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Gaseous Thermal Electron Reactions:
Attachment to SF_6 and C_7F_{14}

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The rates of attachment of thermal gaseous electrons to sulfur hexafluoride and perfluoromethylcyclohexane have been measured using a microwave cavity resonance technique. The measurements are compared to the results of recent electron beam work. The rate constants for attachment to SF_6 and C_7F_{14} are respectively, $3.1\text{x}10^{-7}$ and $9.8\text{x}10^{-8}$ cc/molecule sec. The former rate constant decreases and the latter slightly increases as the electron temperature is raised.

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Recently there has been considerable interest in collisions of low energy electrons with molecules. Most studies[1-4] of electron dissociative attachment and resonant capture have been carried out with pseudo-monenergetic electron beams obtained by the retarding potential difference technique. The difficulties associated with measuring absolute inelastic cross sections, particularly of very sharp resonances, and of obtaining a reliable calibration of the electron energy scale are well known. In view of these considerations it seemed important to investigate the electron attachment phenomenon by a totally different technique. In this paper we report the rates of thermal electron attachment to sulfur hexafluoride and perfluoromethylcyclohexane as measured by microwave cavity resonance. These gases were chosen because they have been studied recently by the electron beam method.[4]

Experimental

The electrons were produced by vacuum ultraviolet flash photolysis of nitric oxide and their concentration measured as a function of time by observing the departure from resonance of a microwave cavity that contained the reaction vessel. The reaction cell consisted of a quartz tube 2.5 cm in diameter. An end window of lithium fluoride, located just outside the microwave cavity, was attached with epoxy cement, and separated the reaction cell from a light source which consisted of a 2.5 cm diameter tube filled with krypton at 35 mm pressure.

The lamp was powered by a one megawatt square pulse of 2450 Mc microwave power which had a 2.5 microsecond duration. The ionizing radiation emitted by this type of lamp is most intense near 1236 Å (10.0 eV).

The microwave field was approximately uniform over the part of the lamp contained in the excitation cavity. Consequently it is to be expected, and direct visual observation indicated, that the lamp was effectively a thick uniform source 25 mm in diameter. Since the front surface of the luminous area was at least 15 cm from the gas in the microwave detection cavity, any minor spacial nonuniformity in the lamp would not be expected to produce nonuniform illumination of the reaction cell.

The reaction vessel was located axially in a cylindrical microwave cavity which had a resonant frequency of 3154 Mc and a loaded Q of 5000. A low level constant frequency microwave probing signal was delivered to the cavity. Bolometer measurements showed that under experimental conditions, less than 30 microwatts of power entered the cavity. This power level is low enough that the heating of the electron gas is negligible under our experimental conditions, and the electron temperature can be taken as 300°K.

The detection cavity was operated in the TM_{010} mode, and took the position usually occupied by the reference cavity in a Pound klystron stabilizer circuit. In our arrangement, however, the differential error signal from the Pound stabilizer, which indicated the departure of the cavity resonant frequency from the frequency of the probing signal, was fed to the Type D preamplifier of a Tektronix 545 oscilloscope. The error signal is a linear function of the change in the cavity resonant frequency for small departures of the cavity resonant frequency from the frequency of the probing signal. Since the cavity resonant frequency is a linear function of the electron concentration[5] for a lossless electron gas, the error signal displayed on the oscilloscope was directly proportional to the electron concentration in our experiments. This arrangement gave us a continuous record of electron concentration after the light pulse. The fact that the electron attachment reactions follow a pseudo-first order differential rate law made it unnecessary to obtain an accurate absolute determination of the electron concentration in order to obtain rate constants.

Even though the cavity which delivered power to the lamp and the electron detection cavity had different resonant frequencies, there could be considerable power leakage from the lamp into the detector during the 2 microseconds the lamp was on. In some cases this power leakage could be large enough to cause further ionization by the photoelectrons in the reaction cell. This power transfer was avoided by using on both cavities 2.5 cm diameter tubular ears which acted as power attenuators. The ears of the lamp cavity were lined with moist asbestos to increase their attenuation. In addition, use of 35 mm pressure of krypton in the lamp led to increased dissipation of the microwave power in the lamp, and diminished leakage from the cavity. With this arrangement, no significant power leakage from the lamp into the detection cavity could be detected.

