber.*, 1929, **62**, 1335.

¹⁵ Tollefson and LeRoy, *J. Chem. Phys.*, 1948, **16**, 1057.

¹⁶ Wrede, *Z. Physik*, 1929, **54**, 53.

¹⁷ Foner and Hudson, *J. Chem. Phys.*, 1953, **21**, 1608.

The types of leak most often used are a hole sparked in the very thin end of a quartz or glass thimble,¹⁸ or a hole drilled in gold leaf.¹⁹

A serious source of error is the possibility of a molecule's colliding with the hot filament, which is usually a tungsten wire heated electrically to about 2000°C; there is a high probability that any molecule hitting this filament will dissociate, thereby forming radicals, which may be subsequently ionized. This effect can be lessened by differential pumping of the filament region, which, to be effective, requires that the filament be in an enclosure separate from the rest of the ion source, and with its own pump, the only connection between the two regions being the slit by which the electrons enter the ionization chamber. This system was used in the first paper on this subject, by Eltenton;¹⁹ Lossing and Tickner¹⁸ enclose the filament in a chamber which is pumped out by the pump on the analyser tube, *via* a series of holes in the six ion-accelerating plates (see Fig. 5), the sides of this pumping path being closed by glass spacing rings between these six plates.

(ii) *Calibration.* It has already been stated that if the cracking patterns of all the components of a mixture are not known, it is not possible to make a full quantitative analysis of the mixture; knowledge of the cracking pattern of a pure component means not only knowledge of the relative heights of the various peaks, but also the absolute sensitivity under the experimental conditions used. In the case of free radicals, this presents some formidable problems, for it is not possible to introduce into the mass spectrometer pure free radicals at a known pressure. In the rare cases where it is possible to say that only one free radical contributes to the mass spectrum, the spectrum of this radical can be found by subtracting the spectra due to all other components, but it is still necessary to measure the sensitivity for this one radical before its absolute concentrations can be measured. LeGoff and Letort²⁰ obtained the spectrum of the methyl radical, having made the radical by pyrolysis of methyl iodide or tetramethyl-lead on a tungsten filament. They were able to show that peaks at masses 13 and 14 were not due to CH or CH₂ radicals, since the appearance potentials were higher than those of peaks 15 and 16; after subtraction of contributions due to methane and ethane, there remained the following spectra, due to the methyl radical:

Mass	From methyl iodide	From tetramethyl-lead
15	100	100
14	32 ± 4	40 ± 4
13	9 ± 1	8 ± 1
12	3.6 ± 0.3	—

¹⁸ Lossing and Tickner, *J. Chem. Phys.*, 1952, 20, 907.

¹⁹ Eltenton, *J. Chem. Phys.*, 1947, 15, 455.

²⁰ LeGoff and Letort, *J. Chim. phys.*, 1956, 53, 480.

In simple cases such as these, it is possible to obtain a value for the sensitivity for the radical by assuming a 100% material balance; e.g., in the pyrolysis of dimethylmercury, the pressures of methane and ethane and the reactant can be obtained from their (known) mass-spectrometric sensitivities under the conditions of the experiment, and, a perfect carbon balance being assumed, the pressure of methyl (the only other product) can be calculated. In this way Lossing and Tickner¹⁸ found the sensitivity of their instrument for methyl radicals to be 0.47 ± 0.07 of the sensitivity for methane.

The difficulty of such a calibration is increased when, as is often the case, the reaction producing the radicals is at a high temperature; the magnitude of a mass-spectral peak decreases with increasing temperature. This decrease is largely due to a change in the flow through the sampling leak, caused by the temperature coefficient of viscosity of the gas, but there is

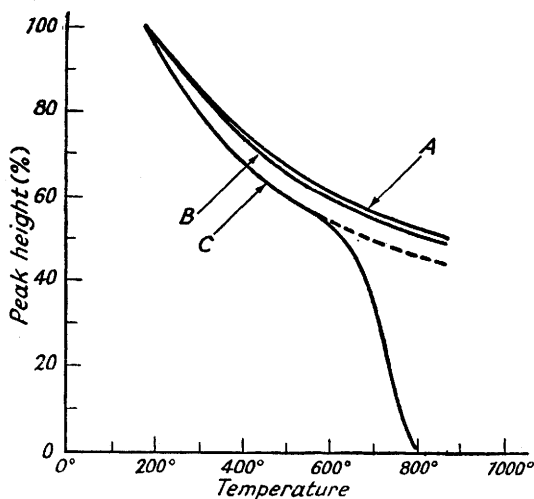


FIG. 3 *The temperature coefficient of sensitivity.* A, Methane; B, ethane; C, dimethylmercury. (Reproduced, by permission, from *J. Chem. Phys.*, 1953, 20, 907.)

