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Ion - Molecule Reactions Studied by Time-of-Flight Mass Spectrometry

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Many reactions between ions and molecules in the gas phase have been studied during the last ten years; this field has been extensively reviewed by Lampe, Franklin, and Field,[1] and by Talroze[2]. The usual

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1. F. W. Lampe, J. L. Franklin, and F. H. Field, Progress in Reaction Kinetics, vol. 1 (ed. G. Porter) Pergamon Press, New York, 1961; pp. 67ff.

2. V. I. Talroze, Pure and Appl. Chem. 5, 455 (1962).

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experimental method[1] of obtaining rate constants for such reactions has been to operate a mass spectrometer at relatively high pressure (10^{-4} - 10^{-1} Torr.) in the source region. The primary ions (those formed by electron impact in the mass spectrometer) undergo reactive collisions with neutral species as they pass from their point of formation to the exit slit under the influence of the electric field. The average residence time of an ion in the high pressure source region can be calculated from a knowledge of the source geometry and the electric field; the rate constant for the reaction under investigation is then obtained from the residence time, the experimentally determined pressure, and the ion currents measured at the detector.

We have developed a method in which time, rather than pressure or potential gradient, is the experimental variable. The basic instrument

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is a Bendix model 14 time-of-flight mass spectrometer which has been modified as follows. 1) A stainless steel box of dimensions 1.5"x1.5"x 0.~~375~~ .240" was constructed around the ion source region, forming a reaction chamber with the short side parallel to the ion trajectories. The chamber is provided with a 0.1" dia. ion exit orifice, 0.030"x0.200" electron beam entrance and exit slits, a 0.125" dia. gas inlet tube, and a 0.250" dia. orifice for pressure measurement. An auxilliary 6" diffusion pump was installed so that the source region could be differentially pumped. The instrument can be operated with up to 0.080 Torr. in the source region, while the pressure in the rest of the instrument remains less than 2×10^{-5} Torr. Pressures in the source region are measured with a McLeod gauge and/or a Consolidated micromanometer. 2) A delay circuit (available from the Bendix Corp. as the Time Lag Focus Modification) was provided to allow the introduction of a variable and accurately known delay between the ionizing electron pulse and the pulse which withdraws the ions for analysis. Thus primary ions formed in the electron beam react for a known time at thermal velocities in a field-free space.

To test the method we have reinvestigated the reaction $CH_4^+ + CH_4 = CH_5^+ + CH_3$. With the usual assumptions that competitive and consecutive reactions are negligible[3], that the ions CH_4^+ and CH_5^+ are collected by the detector with equal efficiency, and that these ions are

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3. F. H. Field, J. L. Franklin, and F. W. Lampe, J. Am. Chem. Soc. 79, 2419 (1957).

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lost at equal rates by neutralization at the walls and by flow out of the

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reaction chamber, the kinetic equation may be integrated to

$$\log_{10} \frac{I_{16} + I_{17}}{I_{16}} = \frac{k\,[CH_4]\,t}{2.303}$$

where I_m is the measured intensity of the ion current of mass m, k is the bimolecular rate constant, and t is the time.

Figure 1 shows a typical plot of log $\frac{I_{16} + I_{17}}{I_{16}}$ vs. time between formation and analysis of the ions; the data were obtained at a source pressure of 0.049 Torr. and result in a rate constant of $k=10.5 \times 10^{-10}$ cc./molecule-sec. Table 1 shows rate constants for this reaction determined at various pressures. The average value of the rate constant, 11×10^{-10} cc./molecule-sec., is in good agreement with the value $k=8.9 \times 10^{-10}$ cc./molecule-sec., obtained by Franklin, Field and Lampe[3], over a pressure range of 10^{-4} - 10^{-2} Torr. Talroze[4], using a pulse technique similar to

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4. V. I. Talroze, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1351 (1959); C.A. 53, 21184e (1959).

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ours but with a conventional rather than a time-of-flight instrument, obtained $k = 11.6 \times 10^{-10}$ cc./molecule-sec. over a pressure range 10^{-4} - 10^{-3} Torr.

In view of the good agreement with the literature we feel that the method represents a valuable addition to the tools available for study of ion-molecule reactions.

