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A Mass Spectrometric Study of Flash Photochemical Reactions. I

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A time-of-flight mass spectrometer is described briefly which presents the spectrum of a gas effusing through a pinhole from a reaction cell. The instrument produces a complete mass spectrum every 50 μsec. and the mass resolution is about $^{1}/_{40}$. The sensitivity is such that a component of the gas present at a mole fraction of 0.005 can be observed in a single spectrum with reasonable certainty. This apparatus is applied to the study of flash photochemical decompositions of ketene and nitrogen dioxide in the presence of inert gases, at total pressures of the order of 1 mm. It is made very probable that the reaction of photochemically generated methylene with residual ketene is exceedingly fast, the reaction probability on collision being at least 10^{-2}. It is also made probable that one of the products of this reaction is a radical or molecule C_3H_4O, which disappears from the reaction cell after several hundred μsec. The reaction of oxygen atoms, which are produced in the primary photochemical process of nitrogen dioxide, with residual nitrogen dioxide to form oxygen molecules and nitric oxide is very fast, the lower limit of reaction probability on collision being about 10^{-2}. No nitrogen trioxide has been observed, but significant amounts of nitrous oxide are formed as fast as are oxygen molecules. It is suggested that the primary dissociation of nitrogen dioxide by radiation of shorter wave lengths results in the formation of "hot" molecules of nitric oxide, which then react by $NO^* + NO_2 = N_2O + O_2$.

The use of a mass spectrometer in conjunction with the steady-state low pressure flow reactors has yielded much important information on unstable reaction intermediates. There are, however, significant kinetic problems, *e.g.*, flash-photochemical reactions, reactions in shock waves, some explosion phenomena, etc., to which steady-state technique is not readily applicable and a direct observation of the course of the reactions by a mass spectrometer has substantial advantages. The obstacle to this is that in many cases of kinetic interest the mass spectra must be displayed much faster than it has been possible to achieve[1] with conventional mass spectrometers. The present paper describes a time-of-flight mass spectrometer adapted from the design of Wiley and McLaren,[2] which permits a new mass spectrum of the components of a reacting gas to be recorded every 50 μsec. Results of preliminary investigations of the photochemical decompositions of ketene and of nitrogen dioxide by the flash technique[3] are also reported.

The Apparatus

The equipment consists of four distinct parts: the mass spectrometer proper, the mass spectra recording apparatus, the reaction cell with the usual gas handling attachments and the flash lamp with its power source.

The mass spectrometer is electronically identical with that designed by Wiley, the entire electronic circuitry package having been constructed by the Bendix Aviation Research Laboratories. Since the principles of its design have already been described,[2] a brief recapitulation will suffice. A pulsed electron beam generates a number of ions in a field-free space near a grounded electrode. A high negative potential is then applied to a nearby grid, drawing out the ions. After additional acceleration by a second grid, the ions travel in a field-free drift tube, are then again accelerated and strike the cathode of an electron multiplier some 40 cm. away. By an ingenious arrangement of accelerating potentials, Wiley succeeded in causing all ions of the same mass to arrive at the detector very nearly at the same time, regardless of their point of origin within a small ionizing volume. The times of arrival of ions of different masses vary as the square roots of the masses. Mass resolution becomes worse, therefore, with increasing mass, but xenon isotopes have been fully resolved.[2] Each ion accelerating pulse triggers the sweep of a scope, after a delay matched to the time of flight of the fastest ions to be observed and the amplified current pulses from the groups of ions are displayed as vertical pips on a CRO tube.

This mass spectrometer has two major advantages for the purposes at hand: (1) new mass spectra can be generated at repetition frequencies as high as 20 kilocycles; (2) the ions are generated very near a grounded electrode which, in our design, is made the wall of the reaction cell and is provided with a pinhole through which the gas effuses continuously. By thus locating the ionizing volume very near the effusion pinhole it is possible to produce ions mostly from molecules just escaping from the reaction cell, as contrasted with those which have been in the mass spectrometer

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(1) E. G. Leger and C. Quillet, *J. Chem. Phys.*, **21**, 1310 (1953).

(2) W. C. Wiley and I. H. McLaren, *Rev. Sci. Inst.*, **26**, 1150 (1955).