The gas handling system was of the conventional glass type with a mercury diffusion pump protected by a liquid nitrogen trap. Stopcocks greased with Apiezon N were used. The fact that the gases studied have electron attachment cross sections that are much larger than those of possible contaminants made the use of ultrahigh vacuum technique unnecessary. This was verified by comparing the electron decay rates in gaseous mixtures with and without the SF_6 or C_7F_{14} present. To prepare a reaction mixture, the SF_6 or C_7F_{14} was allowed to evaporate from a trap into a known volume until the pressure as measured by a McLeod gauge had reached a few microns. The gas was then expanded into the reaction cell and its pressure (usually less than 10^{-5} mm) was calculated from known expansion factors. The calibration of the expansion volume was checked at several pressures. Even when the final pressure was in the vicinity of 10^{-5} mm, the pressure as calculated from calibration factors determined at higher pressures agreed to within 10 percent of the pressure as measured directly by McLeod gauges, an error which is within the reading uncertainty of the gauges. The pressures were constant in time, which indicated no detectable absorption or desorption effects. The validity of using the expansion factors to calculate the pressures lower than 10^{-5} mm can be questioned, but is supported by the fact (vide infra) that plots of the pseudo first order rate constants for electron decay as a function of pressure go through the origin of zero rate at zero pressure. Thus the pressure measurements and the derived second order rate constants have an uncertainty of at least 10 percent.

After the SF_6 or C_7F_{14} had entered the cell, 0.090 mm of nitric oxide and 18 mm of helium were delivered to the reaction cell and sufficient time allowed for the gases to mix by diffusion. At this nitric oxide pressure, only one percent of the incident light is absorbed in the cell. Consequently light absorption and thus electron generation was uniform along the reaction cell.

Results and Discussion

Some typical plots of the logarithm of the electron concentration as a function of time are shown in Fig. 1. Initial electron concentrations of over 10^7 cc^{-1} could be achieved, and no electrons were produced when nitric oxide was absent. The principal source of uncertainty in the relative electron concentrations was the finite thickness of the oscilloscope trace, and this was used to determine the size of the error bars in Fig. 1.

There are several features of the experiment that should be discussed before rate constants are deduced. A significant fraction of the electrons generated by photoionization of NO with 10 eV photons may have initial energies up to 0.7 eV. Consequently, it is important to estimate the thermal relaxation time of the electron gas. We follow here the treatment of Oskam.[6] Elastic collisions of electrons with essentially stationary gas molecules lead to a mean energy loss of approximately $(2m/M)(u-u_T)$, where u is the electron energy, u_T is the mean thermal energy of the molecules, and m and M are the electron and molecular mass respectively. If the collision frequency of the electrons is independent of their velocity, the electron energy relaxes according to

$$u = \Delta u_o \exp[-t/\tau] + u_T$$

where

$$\tau = M/(2m\nu)$$

and ν is the collision frequency of the electrons. The quantity Δu_o is the departure of the electron energy from the thermal value at $t = 0$. For Δu_o we take 0.7 eV, the most unfavorable assumption, for most of the photoelectrons have initial energies less than this. In this respect, photoionization is quite obviously superior to the microwave ionization techniques usually used in electron decay studies. The relaxation time τ can be expressed as[6]

$$\tau = 1.4\text{x}10^{-3}\ (\ell_o M)/(pT^{1/2})\ \text{sec}$$

where T is the temperature, p is the pressure in mm, and ℓ_o is the electron mean free path at 1 mm gas pressure. The time after which the energy of the electron deviates less than 10 percent of the thermal average energy is given by[6]

$$t \geq 1.4\text{x}10^{-3}\ (\ell_o M)/(pT^{1/2})\ \ln[(\Delta u_o)/(0.1\ u_T)]$$

For helium at 300°K the electron thermalization time is given approximately by $(100/p)\times 10^{-6}$ sec, if ℓ_0 is taken[7] to be 0.055 cm. Oskam[6] shows that if in contrast one assumes that the mean free path of the electrons is independent of the electron velocity the thermalization time is approximately one third the above value. Thus at the pressures used in our experiment, the electron thermalization time is approximately 5 microseconds.

The duration of the ionizing light pulse is an important factor in this problem. Although the microwave pulse that energized the lamp lasted only 2.5 microseconds, it is to be expected that the light emitted lasts noticeably longer. As shown in Fig. 1, the shape of the electron concentration-time curves for pure NO-He mixtures showed that electron generation became negligible 40 microseconds after the energizing pulse. Thus the thermal relaxation time and lamp duration set 50 microseconds as the lower limit for the reaction time constants that can be determined by our present technique. Observations of the electron concentration were carried out over periods that were typically 350 microseconds duration.

