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TIME RESOLVED MASS SPECTROMETRY WITH
THE BENDIX TOF MASS SPECTROMETER

by

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and

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ABSTRACT

Adaptation of the mass spectrometric technique to kinetic analyses of transient chemical processes has been limited by low sensitivity for the detection of intermediate species, by long transit paths between the high pressure reaction zone and the low pressure ionization zone, and, in the case of flash photolysis experiments, by a low photochemical conversion efficiency. The present work has provided greatly improved performance of a Bendix TOF mass spectrometer for ion generation, transmission and detection. An ultimate single cycle sensitivity of 1 part in 100,000 has been obtained for pulsed operation at 20 kc. This corresponds typically to an absolute abundance of a reactive species of 0.5×10^{-7} mole/liter. Bimolecular reactions with rate constants approaching 10^{11} liter mole⁻¹sec⁻¹ may be studied with this sensitivity and time resolution. A short transit path of 2 mm is achieved with a reaction vessel fitted into the Bendix ion source and containing a conical, ground glass sampling orifice. Geometrical coupling of the flash lamp and the reaction vessel has permitted efficient transfer of the ultraviolet radiation to the absorbing gases. An incident light flux of 3×10^{18} quanta/cm² for the wavelength band 2000 Å to 4000 Å has been measured by nitrogen dioxide actinometry.

July 1965

TIME RESOLVED MASS SPECTROMETRY WITH THE BENDIX TOF MASS SPECTROMETER

R. T. MEYER and J. M. FREESE

INTRODUCTION

Application of the flash photolysis and time resolved mass spectrometry techniques¹ to kinetic analyses of transient chemical processes has been limited by low sensitivity for the detection of intermediate species and by low photochemical conversion efficiencies. The purpose of this paper is to describe improvements in the technology which have led to successful studies in our laboratory. Only brief reference will be made here to our chemical kinetic results, which include the detection of the OH radical in the NO₂ sensitized reaction between H₂ and O₂² and a study of the photodecomposition of methyl iodide.³

EXPERIMENTAL

The geometry of the flash lamp, reaction vessel and Bendix ion source is shown in Fig. 1. Input energies to the flash lamp ranging from 900 to 3500 joules have been employed, with corresponding flash durations of 18 to 200 μ sec. The thimble configuration of the reaction vessel permits efficient coupling of the ultraviolet radiation. The effective reaction zone is a 1.5 cm long cylindrical volume between a Suprasil window and the sampling orifice. A gold foil reflector surrounds both the cylindrical and orifice plate surfaces of the reaction vessel.

The sampling orifice was prepared by a Tesla coil puncture at the tip of a pyrex cone. An orifice diameter equal to 0.0005 inch permits total gas pressures in the reaction vessel approaching 100 torr, with the spectrometer pressure not exceeding 2×10^{-5} torr. For reaction vessel pressures above 10 torr, the mean free path of the molecules is less than this orifice diameter. Therefore, gas flow into the ionization zone is essentially hydrodynamic. The center of the electron beam has been brought to less than 2 mm from the orifice by removing the backing plate of the Bendix ion gun. Large numbers of ions are produced since the electron beam intersects the gas sample in a region of high molecular density.

Figure 2 shows the principal elements of the Bendix Model 14-101 TOF mass spectrometer, which control the efficiency of ion production, transmission and detection. Increased ion production is obtained by operating the five grid electron gun with a pulse duration of 1.4 μ sec, instead of the standard 0.25 μ sec, and by using strong electron beam collimating magnets. Integrated trap currents in excess of 25 μ amp are possible at 70 ev and 20 kc pulse frequency.

Fig. 1 Geometry of coaxial flash lamp and reaction vessel adapted to ion source of Bendix TOF mass spectrometer.

Fig. 2 Schematic of Bendix TOF mass spectrometer.

Major improvements have been made in the ion gun which have led to greatly augmented ion transmission. First, the loose nickel mesh of the three ion grids has been replaced with tight molybdenum mesh. This reduces the spacial dispersion of ions caused by non-planar accelerating fields. Second, an intermediate accelerating potential, supplied by a separate variable power supply, has been applied to the second ion grid. The absolute value of this potential is critical, depending upon the overall ion source conditions and upon the mass range being investigated. Third, the final accelerating potential, applied to ion grid no. 3, has been increased from -2800 volts to -3300 volts. Transmission of ions is optimized by adjusting the other auxiliary focusing devices: compensating magnets, horizontal and vertical deflection plates; and the ion lens. The bandwidth of the spectrometer, i.e. ion intensity as a function of mass, is best adjusted for the limited mass range pertinent to a particular set of experiments.