(3) (a) K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.* (*London*), **A210**, 439 (1952).

for some time. An order-of-magnitude calculation will illustrate this point. With a pinhole of 0.015 cm. diameter and 1 mm. gas pressure in the cell, about 10^{17} molecules per sec. leak into the spectrometer. We estimate our effective ionization volume to be less than 0.01 cc., subtending about π solid angle from the pinhole and being about 0.1 cm. thick. Thus the number of effusing molecules which are in this volume at any one time is about 10^{11}, which is equivalent to a static gas pressure of *ca.* 3 $\times$ 10^{-4} mm. Beyond the pinhole there is very little resistance to gas flow because of the absence of focusing slits of a conventional mass spectrometer. They are replaced by open grids, although a blind is superposed on the first one, which screens off the electron beam, except for the area directly over the pinhole. The concentration of molecules which have already suffered random collisions with the walls of the spectrometer is therefore nearly the same throughout the spectrometer chamber. Hence the pressure, as read on a nearby ionization gage, may be taken as the measure of the concentration of the randomly moving molecules in the ionization space proper. This pressure did not exceed 2 $\times$ 10^{-5} mm. when the gas was effusing from the pinhole and therefore one may estimate that more than 90% of the ions formed came from molecules in direct flight from the pinhole.

The vacuum system of the spectrometer (see Fig. 1) was designed for fast pumping. The main chamber (1 in Fig. 1) is a 19″ long, 10.25″ i.d. pipe, with a flange and lid (2) on top and a flat bottom, through which is welded a short length of flanged 6″ i.d. pipe (3). A 6″ throat Consolidated Vacuum Corp. MCF-700 pump (4), operating on Octoil S, is fitted to this flange. A 6″ flap valve (5) over the 6″ i.d. pipe can separate the spectrometer from the diffusion pump. The latter is backed by a Welch Duoseal two-stage mechanical pump (6); a bypass (7) with suitable valves serves to evacuate the spectrometer directly by the mechanical pump. Suspended from the lid by two thin-walled necks (8), 6″ long and $^3/_4$″ i.d. is a cylindrical cold trap of 2 liter volume (9) with fins, so arranged that oil vapor molecules cannot pass to the upper part of the chamber without striking cold surfaces. For reasons of convenience the trap is cooled by liquid Freon, supplied by a commercial refrigeration unit. The vacuum in the trap is maintained at 22″ mercury, corresponding to *ca.* −55°. The construction is welded stainless steel throughout, with gold wire gaskets to allow baking out. After a moderately short evacuation the pressure drops to 10^{-6} mm., as read on a VG 1A ionization gage (10). When gas is streaming from the pinhole, the pressure rises to 1-2 $\times$ 10^{-5} mm.

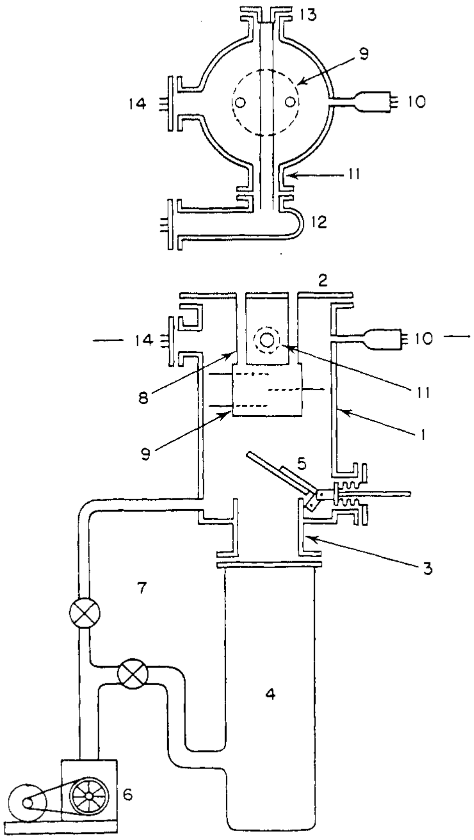

Fig. 1.—A schematic drawing of the general layout of the spectrometer.

On the diameter normal to the plane of the necks of the cold trap and near the top of the chamber are welded two flanged pipes, 1.50″ long and 2″ i.d. (11, 13). To one of these ports is bolted an elbow shaped pipe (12) containing the electron multiplier detector. The other (13) is closed by a lid which carries the reaction cell and all the control elements of the spectrometer. Electrical connections to these are brought out through a third flanged port (14) of the chamber.