The absorption spectra of SF_6 and C_7F_{14} in the vacuum ultraviolet are not known. It seems unlikely, however, that either molecule has metastable excited states with lifetimes greater than 10^{-5} sec. Thus any photoexcited electronic states of these molecules should either decay by fluorescence, collisional quenching or dissociation before the measurements of electron concentration begin. Similarly, if any vibrationally excited states of SF_6 or C_7F_{14} are produced, they should be collisionally quenched in a few tens of microseconds, since vibrational relaxation in such complex molecules is relatively rapid.

One must also consider the possible depletion of the SF_6 or C_7F_{14} by the photolysis flash. Rate constants for electron decay were obtained for the first, tenth, and one hundredth flash of any given mixture. The pseudo first order rate constants decreased as the number of flashes increased, and after 100 flashes were typically 0.6 of their value on the first flash. Only rate constants for the first flash are reported here.

Although the plots of the logarithm of relative electron concentration as a function of time were linear within experimental error over a factor of ten change in electron concentration, there was a noticeable tendency for the slope to increase in the very last stages of the reaction. This occurred whether or not SF_6 or C_7F_{14} were present, and is apparently associated with the transition from ambipolar to free diffusion of electrons that occurs when a substantial number of electrons have become attached. Free diffusion of electrons becomes increasingly important as the Debye length of the plasma approaches the smallest vessel dimension. If the electron concentration is as low as 10^6 cc^{-1} the smallest concentration we could measure, the Debye length is 0.1 cm, which while still small compared to the vessel radius of 1 cm, is large enough that free electron diffusion should begin to occur as the electron concentration approaches the detectability limit. The rate constant for electron loss by free diffusion can be written as

$$k_D = D[(2.4)/(r_o)]^2$$

where D is the electron diffusion coefficient, and r_o is the radius of the reaction vessel. If we evaluate D approximately from $D = \frac{1}{3}\bar{v}\ell$, where $\bar{v}$ is the mean speed and ℓ is the electron mean free path, we find $k_D \cong 4\times10^4$ sec^{-1} at a pressure of 18 mm helium if we take $\ell_o = 0.055$ cm. This diffusional decay rate constant is equal to or up to an order of magnitude greater than the attachment rate constants we find, and consequently the effects of free electron diffusion should begin to appear at the lowest measured electron concentrations, as the data in Fig. 1 suggest is the case. In drawing the lines to deduce the attachment rate constants, emphasis was placed on the data obtained early in the decay, before free diffusion became apparent. As a further check on the rate constants determined this way, the pressure of helium was varied at a constant SF_6 concentration in one of the experiments. Rate constants obtained at 2.7, 15, and 18 mm of He agreed well within experimental error, which indicates diffusional loss of electrons does not affect the value of our rate constants noticeably.

First order rate constants were derived from plots of the logarithm of the electron concentration as a function of time, and the resulting data are shwon in Fig. 2 and Table 1. A very small correction determined from experiments with pure NO-He mixtures has been made to account for ambipolar diffusional loss and attachment to nitric oxide. It is clear that the first order rate constant increases linearly with the pressure of SF_6. The lifetime of the ion $(SF_6^-)^*$ with respect to electron ejection is greater than the time between collisions, for mass spectrometer studies[8] show the lifetime of $(SF_6^-)^*$ under collision free conditions is at least 10^{-6} sec, while the time between collisions at 18 mm pressure is approximately 10^{-8} sec. Thus the attachment mechanism is

$$e + SF_6 \longrightarrow (SF_6^-)^* \qquad (1)$$

$$(SF_6^-)^* \longrightarrow SF_6 + e \qquad (2)$$

$$(SF_6^-)^* + He \longrightarrow SF_6^- + He \qquad (3)$$

with $k_3[He] \gg k_2$. Consequently our measurements give the rate constant for reaction (1) as $k_1 = 3.1 \times 10^{-7}$ cc/molecule sec.