also an instrumental effect. Fig. 3 shows the variation of sensitivity with temperature for methane, ethane, and dimethylmercury;¹⁸ the sudden drop in the curve for dimethylmercury is due to its disappearance by decomposition, the broken curve being an extrapolation of the low-temperature part of this curve, obtained from the almost linear plot of sensitivity against $1/T$. The temperature sensitivity of methyl, which cannot be measured, was assumed to be the same as that for methane; since their masses are nearly equal, the temperature variation in viscosities would be expected to be very similar.

(c) **Apparatus.**—In this section three apparatuses will be described which illustrate many of the general principles outlined above; they are

the first apparatus used in studying free radicals in chemical reactions, by Eltenton,¹⁹ a more typical, later, apparatus developed by Lossing⁵ and extensively used throughout Canada, and the molecular beam sampling system of Foner and Hudson.²¹

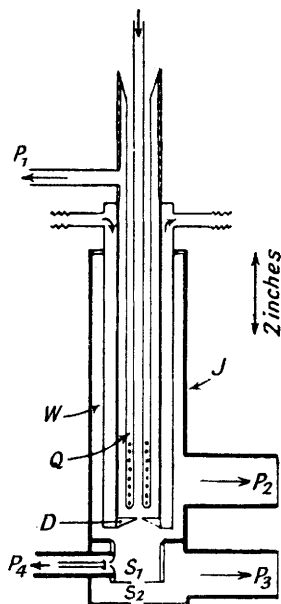


FIG. 4 *Eltenton's reaction vessel and ion source.* (Reproduced, by permission, from *J. Chem. Phys.*, 1947, 15, 455.)

Eltenton's apparatus is shown in Fig. 4; a considerable limitation, in this case, was imposed by the use of a 180° Dempster-type mass spectrometer²² in which the whole of the ion source is contained in the magnetic field, and is less accessible. This apparatus is, nevertheless, noteworthy for the fact that the ionization and ion-accelerating chambers were evacuated by two, separate, large diffusion pumps (P_2 , P_3), while the filament (P_4) and analysing chambers were separately evacuated by smaller pumps. The reaction vessel consisted of a spiral heater wound in a double-walled quartz tube (Q) down the centre of which the reactant was introduced. The reaction zone was sampled through a gold-leaf diaphragm (D), the remaining gases being pumped out by P_1 through the annular space between Q and the water jacket (W). The ion-source pressure was maintained at 1 micron, which is considerably higher than would be the case in a more modern instrument, and dangerously high if one wishes to avoid all ion-molecule reactions; the pressure in the reaction vessel could be as high as 10 cm. Low electron energies were used for detecting radicals.

²¹ Foner and Hudson, *J. Chem. Phys.*, 1953, 21, 1374.

²² Dempster, *Phys. Rev.* 1918, 11, 316.

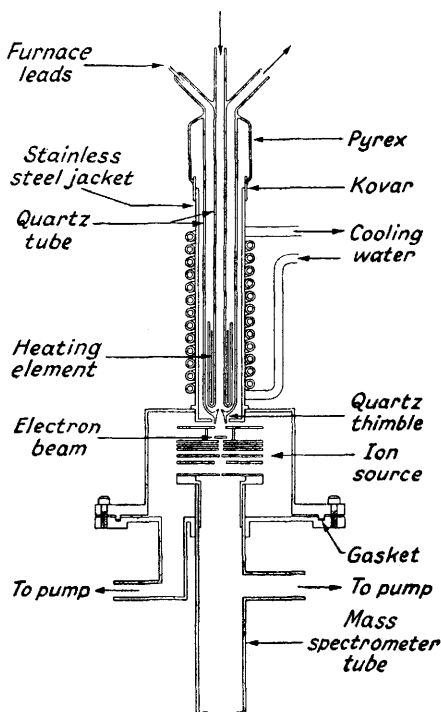


FIG. 5 Lossing's reaction vessel and ion source. (Reproduced, by permission, from *Ann. New York Acad. Sci.*, 1957, 67, 499.)

