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Rate of Attachment of Gaseous Electrons to Nitrogen Dioxide

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The rates of attachment of gaseous thermal electrons (300°K) to NO_2 in the presence of several inert gases have been measured. In the pressure range from 3 to 70 mm, the rate of attachment is independent of the pressure, but dependent on the nature of the inert gas. A mechanism is proposed that accounts for these observations.

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It is known that NO, because of its low ionization potential, is important as a 'sink' for positive charge in the upper atmosphere. It now seems that NO_2, which has a very high electron affinity (~4 eV)[1] plays a similar role toward electrons. Indeed, NO_2^- is the only negative ion detected by rocket-borne mass spectrometers.[2] It is therefore of some interest to examine electron attachment processes in NO_2, particularly at low electron energies. In this investigation, we have measured the rate at which free thermal electrons attach to NO_2 in the presence of a non-attaching gas.

EXPERIMENTAL

Electrons were produced by the 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 technique has been described in detail in a previous publication.[3] Briefly, the reaction vessel is a quartz cylinder located axially within a microwave cavity. The cavity is part of a Pound discriminator circuit, occupying the position usually taken by the reference cavity. A low level microwave signal whose frequency is near that of the TM_{010} mode of the cavity (in this case 3080 MHz) is fed into the cavity. A small difference in frequency between probing signal and resonance produces a differential error signal which is fed into the type D preamplifier of a Tektronic oscilloscope. This error signal is directly proportional to the difference between the

probing and cavity resonance frequencies. The presence of electrons within the cavity causes a shift in its resonance frequency, the shift being proportional to the mean electron density in the cavity. The rate at which electrons disappear after the ionizing flash is equivalent to the rate at which resonance frequency approaches its original value and this is recorded photographically from the scope trace of error signal vs. time.

The gas-handling system was of glass and metal, employing Granville-Phillips Type C ultra-high vacuum valves. The reaction cell was a cylinder, 1" dia, closed at one end by an LiF window. This was attached to the quartz via a silver thimble with silver chloride as sealant.[4] The system was bakeable at temperatures up to 200°C. It was evacuated by a 2" oil diffusion pump backed by a mechanical pump and the ultimate pressure attained was 10^{-7} Torr as measured on an Alpert gauge. Working gas pressures were measured on C.E.C. capacitance manometer.

The ionizing radiation was produced by an H_2 filled lamp. This lamp was also a 1" dia quartz cylinder with an LiF window positioned about 2 mm from the window of the reaction cell. The lamp was powered by a 1 MW square pulse of 2450 MHz microwave power which had a 2.5 microsecond duration. The most intense radiation from this lamp is at 1216 Å (10.2 eV) The ionization potential of NO is 9.3 eV and that of NO_2 is 9.8 eV. However, at about 10 eV the ionization cross-section of NO_2 is so low that no electrons could be detected on flashing

in the absence of NO. Radiation that might dissociate rather than ionize NO and NO_2 was attenuated by the atmospheric oxygen in the 2 mm path between lamp and cell.

The electrons from photoionization of NO can have up to about 1 eV initial energy. Calculations show, however, that thermalization times are only a few microseconds[3] and, in estimating rate constants, concentration measurements were made only for times longer than 50 microseconds after the flash. Thus, the electrons were assumed to be at the gas temperature, 300°K. Deliberate attempts to heat the electrons by increasing the microwave power produced no change in attachment rate constant.

The NO and NO_2 employed were Matheson gases of 99.5% stated purity and the inert gases were reagent grade obtained from Airco. All were used without further purification.

In any experiment, NO_2 from a lecture bottle was let into the system through an acetone/CO_2 cold trap. The gas was then condensed in a liquid N_2 trap and pumped on for several minutes. The liquid N_2 was removed and the NO_2 pressure measured with the capacitance manometer. The liquid N_2 was replaced and NO allowed to diffuse into the system through another liquid N_2 cold trap. Usually about 85 microns NO were admitted. Finally, the desired pressure of diluent gas M was added. At least 30 minutes were allowed to ensure mixing before flashing. The scope trace was photographed and a plot of ln (signal) vs. time drawn to give the first order rate constant for electron decay. An example of such a plot is given in Fig. 1. In general,