The principal elements of the spectrometer proper are attached to a steel block welded to the port lid. The ion current amplification ($10^5 \rightarrow 10^6$) by the electron multiplier is sufficient for direct presentation by a Tektronix 541 scope with a 53-54 B preamplifier. Adjustable delay and speed of the sweep permit the presentation of the entire mass spectrum or of any portion of it. The available circuitry allows the selection of 20, 10, 5, 2.5 or 1 kilocycles repetition frequencies.

Recording Apparatus.—The selection of a short-persistence P11 CRO tube has permitted the photography of successive traces by a simple rotating drum camera, using Eastman Kodak Linograph Pan 35 mm. film. The camera is equipped with an f 2.8 lens and a mechanical shutter which opens for somewhat less than the duration of one revolution of the drum (0.01 sec.) and which triggers the discharge of the flash lamp after a delay of a few milliseconds, intended to register several mass spectra of unreacted gases.

Reaction Cell.—The reaction cell is formed in the rectangular stainless steel block welded to the port lid. The block is bored to standard taper dimensions (*ca.* 2.9 cm. max. i.d. by 2.8 cm. length). Into this hole is fitted a ground quartz thimble with a flat bottom brought flush with the end of the steel block. Over the bottom, in which there is a centrally located hole of *ca.* 2 mm. diameter, is cemented a 0.001″ thick gold foil, provided with a pinhole in the center. On the inside the quartz thimble is aluminized to add to reflectivity and finally is quartz coated (including the portion of the gold foil exposed by the hole), to minimize surface reactions. The open end of the reaction cell is closed by a Teflon plug which has a large central hole containing a short quartz thimble. Through another smaller hole in the plug passes a glass tube connecting the cell to the gas handling system. This needs no detailed description, being of conventional glass design and adapted to the particular problem being investigated. It includes a fairly large flask which is in communication with the reaction cell during a run because the effusion of the gases through the pinhole is quite rapid, the sojourn time of the gas in the cell being a few seconds. The gas handling system is evacuated by its own pumping system which includes a diffusion pump.

Flash Lamp.—The central portion of the quartz flash lamp is coaxial (*i.e.*, like a conventional cold trap), the end of this portion fitting into the thimble within the reaction cell. The power supply consists of a bank of condensers (10 $\times$ 1 μfd. and 1 $\times$ 25 μfd.) and a high voltage transformer-rectifier, which charges one side of the condensers positive, the other equally negative. Any voltage up to 15,000 v. may be used, but the normal operating conditions have been 10 μfd. at 10,000 v. or 500 j. The flash is set off by a triggered spark gap in series with the condensers and the lamp, the trigger pulse being synchronized with the mechanical shutter of the drum camera. A glass rod pipes a little radiation from the flash lamp to the rotating drum, where it is recorded on the film to identify the exact instant and the duration of the flash. The latter in final experiments was about 10 μsec.

Preliminary Experiments

In adapting the Wiley mass spectrometer design to the purpose of present research, the collection of only those ions which are formed in a small volume immediately over the pinhole, design compromises were made which resulted in a less-than-optimum performance. This can be substantially improved by comparatively small modifications, which are being incorporated into the second version of the internal parts of the spectrometer.

In a time-of-flight mass spectrometer, in which the spectrum produced by each pulse is separately observed, the sensitivity is ultimately limited by the number of ions generated by a single electron pulse and is therefore roughly proportional to the duration of the pulse. The resolution of the spectrometer, however, is adversely affected by lengthening the pulse because of the drift of the ions out of the small volume in which they are formed. The ionization of molecules effusing from a pinhole is more favorable in this respect than that of randomly moving molecules because all of the former have a forward component of velocity. It was found, however, that the selection of electron beam dimensions as 1 × 4 mm., when combined with a pulse duration of 1.5 μsec., gave spectra in which only masses below 40 were fully resolved. It seemed inadvisable to work with still poorer resolution and therefore this pulse duration was chosen for all experiments. Figure 2 shows several consecutive spectra of gas mixture No. 1 (see below) covering the range from mass 12 to mass 29, taken at 10 kc. repetition frequency. The smaller peaks show random fluctuations in height, one cause of which is the statistical fluctuation in the number of ions produced in consecutive pulses.