Operational stability of the electron multiplier detector has been improved by providing a separate regulated power supply for the dynode and field strips. This provides independent control of the multiplier gain and eliminates current loading effects from perturbing other elements of the mass spectrometer. The mass spectrometer output is displayed on a modified Tektronix 517A oscilloscope with a P16 phosphor.

The successive mass spectral analyses, appearing every 50 μ sec, are time resolved with a Beckman and Whitley Model 364-2 oscillographic drum camera.⁴ Conventional circuits have been employed to synchronize the flash lamp, the mass spectrometer, the oscilloscope and the drum camera.⁵

RESULTS AND DISCUSSION

Mass Spectrometer Sensitivity

For present purposes, sensitivity is gauged in terms of the maximum number of ions that can be produced, transmitted and collected per cycle of spectrometer operation. The method of ascertaining the number of ions being detected is based upon the theory of statistical fluctuations. The relative fluctuation F in the measurement of a number of gaseous molecular species N is given by

$$F = \left[\frac{(\overline{(\delta N)^2}}{\bar{N}^2} \right]^{\frac{1}{2}} = (1/\bar{N})^{\frac{1}{2}}.$$

$\bar{N}$ is the average value of N and $(\delta N)^2$ is the mean square deviation of the measured values. Thus, the average number of species is equal to the reciprocal square of the relative statistical fluctuation.

Data illustrating the improved sensitivity of the mass spectrometer are summarized in Tables I and II. The single cycle sensitivity prior to the improvements was obtained by measuring the statistical fluctuations in mass spectral signal amplitudes for 100 consecutive cycles. Using a pure argon sample at an optimum spectrometer pressure of 1.0×10^{-5} torr, the Ar^{36} and Ar^{38} isotope peaks were monitored. Relative fluctuations of 0.38 and 0.92, respectively, were obtained. Therefore, calculating the absolute number of ions/cycle specifically for Ar^{36} and Ar^{38} and dividing by the known natural abundance of these species gives the total number of ions of all argon isotopes. An average value of 2000 ions/cycle is obtained. The assumption that the fluctuations are purely statistical is justified by the good agreement between the calculated ion/cycle abundance ratio of 5.8 and the natural abundance ratio of 5.4.

TABLE I. Spectrometer sensitivity in total number of ions/cycle for the original Bendix mode of operation (including ions lens at drift tube potential), based upon argon isotope abundance measurements.

Isotope	Natural abundance	Rel. fluct.	Ions/cycle	Total no. of ions/cycle
Ar ³⁶	0.337	0.38	7.0	~2100
Ar ³⁸	0.063	0.92	1.2	~1900
Abundance ratio	5.35		5.8	

TABLE II. Statistical fluctuation in Ar⁴⁰ ion intensity as a function of sample pressure and mode of ion transmission.

Ar sample pressure torr	Spectrometer pressure torr	Rel. fluct.	Ar ⁴⁰ ions	Transmitted ion ratio
		Bendix	Improved	
9.7	1×10^{-5}	0.093	0.018	27
4.2	5×10^{-6}	0.14	0.027	25
1.2	1.5×10^{-6}	0.28	0.040	49
0.35	6.5×10^{-7}	0.36	0.064	31
			Average	32

Table II shows the increase in the ion transmission obtained for the improved mode of operation. This result is based upon measurements of the statistical fluctuation in the Ar^{40} ion intensity for various sample pressures. The relative statistical fluctuation in the argon amplitudes decreased by an average factor of 5.7. This corresponds to a gain of 32 in the number of ions transmitted and detected.

Although the 1.8% fluctuation recorded at the optimum spectrometer pressure of 1×10^{-5} torr is a respectably small value, it represents the sum of both statistical and systematic fluctuations. A plot of relative fluctuation versus the reciprocal of the sample pressure, extrapolated to infinite pressure, shows the systematic error contributions to be approximately 2%. This figure agrees with the estimated film reading error.

Therefore, a calculation of the absolute number of ions per cycle is best obtained by multiplying the improvement factor of 30 times the number of ions per cycle established from the isotope abundance experiments. The number of ions/cycle calculated in Table I must be raised by a factor of two to 4000 ions/cycle to account for another known difference in sensitivity between the data of Tables I and II. Thus, a level of ion production, transmission and collection exceeding 100,000 ions/cycle is obtained. Since a minimum of 1 ion/cycle can be detected with an oscilloscope readout, this is equivalent to a sensitivity of 1 part in 100,000 per cycle.