Fig. 5 shows a recent version of the apparatus developed by Lossing and Tickner,¹⁸ which differs from Eltenton's mainly in being built around a 90° Nier-type mass spectrometer. The filament pumping, *via* a series of holes in the ion-accelerating plates, has already been described. The sample leak consists of a quartz thimble, through the thin top of which a hole is sparked by a Tesla discharge; the holes used are about 30 microns in diameter, and 10–20 microns long.

The simple pinhole leak gives a beam of molecules distributed over a very wide angle, many of which will, therefore, collide with the walls of the ion source before being ionized; Foner and Hudson's molecular beam system²¹ (Fig. 6) greatly reduces the beam spread and increases the chance of a molecule's entering the electron beam before striking a wall. Slits 1 and 2 are circular holes; the space between slits 1 and 2 was maintained at about 5×10^{-3} mm. pressure, and the ion source at about 10^{-6} mm. The molecular-beam intensity was a maximum when the mean free path in the first (scattering) region was equal to the distance between slits 1 and 2. The molecular beam passed through the ion source along the path of the electron beam, instead of at right angles to it.

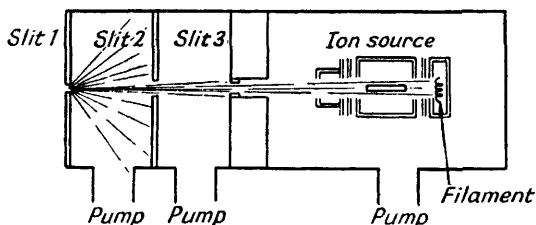


FIG. 6 *Molecular beam sampling system.* (Reproduced, by permission, from *J. Chem. Phys.*, 1953, **21**, 1374.)

The sensitivity of the instrument to the sample was greatly increased by "chopping" the sample beam in the first region, by means of a vibrating reed driven electronically, and by amplifying the oscillatory component of the ion current at this same frequency. A discrimination of 10,000 in favour of the sample beam rather than the background, was obtained; if the background arose from beam scattering an additional tenfold discrimination was obtained by using the molecular beam system, since the density in the beam was about ten times that in the rest of the apparatus. The sensitivity was still further increased by the use of an electron multiplier on the ion collector, and by using pulse-counting techniques for very weak signals.

The majority of experiments on free radicals with mass spectrometers have employed a flow reaction system and slow scanning of the mass spectrum. A few investigators have made use of the fast scanning possibilities of the mass spectrometer. With a conventional instrument, this can be achieved with electrostatic scanning, by applying a sawtooth voltage waveform to the ion-accelerating plates, the resulting modulated ion current being displayed on a cathode ray tube, whose time-base is derived from the sawtooth wave; such an arrangement was used by Foner and Hudson.²¹ Fast scanning is also a feature of the time-of-flight mass spectrometers, which are based on the principles of the cyclotron or the drift tube.²³ Kistiakowsky and Kydd²⁴ have used a drift tube type of spectrometer to scan a spectrum every 50 microseconds, but the reproducibility of the spectrum is sacrificed for speed, owing to statistical variation in the number of ions formed in each pulse.

Examples

Mass spectrometers have been used to study free radicals in pyrolyses, photolyses, combustion reactions including flames, and heterogeneous reactions. The identification of free radicals in these processes has proved of great assistance in determining the mechanisms of the reactions, but, since the failure of the mass spectrometer to detect a particular radical

²³ Ref. 3, pp. 74-85.

²⁴ Kistiakowsky and Kydd, *J. Amer. Chem. Soc.*, 1957, **79**, 4825.

cannot be taken as evidence that the radical is not present in the reaction, it is rare for any reaction mechanism to be unequivocally determined by this technique. In some favourable cases it has been possible to obtain an estimate of the rate of an elementary radical reaction, but considerable difficulty is found, not only in the measurement of absolute concentrations in the mass spectrometer, but also in the estimation of contact times and temperatures in the flow types of reaction vessel usually used. These points will be illustrated in the following sections of this Review; the measurement of ionization potentials of free radicals, and the subsequent estimation of bond dissociation energies will also be discussed.