The extent of these fluctuations is shown by the following calculation. The abundance of mass 22 neon isotope is 9.73%. The root mean square deviation from the mean of 16 consecutive M 22 peak heights obtained with a partial pressure of neon of 0.4 mm. was found to be 13%. If these fluctuations are regarded as being solely due to the fluctuation in the number of M 22 ions reaching the collector, this number must be 60. The actual number is considerably larger because at least the first stage of multiplication in the detector contributes substantially to the fluctuations and there are additional contributions from peak height measurements, etc. Disregarding all of these, the total effective number of neon ions formed is about 700. Neon has a comparatively low ionization cross section and hence one might expect that over a thousand ions are formed from other gases at the same pressure in the reaction cell. This sets a somewhat disappointingly high lower limit of 0.005 to the mole fraction of a gas mixture component that can still be detected reliably in a single spectrum. Averaging peak heights of several consecutive spectra improves the sensitivity but, of course, spoils time resolution. We have chosen therefore to perform several experiments under nearly identical conditions and to average the measurements of spectra which were obtained at (nearly) the same time interval after the flash of the lamp.

The relatively low sensitivity of the instrument calls for a high degree of reaction in flash photochemical experiments. The initial design of the reaction cell included a flat window on the side opposite the pinhole and an externally situated flash lamp. Extensive experimentation with various forms of flash lamps, using low and high voltages and several types of reflectors, failed to produce a design which gave more than a few per cent. decomposition of ketene. In the next series of experiments a coaxial lamp was inserted directly into the reaction cell through the Teflon plug mentioned earlier. Using a small pinhole and total gas pressures of the order of 20 mm., decompositions of ketene present at a pressure of 10 mm. as high as 5–8% were observed with the spectrometer. In some of the runs 50 volt electrons were used for ionization. Under these conditions a rather high intensity of M 14 peak (CH_2^+) was observed prior to irradiation, due to the breakup of the parent ketene ions. Irradiation caused only a slight reduction in the intensity of this ion peak, due to decomposition of some ketene. With 15 volt electrons M 14 peak was virtually absent both prior to and after irradiation, but low sensitivity of the spectrometer made this result of limited significance. In general, this method did not prove fruitful with this instrument for the reason given and all other experiments were performed at an electron energy of 50 v. The important observation made was that the ratios of the M 28 and M 26 peaks (CO^+, $C_2H_4^+$ and $C_2H_2^+$) to that of neon 20 reached their full intensity in the first spectrum recorded after the irradiation, *i.e.*, *ca.* 50 μsec. later. Since in a mixture of ketene with inert gases the reaction mechanism is essentially[4]

$$CH_2CO + h\nu = CO + CH_2 \quad (1)$$

$$CH_2 + CH_2CO = C_2H_4 + CO \quad (2)$$

the above result means that as soon after the flash as it was possible to make observations the reaction was complete. Methylene molecules suffer approximately 10^4 collisions with ketene molecules in 50 μsec. under the conditions chosen.

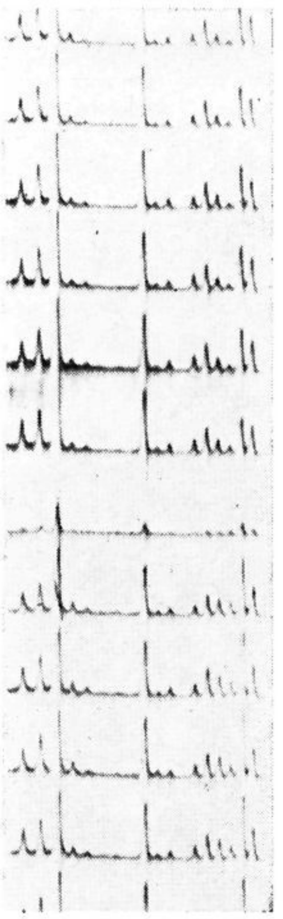

Fig. 2.—Consecutive mass spectra obtained with mixture No. 1. The region displayed is from M 12 to M 29. The weak spectrum in the center follows the lamp flash.

It was therefore decided to enlarge the pinhole to the spectrometer and to work with much lower gas pressures, to reduce collisional frequency and so to gain more information on the rate of this very fast reaction. The experiments described in the next section were made with a 0.015 cm. diameter pinhole at total gas pressures of less than 1 mm. But when these conditions were established in the reaction cell, it was discovered that the discharge of the flash lamp totally suppressed the ion spectrum for several hundred microseconds. The disturbance disappeared entirely when the cell was evacuated (or was filled with gas at a pressure of 20 mm. or more). There was no disturbance (but, of course, also no photochemical reaction) when the lamp was painted with (non-conducting) black paint. Surrounding the lamp with a grounded grid helped substantially. The best results were obtained by putting a light wire grid between the lamp and the thimble and biasing this grid 400 v. negative. The first spectrum after the flash was usually uniformly weakened, but the following spectra were not visibly affected. With nitrogen dioxide, instead of ketene in the cell, the disturbance was less pronounced and the same remedial actions resulted in its virtual elimination.