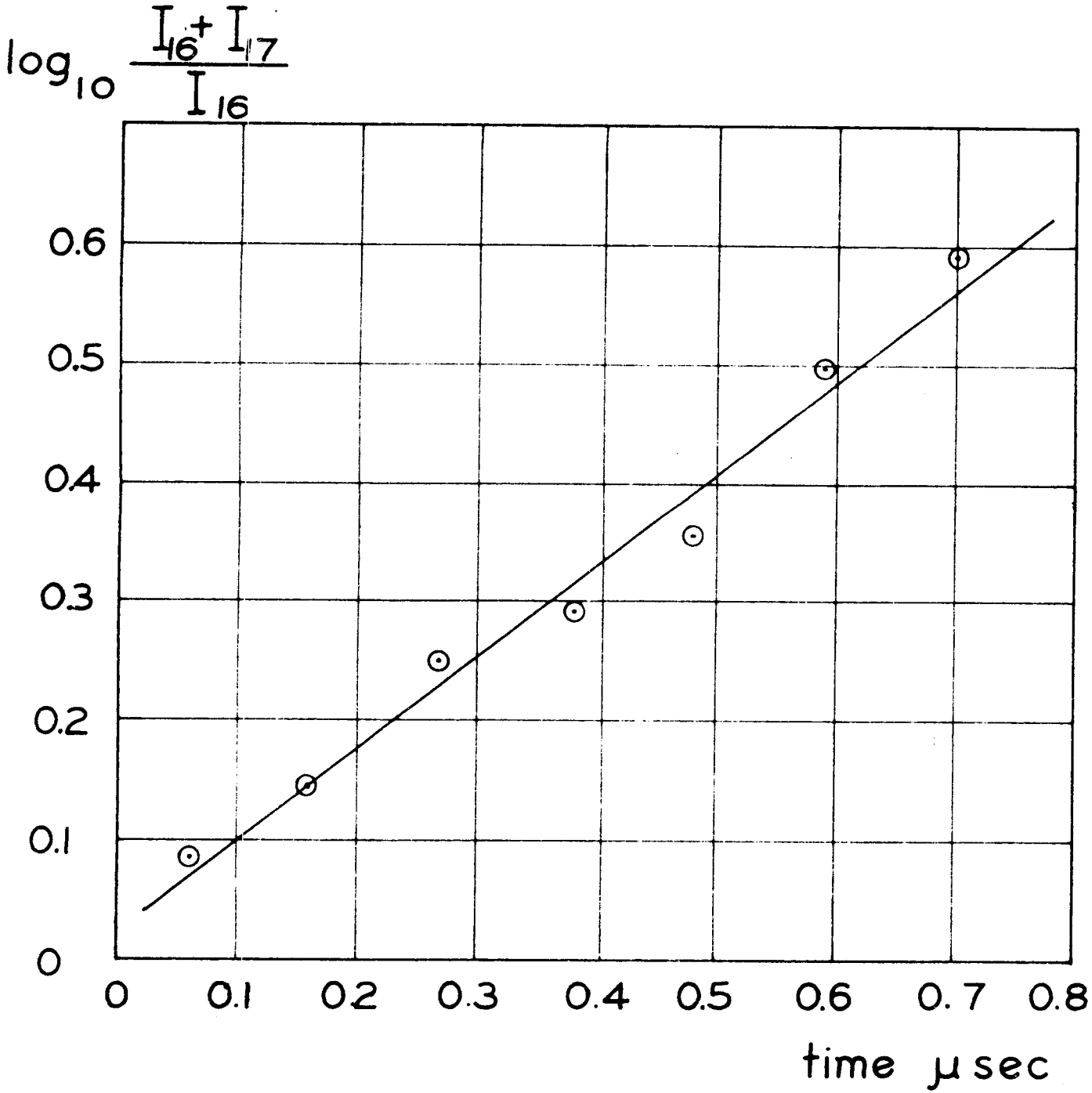
$\log_{10} \frac{I_{16} + I_{17}}{I_{16}}$
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
time μ sec

fig. 1

Caption

Fig. 1. $\log_{10} \frac{I_{16} + I_{17}}{I_{16}}$ vs time. Source pressure 0.049 Torr.

$k = 10.\cancel{5}\,3 \times 10^{-10}$ cc./molecule-sec.

Table 1.

Pressure (Torr. x 10^3)	k(cc/molecule-sec. x 10^{10})
3.4	12.3
3.8	14.7
8	13.5
10	7.0
17	9.5
19	9.95
25	11.2
49	10.3
	Average: 11.1