The results of the experiments with perfluoromethylcyclohexane are also shown in Fig. 2 and Table 1. The ion $C_7F_{14}^-$ has been observed in a mass spectrometer,[4] so its lifetime under collision free conditions must be at least one microsecond. Consequently our measurements give the rate constant for the capture reaction

$$e + C_7F_{14} \longrightarrow (C_7F_{14}^-)^* \qquad (4)$$

for which we find $k_4 = 9.8 \times 10^{-8}$ cc/molecule sec.

The uncertainty in any determination of the slope of the logarithmic plots introduces an uncertainty of approximately ±10% in any of the pseudo first order rate constants. The simultaneous uncertainty of ±10% in the pressure measurement means that any second order rate constant is uncertain to at least 15%, and a more generous error estimate might be 25% in any one rate constant. The mean of the nine values of each second order rate constant will have a smaller uncertainty of the order of 10%. The average deviation of the values of k_1 and k_4 from their respective means is in fact less than 10%.

It is interesting to compare the results of our experiments with those obtained with electron beam techniques. Ideally, electron beam experiments yield the velocity dependent cross section $\sigma(v)$ as a function of electron energy. The rate constants we measured are related to these attachment cross sections by

$$k = \int_0^\infty v\ \sigma(v)\ fdv \qquad (5)$$

where fdv is the normalized thermal velocity distribution function. If $\sigma(v)$ were available from electron beam measurements, rate constants could be calculated that could be compared directly to our measured values. In fact, the electron beams employed to date have energy spreads of the order of 0.1 eV, and consequently do not necessarily reveal the true velocity dependence of the cross section, particularly when the latter varies rapidly with energy.

To effect an approximate comparison between the electron beam and thermal electron experiments, we can assume $\sigma(v)$ is constant over the range of the more probable thermal velocities. From Eq. (5) we get

$$\bar{\sigma} = k/\bar{v}$$

where $\bar{v}$ is the average electron speed. Although this assumption may be quite incorrect, it may lead to an average cross section comparable to those derived from electron beam experiments for the following reason. In many electron beam experiments the width of the electron energy spread is approximately 0.1 eV. Since in a thermal electron gas at 300°K ninety percent of the electrons have energies less than 0.08 eV, the thermal spread of energies is comparable to the spread in energies of an electron beam of approximately 0.04 eV energy.

Our data give an average cross section of $2.6\text{x}10^{-14}$ cm^2 for electron attachment to SF_6. From electron beam experiments Asundi and Craggs[4] report $1.3\text{x}10^{-15}$ cm^2 at 0.03 eV, while Buchelnikova[2] gives $5.7\text{x}10^{-16}$ cm^2. The lack of agreement between these determinations and the fact that they are smaller than our value of $2.6\text{x}10^{-14}$ cm^2 are understandable if the capture cross section is greatest near zero energy and drops rapidly with increasing energy. In fact, we observed that if the microwave power to the detection cavity was increased to the point where the electron temperature surely was raised, the rate of attachment to SF_6 decreased. This confirms the idea that the resonant attachment cross section has a sharp maximum at energies near zero.

For C_7F_{14}, our data give 8.2×10^{-15} cm^2 for the average electron attachment cross section. Asundi and Craggs[4] found a maximum attachment cross section of 7.5×10^{-15} cm^2 at 0.15 eV for C_7F_{14}. The fact that we find a cross section of similar magnitude for electrons of 0.039 eV average energy suggests that the cross section at 0.15 eV may have been underestimated, or that the maximum in the cross section may occur in the range 0.05-0.10 eV instead of at the higher energy. Some support for the latter point of view comes from our observation that increasing the electron temperature leaves the attachment rate unchanged or slightly increased. If the maximum cross section lay at 0.15 eV, we surely would expect the attachment rate to increase markedly with electron temperature.

The agreement and contrasts between our determinations of electron attachment cross sections and those obtained from electron beam measurements suggests that experiments with thermal electrons can be a valuable supplement to electron beam work, particularly if it proves possible to achieve a range of known electron temperature and better energy resolution can be achieved in the beam experiments.

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Table I

First order rate constants for electron decay.[a]

Run	Pressure SF_6 $\times 10^6$ mm	k $\times 10^{-4}$ sec^{-1}	Run	Pressure C_7F_{14} $\times 10^6$ mm	k $\times 10^{-4}$ sec^{-1}
1	6.49	5.91	8	0.972	0.294
2	3.73	2.76	9	1.73	0.531
3	3.12	2.43	10	3.42	0.98
4	1.95	1.74	11	4.92	1.30
5	1.73	1.55	12	6.08	1.72
6	0.675	0.553	13	6.91	2.05
7	0.547	0.442	14	7.35	2.46
17	6.49	5.52	15	8.27	2.03
18	6.49	5.64	16	8.27	2.33

[a] A correction of -0.06×10^4 sec^{-1} has been made on each k to account for diffusion and attachment. All runs were carried out at 18 mm He pressure except runs 17 and 18 for which the He pressures were 2.6 and 15 mm respectively.