(a) **Detection of Radicals and Measurements of Concentration.**—

(i) *Pyrolyses.* The first study of radicals formed by pyrolysis was made by Eltenton¹⁹ in the pyrolysis of some simple hydrocarbons. Using a quartz vessel, he found methyl radicals to be present in the pyrolysis of methane at 10–300 microns pressure and 800–1100° C. The production of methyl radicals had an activation energy of 46 kcal./mole; methylene was not found, although it could easily be detected, in the same apparatus, from the pyrolysis of diazomethane. This was interpreted in favour of a split of the methane molecule into a methyl radical and a hydrogen atom; the latter species was not found, being presumed to recombine rapidly to form molecular hydrogen, which was detected.

The ethyl radical proved difficult to detect in Eltenton's instrument, owing to the fact that ethylene, which was almost always present with ethyl, has an ionization potential only about two volts higher than that of ethyl, and the isotope $^{13}\text{CH}_2\text{-}^{12}\text{CH}_2$ at mass 29 interferes with the parent peak of C_2H_5 . Some radicals which might confidently have been expected to be present were undetected, e.g., vinyl in the pyrolysis of propene, which yielded abundant methyl radicals.

Lossing and Tickner¹⁸ studied the pyrolysis of dimethylmercury and di-*t*-butyl peroxide, using a few microns of reactant in 5 to 10 mm. of helium; the carrier gas reduces the probability of wall reactions by hindering diffusion to the walls, and also assists in obtaining a high flow rate. The instrument was calibrated for methyl radical concentrations, as described above, and it was then possible to study the first-order decomposition rate of the di-*t*-butyl peroxide; the decomposition was found to have an activation energy of 37 kcal./mole, in good agreement with previous work.²⁵ All the ethane formed in the decomposition of dimethylmercury being assumed to come from the recombination of methyl radicals, the collision efficiency of this process at 859° was of the order of 10^{-2} ; this calculation neglected concentration gradients in the furnace. Ingold and Lossing,²⁶ who studied this radical recombination more extensively, found it to consist of a second-order, homogeneous, reaction,

²⁵ Raley, Rust and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88; Szwarc, *J. Chem. Phys.*, 1951, **19**, 698.

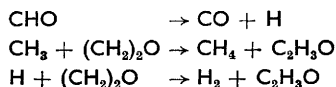
²⁶ Ingold and Lossing, *J. Chem. Phys.*, 1953, **21**, 1135; Ingold, Henderson, and Lossing, *ibid.*, p. 2239.

and a first-order reaction, presumed to be heterogeneous. Considerable difficulty was encountered in the measurement of contact times in the furnace; by taking measurements with a retractable furnace at several distances from the sampling leak, the amount of reaction corresponding to the reaction zone formed by retracting the furnace could be measured, and the unknown concentration gradients in the furnace itself could be ignored. From a knowledge of the temperature gradient in the relevant zone, the appropriate contact time could be calculated. The recombination of methyl radicals was then found to be proportional to the total pressure, and had an activation energy of -1.5 kcal./mole, attributed to the decrease in the lifetime of the activated $C_2H_6^*$ complex, with increasing temperature.

Lossing, Ingold, and Henderson²⁷ studied the pyrolysis of some simple compounds containing the C-O-C linkage. They found methyl radicals in the decomposition of ethylene oxide, but very few in the case of dioxan; no other radicals were detected. In the case of ethylene oxide, they suggested a mechanism based on the primary reactions:



followed by:



and rapid decomposition of the C_2H_3O radical, plus various radical-radical reactions. Failure to detect H, CHO, or C_2H_3O implies that these species, if present, react very rapidly under the conditions used (*ca.* 10 microns of reactant in 15 mm. of helium at about 900°). No stable products of higher molecular weight than $(CH_2)_2O$ were found, implying that the C_2H_3O radical, if it exists, decomposes. It being assumed that there are no reactions for the formation of methane or the removal of hydrogen atoms other than the above, reaction (iv) occurred in at least 37% of the molecules decomposed; the absence of methylene was regarded as evidence against the reaction:



proposed by Fletcher and Rollefson.²⁸

The pyrolysis of several aromatic compounds has been studied at over 1000° , and many aromatic radicals were detected, together with considerable free carbon and hydrogen, suggesting the occurrence of heterogeneous processes.²⁹

(ii) *Photolyses*. The study of high-temperature reactions entails the

²⁷ Lossing, Ingold, and Henderson, *Discuss. Faraday Soc.*, 1953, 14, 34.