these plots were linear over a five-fold decrease in electron concentration, which indicates that electron decay by electron-ion recombination and higher order diffusion was negligible. The measured rate constant was independent of the number of flashes, so dissociation of NO and NO_2 was not important. As a result, the pressure of M could be increased and several runs performed with any one NO/NO_2 mixture at different pressures of M. Corrections for loss by diffusion and attachment to NO were obtained by doing runs in NO and M only. In general, this correction factor was 3%-5% of the measured rate constant, but in low pressures of He, where diffusion losses were high, it approached 20% of the measured value. The pseudo first-order rate constant for electron attachment to NO_2 thus obtained was shown to be independent of the concentration of NO. Therefore, attachment to trace quantities of N_2O_3 present because of the equilibrium $NO + NO_2 \rightleftharpoons N_2O_3$ was not important.

RESULTS AND DISCUSSION

The pseudo first-order rate constants corrected for diffusion and attachment to NO are displayed as functions of total gas pressure in Fig. 2. It is clear than in the pressure range studied, the pseudo first-order rate constant for electron attachment to NO_2 depends on the nature, but not on the concentration of inert gas. In Fig. 3 the same rate constants are shown to increase linearly with increasing NO_2 pressure. Consequently the rate law for the attachment reaction is

$$-\frac{d(e)}{dt} = k(NO_2)(e)$$

where k depends on the nature of the inert gas. The values of k are given in Table I.

The dependence of the attachment role on the nature but not the concentration of inert gas is similar to the behavior found for some atom-diatomic molecule radiative association reactions.[5] By analogy to these cases we can postulate the electron attachment mechanism is

$$NO_2 + e \longrightarrow (NO_2^-)^* \qquad (1)$$

$$(NO_2^-)^* \longrightarrow NO_2 + e \qquad (2)$$

$$(NO_2^-)^* + M \longrightarrow NO_2^- + M \qquad (3)$$

$$(NO_2^-)^* + M \longrightarrow NO_2 + M + e \qquad (4)$$

Making the steady state assumption for $(NO_2^-)^*$ we find

$$-\frac{d(e)}{dt} = \frac{k_1 k_3 (NO_2)(M)(e)}{k_2 + (k_3+k_4)M} \quad . \qquad (5)$$

If the lifetime with respect to electron ejection is longer than the time between collisions, we have $k_2 << (k_3+k_4)M$, and Eq. (5) reduces to

$$-\frac{d(e)}{dt} = \frac{k_1 k_3 (NO_2)(e)}{k_3+k_4} \quad . \qquad (6)$$

Equation (6) is consistent with the experimentally observed order of the reaction, and with the dependence of the rate constant on the nature of the inert gas.

If the stabilization of the excited ion is pictured as a vibrational deactivation of a highly excited molecule similar to those that occur in thermal unimolecular reactions, k_3 should be approximately 10^{-10} cc/molecule sec. The value of k_3 might be even larger because of the effect of ion induced dipole forces on the total cross section. It is unlikely that k_4 is much larger than k_3, and if it were much less than k_3, the effect of the nature of the inert gas on the rate would disappear. Thus k_3 and k_4 are of the same order. In the pressure range of our experiments, we then can estimate that $(k_3+k_4)M \geq 10^8$ sec^{-1}, which implies that the lifetime of the ion with respect to spontaneous electron detachment is greater than 10^{-8} sec.

If k_3 and k_4 are of approximately equal magnitude, k_1 must be roughly 10^{-10} cc/molecule sec in order to be consistent with the experimental rate constants. This value for k_1 means that the cross section for the attachment process is 10^{-16} cm^2, which is not an unreasonable value. Therefore the direct attachment mechanism with collisional deactivation and detachment of the excited ion is consistent with the reaction order, the inert gas effect, and with reasonable values of the individual rate constants.

Although the overall attachment rate constant k varies by only a factor of 2.5 for the inert gases investigated, a systematic variation of k with the mass of the inert gas molecule is evident. A plot of k as a function of the mass of the inert shows a clear maximum at the argon mass, with the rate constant

decreasing monotonically for higher and lower masses. This behavior implies k_3/k_4 has its maximum value for argon. The significance of this behavior is not clear. One might expect the rate constant for the detachment process to increase as the strength of the intermolecular forces increase with atomic number. On the other hand, one might anticipate a similar behavior for the deactivation rate constant. Until more is known about the detachment and deactivation processes individually, a detailed interpretation of the overall attachment rate will not be possible.