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Figure Captions

Fig. 1. Electron concentration (arbitrary units) as a function of time for decays in 18 mm He and 0.090 mm NO, and in He-NO-SF_6 and He-NO-C_7F_{14} mixtures. Curves from which these data were drawn were continuous, and a larger number of points could have been plotted.

Fig. 2. First order rate constants for electron attachment as a function of the pressure of SF_6 and of C_7F_{14}.

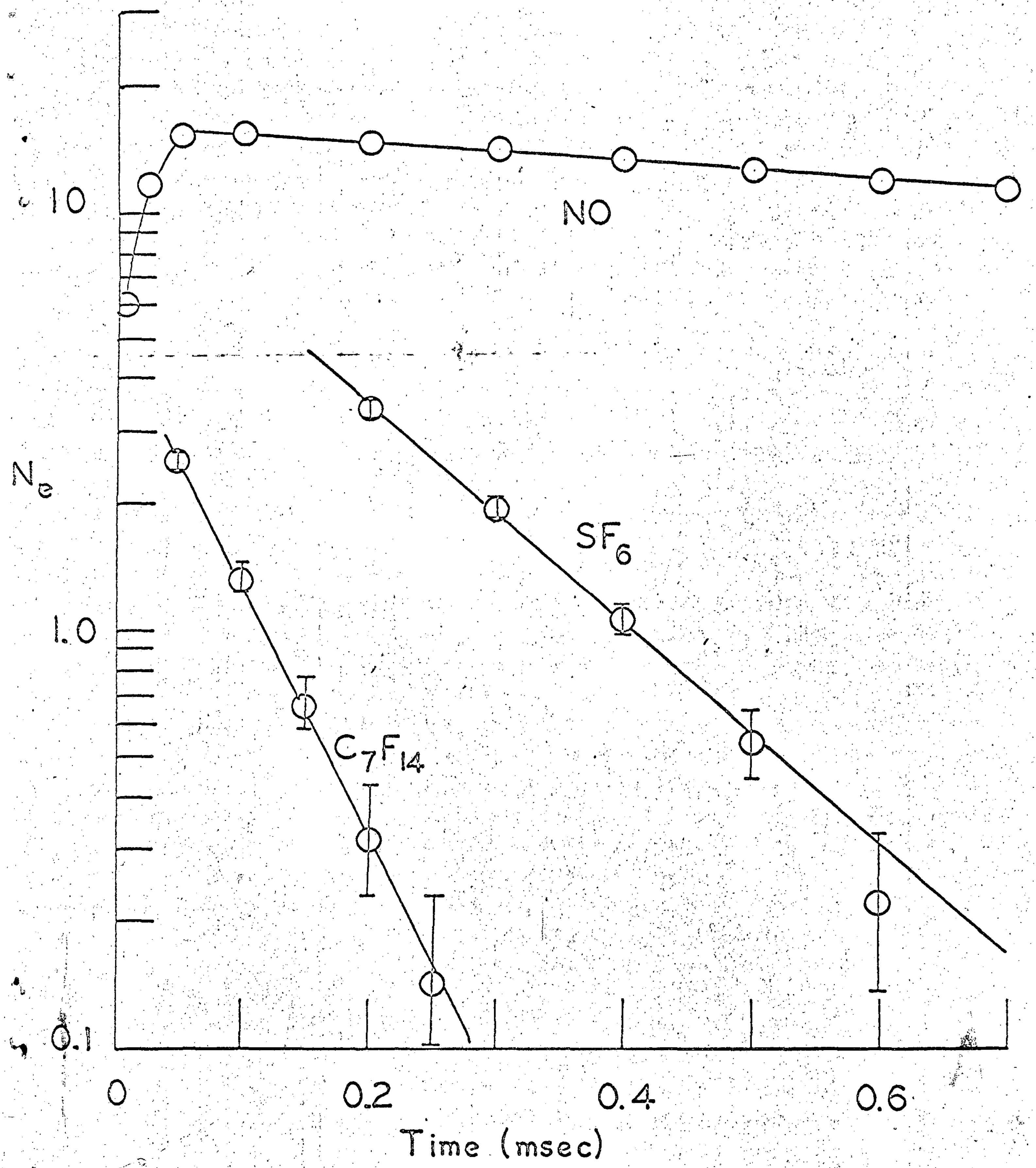

Fig. 1

[illegible] + [illegible] Fig. 1

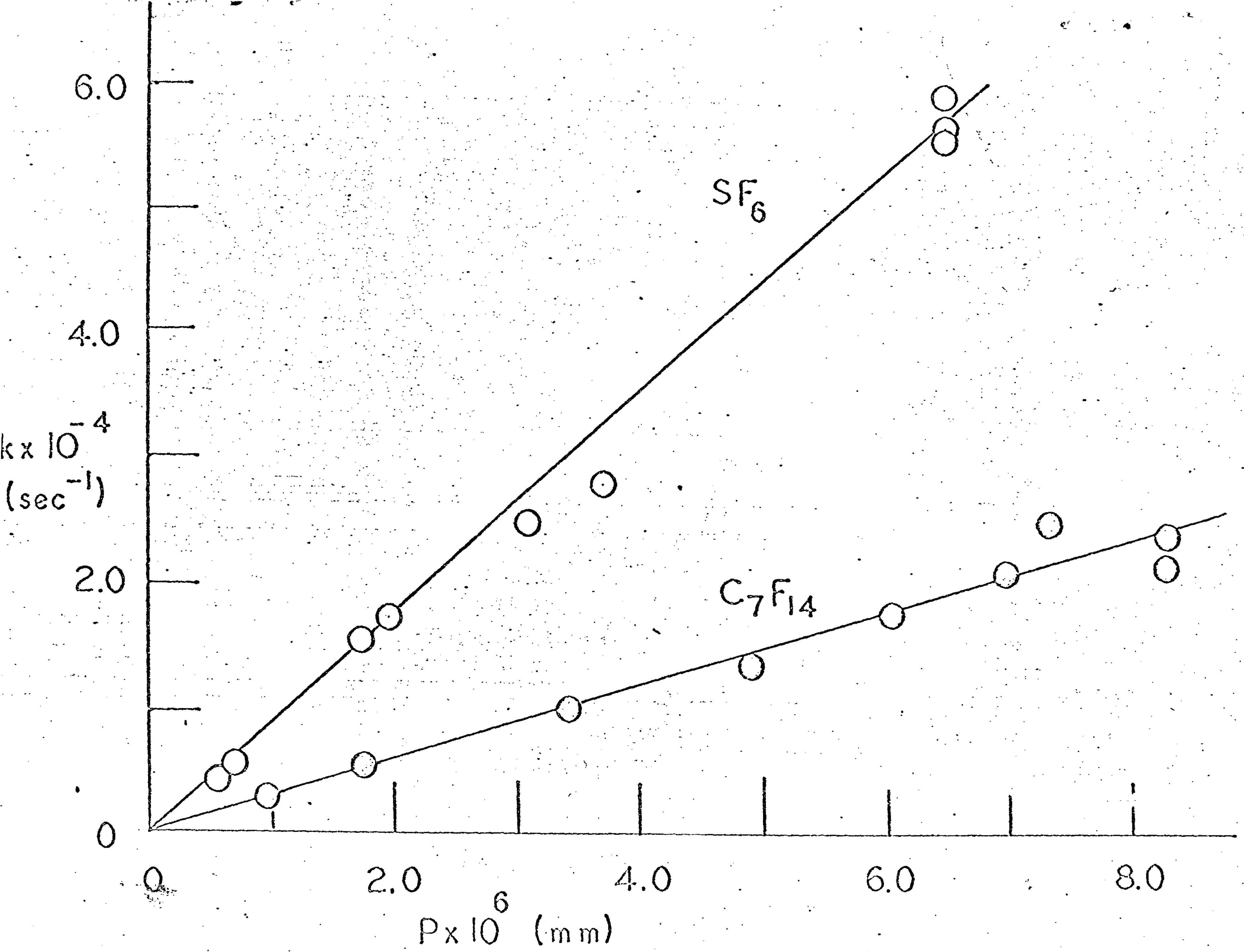

Fig. 2

Maclean + Young Fig. 2