Ultraviolet Light Flux

The effective ultraviolet light flux incident upon the reaction zone was determined from the flash photolysis of mixtures of NO_2 and Ar. The argon was included as an inert, internal standard substance for correcting for systematic variations. Figure 3 shows the time resolved decomposition of NO_2 and formation of NO and O_2 . The average decomposition of NO_2 in several experiments was 78%, which is an order of magnitude greater than that reported by Kistiakowsky and Kydd.¹

A total ultraviolet light flux of 3×10^{18} quanta/ cm^2 is calculated, assuming a quantum yield of two for the NO_2 decomposition. This is comparable to the highest flash intensities that have been reported by Claesson and Lindquist.⁶ Five percent decomposition of a substance with an exponential molar extinction coefficient of only 40 liter mole⁻¹cm⁻¹ should be possible.

In these particular experiments the flash duration was 200 μsec . Figure 3 shows that data points were obtained within this time interval without undue interference from the flash. When interference does occur, its duration never exceeds four times the $1/e$ duration of the flash. With our 18 μsec flash it is possible to obtain mass spectral signals at 50 μsec after the flash peak.

Bimolecular Reaction Rates

From the preceding discussion on mass spectrometer sensitivity, ultraviolet light flux and time resolution, the following statements can be made on the capability for studying bimolecular reactions. For a typical total sample pressure of 10 torr, the single ion detection sensitivity corresponds to a partial pressure of 10^{-4} torr. However, it is

Fig. 3 Time resolved record of the flash photodecomposition of NO_2 into final products NO and O_2 . Data points are referenced to argon, which serves as an internal standard. Time zero corresponds to beginning of flash; flash duration ($1/e$) was 0.20 msec.

estimated that the minimum detectable concentration of a reactive species is more reasonably 10^{-3} torr, or 5×10^{-8} mole/liter. Table III shows maximum rate constants for bimolecular reactions which can be measured with the 50 μ sec time resolution for various limiting conditions. For a reaction between A and B with both concentrations equal to the limiting sensitivity of the spectrometer, then a rate constant approaching the kinetic theory collision limit of 10^{11} liter mole $^{-1}$ sec $^{-1}$ is measurable. If, however, the reacting species are initially present at higher concentrations, only reactions having smaller rate constants of the order of 10^8 to 10^{10} liter mole $^{-1}$ sec $^{-1}$ are capable of being studied. For example, if the primary reactant is present initially at 0.5×10^{-4} mole/liter and undergoes 10% photodecomposition, the reaction rate of a primary transient A with itself must be equal to or less than 4×10^9 liter mole $^{-1}$ sec $^{-1}$ to be observed. A third case is the reaction of an intermediate species B with a primary reactant A, where the reaction half-time is controlled by the concentration of A and the activation energy. An example is the reaction between OH radicals and H₂ to form H₂O, which is believed to have an activation energy of the order of 5 kcal.

In flash photolysis experiments on mixtures of NO₂, H₂ and O₂, we have been able to detect the OH radical and time resolve the formation of H₂O.² Detection of the OH radical in this system required correction for a changing contribution to the mass 17 ion intensity due to dissociative ionization of H₂O. Our increased sensitivity has provided data with sufficient accuracy to achieve this separation. Finally, in a study of the flash photolysis of methyl iodide, we have ascertained the occurrence of a molecular iodine forming reaction which is more rapid than the termolecular iodine atom recombination process. It has been attributed to a bimolecular reaction between excited iodine atoms and methyl iodide.³

TABLE III. Maximum rate constant of a bimolecular reaction, which can be measured with a 50 μ sec time resolution, as a function of initial reactant concentration. The specific examples, in parentheses, have experimental rate constants smaller than the calculated maxima.

Example	Case	Initial concentration a, mole/liter	Maximum rate constant k, liter mole $^{-1}$ sec $^{-1}$
A + B $\rightarrow$ C + D (O + OH $\rightarrow$ O ₂ + H)	a = b	0.5×10^{-7}	4×10^{11}
A + A $\rightarrow$ C + D (OH + OH $\rightarrow$ H ₂ O + O)	a = a	0.5×10^{-5}	4×10^9
A + B $\rightarrow$ C + D (H ₂ + OH $\rightarrow$ H ₂ O + H)	a > b	0.5×10^{-4}	2.8×10^8

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