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Table 1

Rate Constants for Electron Attachment to NO_2.

Added Gas M	k (cc/molecule sec)
He	2.0×10^{-11}
Ne	3.1×10^{-11}
Ar	4.5×10^{-11}
Kr	3.0×10^{-11}
Xe	2.5×10^{-11}
N_2	4.0×10^{-11}

References

1. A. L. Farragher, F. M. Page, and R. C. Wheeler, Discussions Faraday Soc. 37, 203 (1964).
2. C. Y. Johnson, E. B. Meadows, and J. C. Holmes, J. Geophys. Res. 63, 443 (1958).
3. B. H. Mahan and C. E. Young, J. Chem. Phys. 44, 2192 (1966).
4. R. C. Lord and R. S. McDonald, Rev. Sci. Instr. 23, 442 (1952).
5. M. A. A. Clynne and B. A. Thrush, Proc. Roy. Soc. (London) 269, 404 (1962).

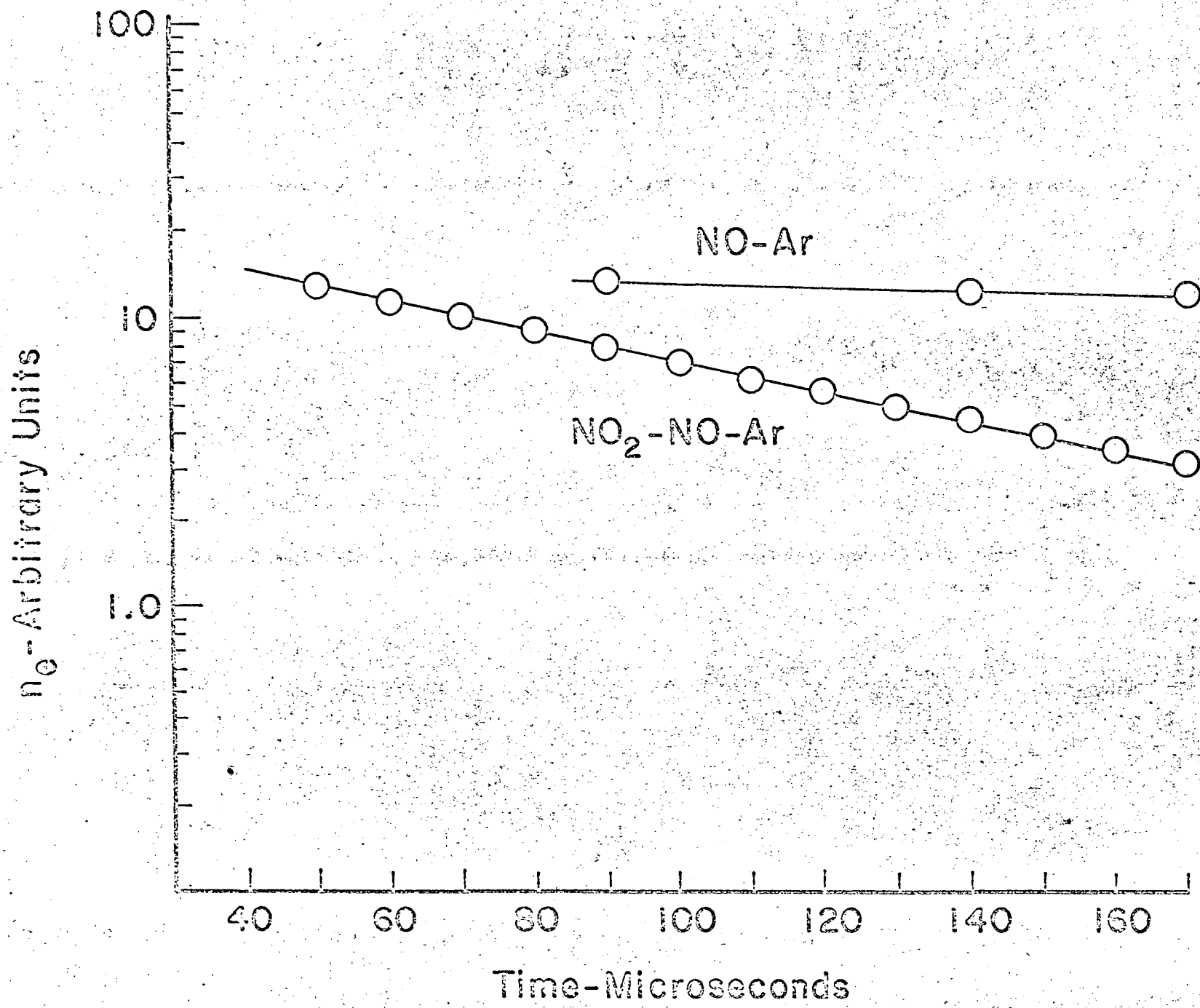

Figure 1. Logarithm of the electron concentration as a function of time for NO-Ar and NO-NO_2-Ar mixtures. Pressures of NO_2, NO, and Ar were 8μ, 85μ, and 10 Torr, respectively.

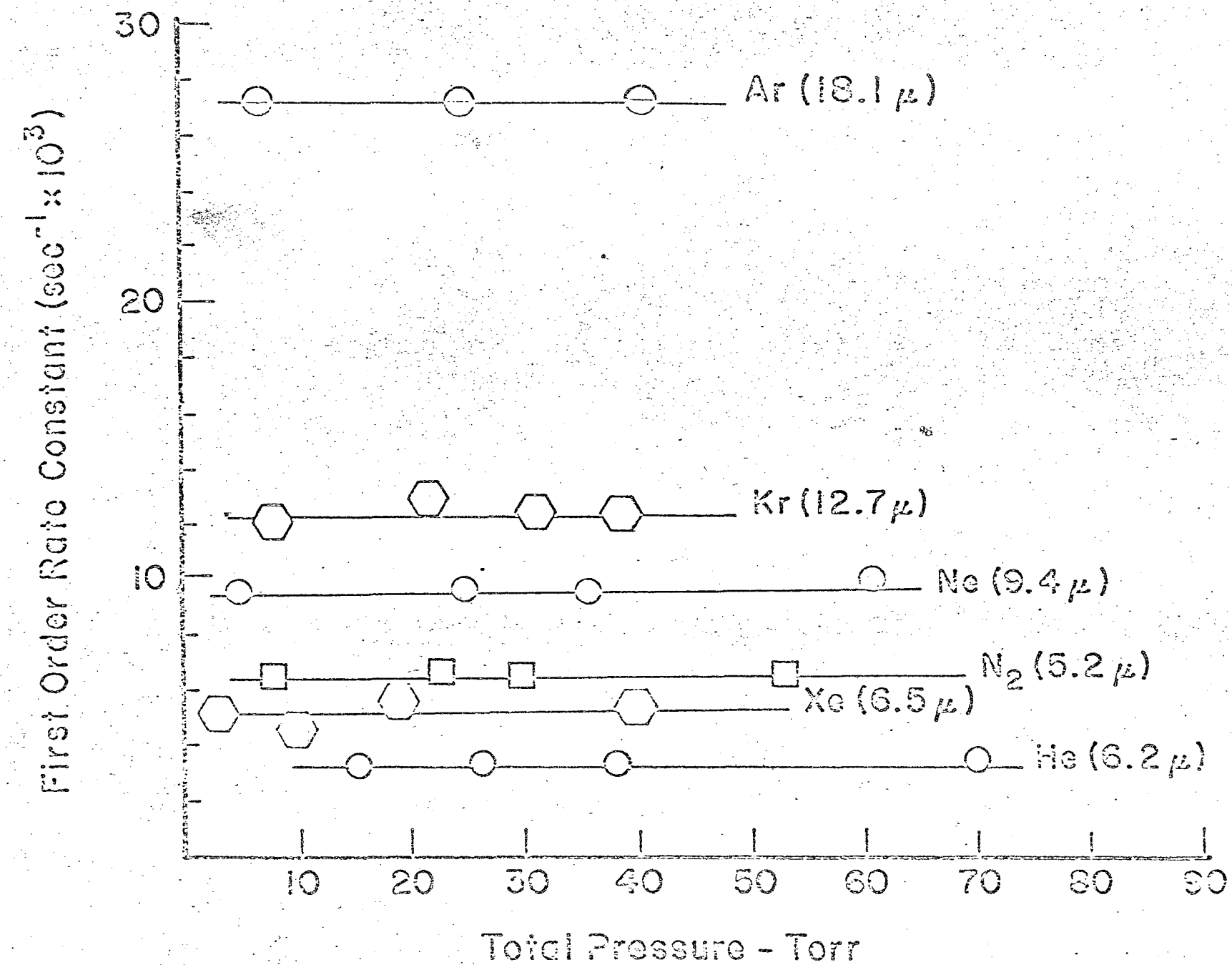

Figure 2. First order rate constant for electron attachment to NO_2 as a function of total pressure in different inert gases. The NO_2 pressure for each run is given in parenthesis. NO pressure was 85 microns.