The nature of the disturbance is not clear in detail, but it evidently involves photoelectric effect by the radiation of the flash, followed by secondary ionization due to field gradients accompanying the discharge. In some way the gaseous ions within the cell then interfere with the formation of the ion cloud within the mass spectrometer.

Ketene Decomposition

The Results.—Experiments were made with three mixtures as follows

Mixture			
I	36.7% CH_2CO	63.3% Ne	
II	11.3% CH_2CO	11.9% Ne	76.8% SF_6
III	7.8% CH_2CO	92.2% Ne	

The inert gases were added to ketene to reduce temperature

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[4] A. N. Strachan and W. A. Noyes, Jr., THIS JOURNAL, **76**, 3258 (1954).

rise caused by the absorption of flash radiation energy; neon isotope peaks were additionally used for reference, being of course unaffected by chemical reactions, but equally subject to variation in mass spectrometer sensitivity, whatever the cause.

In repeated experiments with each mixture the pressure varied in the cell from about 0.3 to 1.2 mm., most being made with a pressure of 0.7 mm. The flash energy was 500 joules at 10,000 v. in all experiments. Approximately 10% of ketene was decomposed per flash, as indicated by a 10% decrease in the ratio of M42/M20 peak heights after the flash.

In Fig. 3 are shown the peak height ratios to neon 20 for mass 28 (CO^+, $C_2H_4^+$) and mass 26 ($C_2H_2^+$) obtained in experiments with mixture No. 1. The points are each the average of ten consecutive runs and the time, in relation to the flash, at which they are shown is a nominal one, since in individual runs it varied by ±50 μsec. The 10 kilocycle repetition rate was used in these experiments since the flash interference spoiled observations closer than 100 μsec. after the flash. Figure 4 shows the change in M28/M20 ratio in experiments with mixtures 2 and 3. In these cases the 20 KC. repetition rate was used and the uncertainty in time is correspondingly less. For these mixtures the mass 26 peak was extremely small because of lower concentration of ketene and it was impossible to measure changes in it.

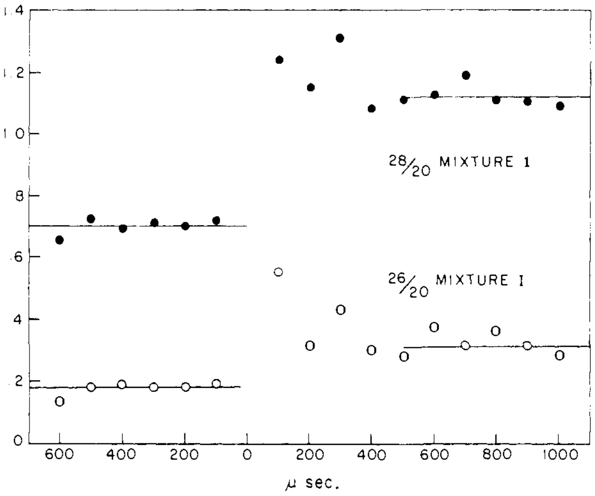

Fig. 3.—The time dependence of peak height ratios 28/20 and 26/20 averaged over several runs with mixture No. I. The horizontal lines show average values of the ratios before and after the flash.

In addition to mass peaks due to ketene and the inert gases present in the cell, peaks of three heavier background ions were relatively prominent in the spectra. They were identified as M 55, 56 and 57. The intensity of the latter two was found not to be significantly affected by the flash except for the electrical interference mentioned previously. Figure 5 shows that the intensity of M55 rises significantly after the flash and then decreases, for both mixtures 1 and 3. To measure these small peaks accurately, only the region of spectrum near mass 50 was presented on the scope and the amplification was increased. It was therefore impossible to form ratios to neon isotopes and the ratio M55/M57 was chosen instead for presentation in Fig. 5. The height of M57 peak was about one third of the M28 peak.

Discussion.—Failure to detect a rise in abundance of M 14 ions after the flash suggests, but certainly does not prove, that methylene is eliminated from the gas phase exceedingly rapidly. The behavior of M 28 peak, however, is rather conclusive: it reaches its full magnitude in the first spectrum after the flash, even at the low pressures used in the final experiments.