²⁸ Fletcher and Rollefson, *J. Amer. Chem. Soc.*, 1936, 58, 2135.

²⁹ Ingold and Lossing, *Canad. J. Chem.*, 1953, 31, 30.

disadvantage that the more unstable radicals will themselves be pyrolysed. For example, the 2- and the 4-methylbenzyl radical, formed almost quantitatively from their iodides at 825° , are themselves pyrolysed at any higher temperatures, being completely dissociated at 1000° ; dissociation of the 3-methylbenzyl radical only becomes appreciable above 1050° .³⁰ Photolysis offers the chance of producing, at low temperatures, radicals which are unstable at the high temperatures necessary for pyrolysis. Unfortunately, in the optimum conditions for mass spectrometric observation of the radicals in a homogeneous system, *i.e.*, at a low pressure of reactant in a carrier gas, most reactants have such low absorption coefficients that sufficient light cannot be absorbed with the available path lengths; it is, therefore, necessary to resort to photosensitisation or to flash-photolytic techniques.

Mercury-photosensitised reactions have been studied by Lossing and his co-workers in the apparatus shown in Fig. 7. The mercury lamp is of

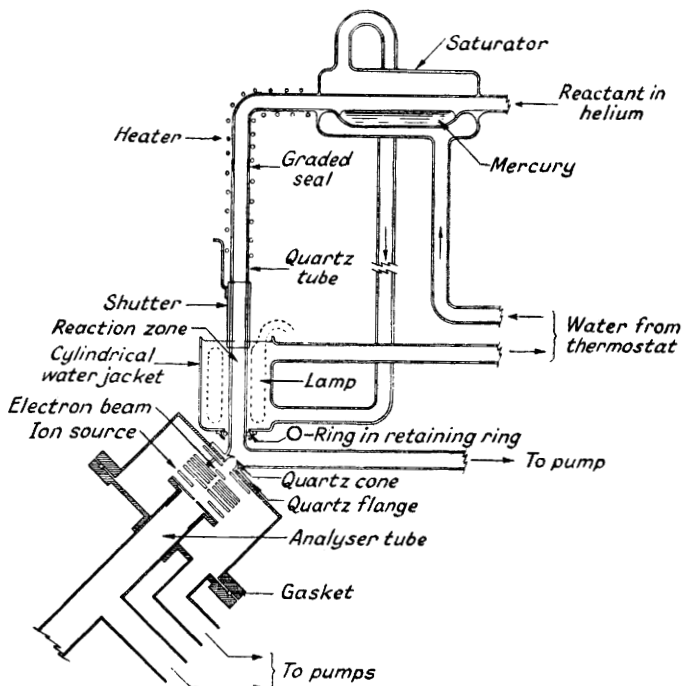


FIG. 7 Reaction vessel for photolytic studies. (Reproduced, by permission, from *Canad. J. Chem.*, 1957, 35, 305.)

special design,³¹ the discharge being constrained in a zig-zag path which almost fills the annular lamp body; the body of the lamp and the mercury

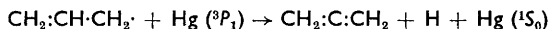
³⁰ Farmer, Marsden, and Lossing, *J. Chem. Phys.*, 1955, 23, 403.

³¹ Lossing, Marsden, and Farmer, *Canad. J. Chem.*, 1956, 34, 701.

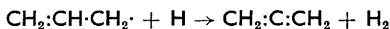
saturator were surrounded by water at 55—60°, so that the partial pressure of mercury in the gas system was 18—25 microns; the absorption of 2537 Å radiation in the reaction volume of 1.39 c.c. was calculated to be greater than 10^{18} photons/sec. As in pyrolytic studies, the various reactants, at partial pressures of a few microns, were carried in a stream of helium at a pressure of about 10 mm.