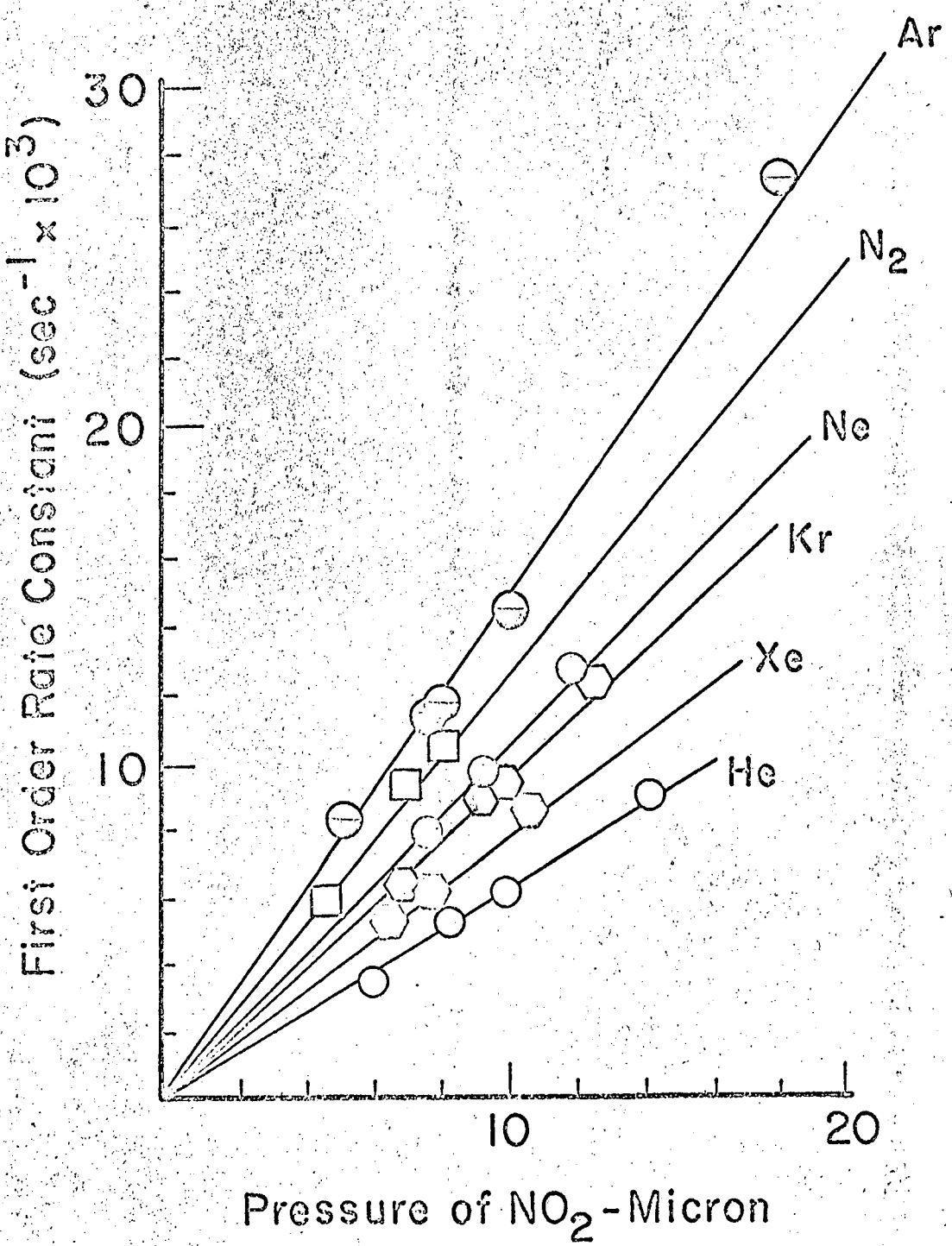

Figure 3. First order rate constant for electron attachment to NO_2 as a function of NO_2 pressure.

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