The M 26 peak (Fig. 3) shows the same behavior and M 26 is a strong fragment ion peak of ethylene. It is therefore more than plausible to conclude that formation of ethylene, as well as of carbon monoxide is essentially completed when the first spectrum after the flash is observed.

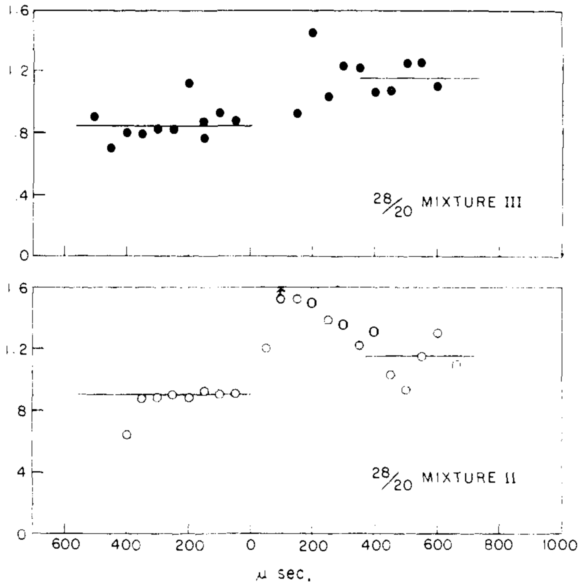

Fig. 4.—Peak height ratios 28/20 obtained with mixtures No. II and III. Horizontal lines show average values of the ratios before and after the flash.

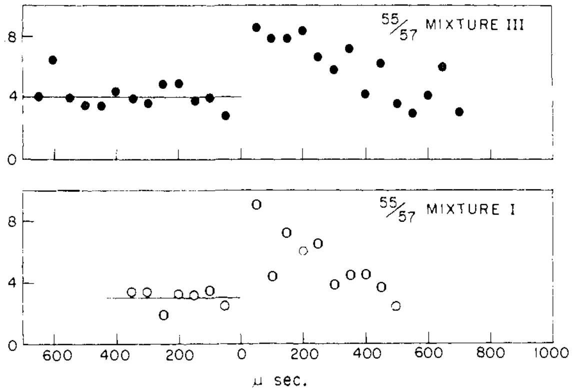

Fig. 5.—Peak height ratios 55/57 averaged over several runs with mixtures I and III. Horizontal lines show average values of this ratio before the flash.

It has been stated recently in a preliminary publication[5] that the reaction

$$CH_2 + CH_2 + M = C_2H_4 + M \quad (3)$$

is unimportant in flash photochemical experiments when the partial pressure of ketene is comparable to those presently used, but the partial pressure of "inert" gas (Xe, SF_6 and CO_2 were used) is of the order of 100 mm. Because of a possible third body effect, reaction 3 can be only less important at total pressures of the order of 1 mm. and therefore the disappearance of methylene cannot be attributed to it. Oxygen was carefully excluded from

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(5) (a) G. B. Kistiakowsky and K. Sauer, This Journal, **78**, 5699 (1956); (b) a more detailed description of these experiments will be shortly submitted to This Journal.

the gas mixtures used and therefore a reaction of methylene with oxygen[4] cannot be appealed to. The most plausible interpretation is that reaction 2 is exceedingly fast and is essentially completed by the time the first mass spectrum after the flash is recorded. The partial pressures of ketene ranged in these experiments from 0.25 to 0.045 mm., the collisional frequencies of methylene with ketene varied therefore from *ca.* 10^7 to 10^6 per sec. The conclusion is that the reaction probability of methylene and ketene on collision is at least 10^{-2}. The major source of doubt—as in all experiments on reactive intermediates with mass spectrometers, in which gas effuses through a pinhole—is that the proximity of the walls alters the effusing gas composition by heterogeneous reactions of intermediates. At the pressures used in these experiments the average displacement of a molecule, due to diffusion, after 100 μsec., is a few mm, and therefore the process by which Porter,[6] explains his observations at low ketene pressures—a diffusion of methylene molecules to the walls—is inapplicable to the present observations. Of course, some of the molecules which effuse through the pinhole suffer previous collisions with adjacent portions of the surface but others arrive at the pinhole directly from the interior of the reaction cell. The most plausible interpretation of the observations, therefore, is that methylene reacts with ketene in the gas phase.