The detection of free radicals at low electron energies could conceivably be falsified in the case of photolyses if any excited molecules were present; the ionization potential of an excited molecule, *e.g.*, $C_3H_6^*$, would be lower than that of the molecule in the ground state, and the appearance potential of any ion, *e.g.*, CH_3^+ , from it might also be lower than the normal appearance potential from the ground state molecule. In fact, no such lowering of the ionization potentials of stable molecules was observed, the lifetimes of any excited molecules being probably too short.³¹

In the mercury-photosensitised decomposition of ethylene only acetylene and hydrogen were detected, supporting the idea of a molecular rearrangement. Propene gave large quantities of allyl radicals, allene, and hydrogen; when the contact time was decreased by lowering the shutter (see Fig. 7) the ratio of allene to allyl decreased rapidly, indicating that the allene is a secondary product from allyl. In view of the high concentration of allyl radicals and Hg (3P_1) atoms, compared with that in conventional photosensitization experiments, the allene was presumed to have been formed by:



The reaction



would be too slow at 60° to form the large amounts of allene found, and, similarly, a unimolecular split of the excited allyl, formed in the initial reaction of propene with an Hg (3P_1) atom, into allene and a hydrogen atom would be expected to have an activation energy of at least 30 kcal./mole.

A mass-spectrometric study of flash-photolytic reactions has been made by Kistiakowsky and Kydd,²⁴ who used a time-of-flight mass spectrometer. It was found that the photolytic flash suppressed the mass spectrum for several hundred microseconds, unless a negatively charged grid were placed between the lamp and the sampling leak; the disturbance was shown to be photochemical rather than electrical, and may be connected with a photoelectric effect's forming ions in the reaction cell, which, in some way, interfere with the working of the ion source. In the flash photolysis of keten, methylene radicals could not be detected, but the formation of ethylene was almost complete in 50 microseconds; this was thought to be due to the rapid reaction:



(iii) *Combustion reactions.* Flames have been studied by Eltenton¹⁹ and by Foner and Hudson.²¹ The former claimed to observe the HO₂ radical (amongst others) in methane, propane, and carbon monoxide flames, but, surprisingly, could not find OH. Foner and Hudson found some H, OH, and O radicals in a hydrogen-oxygen flame, but the maximum radical concentration was of the order of 1%, and HO₂ could not be found, even up to a burner pressure of half atmospheric. In a methane-oxygen flame they measured the spectrum with 15, 18, and 48 v electrons, but were unable to identify all the components, because of the complexity of the spectrum, and the possible occurrence of excited molecules or metastable species (not radicals) of unknown cracking patterns; the only radical definitely identified was methyl, which was shown by the very large peak at mass 15, and by appearance-potential measurements. Identification of HO₂ was complicated by the occurrence of methyl alcohol in unknown amounts, since this has a peak at mass 33 due to ¹³CH₃·OH.

Ingold and Bryce³² confirmed the presence of HO₂ and OH in the hydrogen-oxygen reaction at 1000°, but were unable to find any H or O atoms. They also investigated the reactions of methyl radicals, from the pyrolysis of dimethylmercury, with oxygen³² and with nitric oxide:³³ collision efficiencies of 10⁻⁴ to 10⁻³ were reported in each case, and a large number of products, including free radicals, was observed. In these experiments the heating element was exposed to the gas stream, and heterogeneous reactions were thus highly probable.

The HO₂ radical was first conclusively demonstrated by Foner and Hudson¹⁷ in the reaction of hydrogen atoms, from a Wood's discharge tube, with molecular oxygen carried in an inert gas; the peak at mass 33 increased and decreased as the discharge was switched on and off, although that at mass 32 was unaffected. Large yields of HO₂ were later obtained from the reaction between hydrogen peroxide and the products of a discharge in water vapour.³⁴

Robertson³⁵ also observed HO₂ in the reaction of hydrogen atoms with oxygen; in this case, the reaction products, from the main flow line, diffused down a side tube at the end of which was the leak to the mass spectrometer. Under the conditions used a radical would make many thousands of collisions in the gas phase and on the walls, during this diffusion process; it is, therefore, not surprising that OH and O could not be detected in the reaction. From the fact that the HO₂ concentration increased with increasing pressure in the reaction vessel, Robertson deduced that the excited HO₂* formed in the reaction:



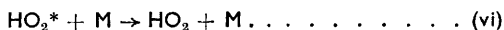
³² Ingold and Bryce, *J. Chem. Phys.*, 1956, **24**, 360.

³³ Bryce and Ingold, *J. Chem. Phys.*, 1955, **23**, 1968.

³⁴ Foner and Hudson, *J. Chem. Phys.*, 1955, **23**, 1364.