Figure 5 supports, but not conclusively, a recent suggestion[5a] that the first event in the reaction of methylene with ketene is the formation of a "hot" cyclopropanone molecule which rearranges, within a time far too short to be observed with the present technique, partly into ethylene and carbon monoxide, and partly into a long-lived radical or molecule C_3H_4O, *i.e.*, M 56. This particular mass peak does not show any significant changes after the flash, but instances are known in which the parent ion of a complex molecule appears in a considerably lower intensity than the ion of one mass unit lower mass.[7] Were this the case with C_3H_4O, changes in M 56 would be obscured by the background ion contribution, whereas those in M 55 might be observable. The magnitude of the nonbackground M 55 peak is seen (Fig. 5) to be highest in the first spectrum after the flash and to decrease below the limit of detectability after a few hundred microseconds. This is in qualitative accord with the results of conventional experiments on the photolysis of ketene, which show that the final products are almost quantitatively ethylene and carbon monoxide. The drop in intensity of M 55 might be therefore interpreted as a measure of the rate of decomposition of C_3H_4O.

There is some suggestion (Figs. 3 and 4) of a decrease in the M 28/M 20 and M 26/M 20 ratios during the first couple hundred microseconds after the initial rise. The cause of it is not known and, treated statistically, the decrease is not very significant, but it does make the above interpretation of the behavior of the M 55/M 57 ratio less conclusive.

Nitrogen Dioxide Decomposition

Results.—Experiments were made with a mixture (IV) of 80% nitrogen dioxide and 20% neon at total pressures of about 1 mm. The degree of decomposition produced by a flash was quite small, 5% or less, as indicated by the decrease in the ratio M 46/M 20. The amplitude of M 16 peak was quite large before the flash, it being a daughter ion of nitrogen dioxide, and Fig. 6 shows that there is no statistically significant change in the ratio M 16/M 20 induced by the flash, when 50 e.v. electrons are used for ionization. Figure 6 shows, however, that the ratio of M 32/M 20 undergoes a sudden increase after the flash and then remains constant. A careful search was made for M 62 (NO_3^+) but this peak did not appear after the flash. On the other hand, it was observed that immediately after the flash the small M 42 peak (N_2O^+) increased in intensity by about a factor of three and then remained essentially constant.

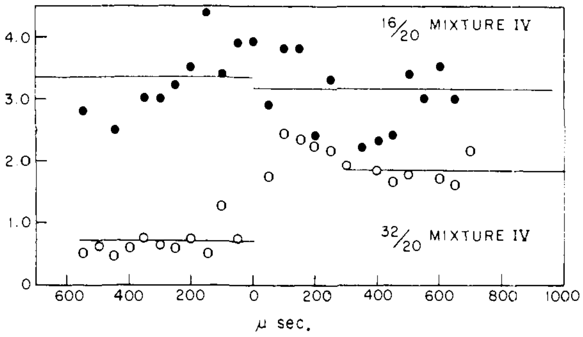

Fig. 6.—Peak height ratios 16/20 and 32/20 obtained with mixture No. IV.

Discussion.—The large magnitude of the M 16 oxygen ion peak resulting from the fragmentation of nitrogen dioxide ions and the small percentile decomposition of nitrogen dioxide by the present flash lamp arrangement account for the failure to note an increase in atomic oxygen after the flash, regardless of whether oxygen atoms are rapidly consumed or not by subsequent reactions. Norrish and Porter[3b] conclude that the reaction

$$NO_2 + O = NO + O_2 \qquad (4)$$

is complete after about 800 μsec. when the pressure of nitrogen dioxide left in the reaction cell after the flash is comparable to that in the present experiments. The reaction probability must therefore be of the order of or larger than 10^{-3} of collisional frequency. The behavior of the parent M 32 ion peak in the present experiments permits a sharper definition of the lower limit of this reaction probability. The peak attains its full magnitude already 100 μsec. after the flash at a partial pressure of NO_2 of about 0.8 mm. and therefore this reaction probability must be of the order of or larger than 10^{-2}. Nitrogen trioxide is not formed in amounts detectable by the present method. A rather interesting new finding is that some nitrous oxide is formed as rapidly as is molecular oxygen. Peak M 44 is quite small and so nitrous oxide must be a relatively minor by-product. The mechanism of this reaction can only be surmised. The radiation

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(6) G. B. Porter, THIS JOURNAL, **79**, 827 (1957).

(7) For instance, formaldehyde, *cf.* National Bureau of Standards Tables of Mass Spectra.

from the flash lamp is rich in short wave lengths. Therefore it is possible that the reaction $NO_2 + h\nu = O + NO$ results in energy-rich, "hot," nitric oxide molecules. These then undergo the reaction

$$NO_2 + NO^* = N_2O + O_2 \qquad (5)$$

The results obtained to date with the time-of-flight mass spectrometer as an analytical device for fast reactions are largely preliminary and qualitative. They show, however, that the apparatus is a useful tool in kinetic research. Further refinements of it and the study of several reactions are continuing, therefore.

We wish to express our thanks to Dr. W. C. Wiley for his many helpful suggestions. This work was supported by a research grant of the National Science Foundation.

CAMBRIDGE, MASS.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of Dimethyl Ketene Vapor

BY RICHARD A. HOLROYD[1] AND FRANCIS E. BLACET

RECEIVED APRIL 19, 1957

The photochemical behavior of dimethyl ketene vapor has been investigated with variations of wave length, pressure and temperature. Propylene and carbon monoxide were found to be the major products but under some conditions small yields of hydrogen, methane and hexene were detected. At 2537 Å. the quantum yield of CO was unity, within experimental error, under all conditions. The quantum yields of C_3H_6 increased (to a limiting value near unity) with either pressure of dimethyl ketene or pressure of added foreign gas. The existence of radical intermediates at this wave length was demonstrated by a tellurium mirror removal experiment. At 3660 Å. the quantum yields were pressure dependent, indicating the formation of a long-lived excited state. The results are interpreted in terms of a wave length dependent primary process.

The behavior of dimethyl ketene under the influence of ultraviolet light was studied as a potential source of isopropylidene radicals. The photolysis of dimethyl ketene had not been reported previous to this investigation. Some work has been reported which involves similar radical intermediates, however. The ethylidene radical has been reported to be an intermediate in the photolysis of methyl ketene[2]; indicating that the primary process is

$$CH_3CHCO + h\nu \longrightarrow CH_3CH + CO \qquad (1)$$

The rearrangement of ethylidene to ethylene appears to be quite rapid but reaction

$$CH_3CH + CH_3CHCO = C_4H_8 + CO \qquad (2)$$

also occurs. Other workers have postulated ethylidene as an intermediate in the pyrolysis of diazoethane[3a] and of ethane,[3b] and in the photolysis of diazoethane.[4,5]

The photolysis of ketene itself has been studied extensively[6] and methylene appears well established as an intermediate. On the basis of the work done on ketene and on methyl ketene, the photolysis of dimethyl ketene was expected to lead to dissociation into CO and isopropylidene

$$(CH_3)_2C{=}C{=}O + h\nu \longrightarrow CH_3\text{-}C\text{-}CH_3 + CO \qquad (I)$$

Thus it would be possible to study the kinetic behavior of this radical.

Experimental

Materials.—Dimethyl ketene was prepared by the pyrolysis of isobutyryl phthalimide in a modified "dimethyl ketene" lamp.[7] It was condensed at −196° and fractionated in a vacuum system to remove impurities, and stored at all times in a trap at −78° to prevent dimerization. A mass spectrogram (see Table IIb) proved the molecular weight to be 70 and also showed no large scale impurities were present. 99.8 per cent. of a sample brought in contact with water was absorbed. The product of this reaction was shown to be isobutyric acid by mass spectral analysis. As an additional check on purity, the ultraviolet spectrum of dimethyl ketene vapor was obtained and found to be similar to the spectrum of diethyl ketene.[8] No ultraviolet spectrum of dimethyl ketene had been reported for comparison. The results are shown in Fig. 1. The infrared spectrum of dimethyl ketene vapor was found to be similar to the published spectrum of ketene[9] as shown in Table I. The carbonyl absorption band at 1700 cm.$^{-1}$ which is typical of

TABLE I

THE INFRARED SPECTRAL BANDS OF KETENE AND DIMETHYL KETENE, CM.$^{-1}$

(s) denotes relatively strong absorption.

Dimethyl ketene	Ketene
	4230
3440	3510
3100	3265
2880(s)	3080(s)
	2540
2380	2290
2120(s)	2155(s)
1960	1967
1450	1402
1390(s)	1376(s)
1335	
1200	1215
	1136(s)
	1111
	1075
990	1048
720	

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