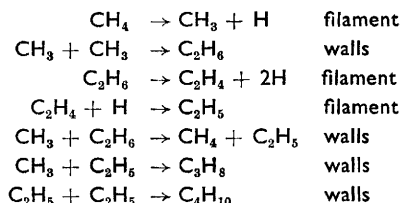
³⁵ Robertson, "Applied Mass Spectrometry", Institute of Petroleum, London, 1954, p. 112.

was stabilised by gas-phase collisions:



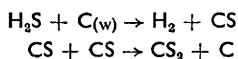
and he showed that a lifetime of 10^{-11} to 10^{-12} seconds for the excited complex, was sufficient if reactions (v) and (vi) occurred at every collision.

(iv) *Heterogeneous reactions.* In studying cracking reactions which occur on heated metal filaments, LeGoff³⁶ and Robertson³⁷ placed the heated filament in the mass spectrometer's ion source, above the top plate or ion repeller, which was replaced by a wire gauze. The reactant flowed over the catalytic filament at a low pressure (10^{-6} to 10^{-3} mm.) so that homogeneous reactions were a minimum. The catalytic filament and the surroundings need to be at the same potential as the ionization chamber, to prevent electrons from the catalytic filament being accelerated so that they might ionise gas molecules in the reaction vessel (*i.e.*, above the ion repeller.³⁸ Robertson³⁷ found methyl radicals in the decomposition of methane on a platinum filament at about 1000° ; the formation of ethane, propane, and butane was attributed to secondary reactions on the cold walls of the mass spectrometer, the overall reaction scheme being:



Ethyl radicals were not detected in the decomposition of ethane, only ethylene and hydrogen being observed; this was attributed to a molecular dehydrogenation process on the filament.

Blanchard and LeGoff³⁹ showed that there was a difference in the mechanisms of pyrolysis of some substances on clean and carburised tungsten filaments. On clean tungsten, only H_2 and S_2 were detected in the decomposition of H_2S , whereas on carburised tungsten, CS and CS_2 were also found, being formed by the reactions:



Recently, some attempts have been made to use field emission as a source of ions for a mass-spectrometric study of species adsorbed on metal surfaces; this method of ionization has the great advantage that fragment ions are produced only in very small quantities, compared with electron-impact ionization; it is, therefore, much easier to identify free

³⁶ LeGoff, *J. Chim. phys.*, 1953, **50**, 423.

³⁷ Robertson, *Proc. Roy. Soc.*, 1949, *A*, **199**, 394.

³⁸ LeGoff, *J. Chim. phys.*, 1956, **53**, 369.

³⁹ Blanchard and LeGoff, *Canad. J. Chem.*, 1957, **35**, 89.

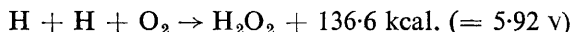
radicals. Gomer and Inghram⁴⁰ detected the $\text{CH}_3\cdot\text{O}$ radical from methyl alcohol adsorbed on the surface of tungsten, and Beckey⁴¹ has found the $\text{C}_2\text{H}_5\cdot\text{O}$ radical from ethyl alcohol on tungsten.

(b) **Ionization Potentials and Bond Energies.**—The experimental difficulties in measuring ionization potentials have already been described; even if they can be overcome, electron-impact ionization potentials are thought to correspond to “vertical” Franck–Condon transitions, and may be appreciably higher than the “adiabatic” spectroscopic values. For free radicals, apart from methyl, spectroscopic values are not available, and there is no alternative to electron-impact data; for the methyl radical the electron-impact value^{36,42} of 9.85 v is only 0.01 v above the spectroscopic value.⁴³ It should be noted that the errors quoted by most workers for electron-impact values represent limits of reproducibility, and are not estimates of the absolute errors, which are often much larger.

Foner and Hudson³⁴ measured the ionization potential of the HO_2 radical as 11.53 ± 0.1 v, and its appearance potential from H_2O_2 as 15.41 ± 0.1 v; the difference between these values is the O–H bond energy in H_2O_2 , if the fragments have zero kinetic energy in the process:



Since $I(\text{H}) > I(\text{HO}_2)$, Stevenson's rule¹³ is satisfied, and the assumption of zero kinetic energy is most probably satisfactory. This gives the bond energy $D(\text{HO}_2\text{--H}) = 3.88$ v = 89.5 kcal./mole. From the (known) heat of reaction:



Foner and Hudson derived the bond energy $D(\text{H--O}_2) = 2.04 \pm 0.1$ v = 47 ± 2 kcal./mole.

The ionization potential of the NH_2 radical is 11.4 ± 0.1 v,⁴⁴ and its appearance potential from ammonia is 16.0 ± 0.1 v, giving a bond energy $D(\text{NH}_2\text{--H}) = 4.6 \pm 0.15$ v = 106 ± 3 kcal./mole, in excellent agreement with thermochemical and spectroscopic data.⁴⁵ Similarly, investigation of hydrazyl, N_2H_3 , from hydrazine gave a bond energy $D(\text{N}_2\text{H}_3\text{--H}) = 76 \pm 5$ kcal./mole.⁴⁴

Use of ionization and appearance potentials to estimate bond energies depends on a knowledge of the nature of the non-ionized, undetermined, fragments. In the above cases, there was no difficulty, as the radical formed by electron impact was simply a hydrogen atom. If the non-ionized fragment is polyatomic, there is always the possibility of its dissociating, in which case the relevant bond dissociation energy must be taken into account; there is also a possibility of the formation of negative ions, which would normally be undetermined, but which could, in principle, be

⁴⁰ Gomer and Inghram, *J. Amer. Chem. Soc.*, 1955, **77**, 500.

⁴¹ Beckey, *Naturwiss*, 1958, **45**, 259.

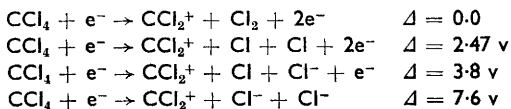
⁴² Langer, Hipple, and Stevenson, *J. Chem. Phys.*, 1954, **22**, 1836.

⁴³ Herzberg and Shoosmith, *Canad. J. Phys.*, 1956, **34**, 523.

⁴⁴ Foner and Hudson, *J. Chem. Phys.*, 1958, **29**, 442.

⁴⁵ Altshuller, *J. Chem. Phys.*, 1954, **22**, 1947.

detected. In an attempt to estimate the bond energy in the CCl_3 radical, Blanchard and LeGoff³⁹ measured the ionization potential of the CCl_2 radical formed by the pyrolysis of carbon tetrachloride on tungsten. In this case, the required bond energy is very dependent on the processes assumed for the appearance of CCl_2^+ and CCl^+ from CCl_4 ; in the former case, for instance, the possibilities are:



The values of Δ show the magnitude of the energy differences between these processes. The authors were able, by considering also the appearance of the ion CCl^+ , to restrict the possible solutions to two only, *viz.*, $D(\text{CCl}_2-\text{Cl}) = 62 \pm 7$ or 93 ± 7 kcal./mole.

A list of electron-impact ionization potentials of free radicals is given by Lossing.⁵

Conclusion

The mass spectrometer has made available considerable information on the radicals present in a wide variety of homogeneous and heterogeneous gas reactions. Many of the possibilities of the method have not yet been exploited, owing to the formidable experimental difficulties. A greater use of the molecular beam sampling system²¹ seems to be desirable to overcome the sampling problem, and electron multipliers or the use of pulse counting techniques would increase the sensitivity of the instruments used. Time-of-flight mass spectrometers have yet to prove their value, especially as fast scanning can be obtained on a Nier-type instrument without the disadvantages of the time-of-flight instrument.

An extension of the principle of low electron energy detection of free radicals should allow one to detect the presence of excited molecules, since their ionization potentials are lower than those of ground-state molecules by the amount of the excitation energy. More accurate measurements of ionization and appearance potentials will be required, and it is desirable to use a technique which eliminates the wide Boltzmann energy distribution of the electron beam²² or, alternatively, photo-ionization.⁴⁶ Excited molecules will also present more acute sampling difficulties, since they are, in general, more unstable towards wall collisions than the radicals so far detected. With these improvements in technique, which may confidently be expected within a few years, mass spectrometry should prove one of the most useful methods of following unstable intermediates in gas-phase reactions.

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⁴⁶ Lossing and Tanaka, *J. Chem. Phys.*, 1956, **25**, 1031; Hurzeler, Inghram, and Morrison, *J. Chem. Phys.*, 1958, **28**, 76.