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Measurement of the Rate Coefficient of the Reaction $CO^+ + 2CO \rightarrow CO^+ \cdot CO + CO$ in a Drift-Tube Mass Spectrometer*

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The rate coefficient for the ion-molecule reaction $CO^+ + 2CO \rightarrow CO^+ \cdot CO + CO$ was measured with a drift-tube mass spectrometer at a gas temperature of 300 °K. The range of E/N which was covered extended from 75 to 150 Td. [Here E/N is the ratio of the electrostatic-drift-field intensity to the gas number density and is measured in Townsend (Td), where 1 Td $= 10^{-17}$ V cm^2.] The technique used to evaluate the rate coefficient was the comparison of detailed "arrival-time" profiles for the product ions with analytical solutions to the differential equation governing the motion of the ions. The measured values of the rate coefficient varied from a high of 1.35×10^{-28} cm^6/sec at an E/N of 75 Td to 1.1×10^{-28} cm^6/sec for values of E/N between 110 and 150 Td.

I. INTRODUCTION

This paper presents the results of measurements of the rate coefficient of the reaction

$$CO^+ + 2CO \rightarrow CO^+ \cdot CO + CO \, . \qquad (1)$$

The data were obtained with a drift-tube mass spectrometer of ultrahigh-vacuum construction. The rate coefficient was evaluated at 300 °K as a function of E/N over the range of 75 to 150 Td. In these measurements, the gas pressure was varied from 0.078 to 0.159 Torr. The technique used to evaluate the rate coefficient was the comparison of product-ion "arrival-time" profiles for various values of E/N and pressure, with analytical solutions to the differential equation governing the motion of the ions.

Chong and Franklin[1] have also measured the rate coefficient for the conversion of CO^+ into $CO^+ \cdot CO$. A mass spectrometer with a high-pressure ion source was used. In their apparatus, the drift field inside the ion source was fixed at 11.5 V/cm, and the pressure was varied from 0.1 to 1.2 Torr. The rate coefficient was obtained by analyzing the variation of the intensity of the observed ions with gas pressure. The influence of several impurities, notably CO_2 and H_2O, was considered. The forward (attachment) reaction rate was determined from the decrease in CO^+ intensity along with the increase in $CO^+ \cdot CO$ intensity as the pressure was increased. This rate coefficient was determined to be 1.43×10^{-28} cm^6/sec. At high pressures, an equilibrium constant was determined, and thereby a backward (detachment) reaction rate was obtained.

Several comments are relevant here. First, the rate coefficients of many reactions, especially dissociation or detachment reactions, are very sensitive to the mean energy of the collisions. Hence, it is desirable that each separate determination of a rate coefficient be based on measurements all made at a fixed value of E/N, i.e., fixed-ion energy. A series of such measurements at various values of E/N can then provide the rate coefficient as a function of E/N. Second, if both formation and breakup occur in a reaction scheme, then an analysis involving both the forward and backward reactions needs to be employed. The influence of the production of parent ions due to product-ion breakup within the drift region must be considered. Third, in the determination of equilibrium constants, ion-intensity studies need to be made that are independent of mass discrimination in the ion sampling. Also if the product-ion species is a weakly bound molecular system, extreme care must be used in the extraction of the ions from the drift region in order to prevent their breakup before mass analysis. In the present research, care was taken to prevent any of these effects from disturbing the results of the measurements.

The drift-tube mass-spectrometer apparatus employed here has been described briefly in the preceding paper[2] (Paper I) and in detail elsewhere.[3–7] It will suffice here to state that the data it provides take the form of high-resolution time profiles of ion swarms as they drift in an electric field past a fixed sampling point. The sampling involves a mass selector, so that separate profiles, or "arrival-time spectra," are obtained for each distinct molecular species of ions present in the swarm. An important feature of the apparatus is a movable ion source, which permits the drift distance (the distance between the point at which ions are introduced and the point at which they are sampled) to be varied over the range of 1–44 cm.

The positions, intensities, and detailed shapes of these profiles, and the manner in which they vary with the drift distance and the gas number density N, evidently depend on the mobilities, diffusion coefficients, and rates of ion-molecule reactions which create or destroy ions of a given species. Methods of analyzing the profile data to evaluate mobilities and diffusion coefficients have been briefly outlined in Paper I. In Sec. II, the analysis used to determine reaction-rate coefficients from the arrival-time profiles will be discussed.

II. ANALYSIS

As outlined in Paper I, ions are introduced into a drift space filled with a low-pressure gas and are subjected to a static uniform electric field. The electric field produces a net transport of the ions through the gas, characterized by the ionic mobility, which is the ratio of the drift velocity to the electric field strength. Superimposed upon this net transport is a rapid random motion due to the frequent collisions of the ions with the gas molecules. If there exists a number-density gradient of ions in the gas of uniform total pressure, there will be a motion of the ions to eliminate the gradient, characterized by the diffusion-coefficient tensor $\overleftrightarrow{\mathrm{D}}$.

During the drift and diffusion of the ions, collisions between ions and gas molecules can produce chemical reactions. Within the ion swarm, ions of a particular species may be disappearing and appearing due to conversion to and from other species. The rate (per ion) at which a given reaction occurs is denoted by the reaction frequency α in units of sec^{-1}. The reaction frequency depends on the collision frequency and, hence, on the number density N of the gas. The dependence of α on N is determined by the interactions involved. If α is proportional to N, the reaction is said to be two body, while if α is proportional to N^2, the reaction is said to be three body. The constant of proportionality k is called the reaction-rate coefficient.

If we consider the drift, diffusion, and reaction of a coupled pair of ionic species, A and B, whose number densities are sufficiently low that ion-ion interactions can be neglected, the coupled differential equations governing their number densities n_A and n_B are

$$\frac{\partial n_A}{\partial t}=\mathfrak{D}_A n_A+\alpha_{AB}n_B+\beta_A \tag{2}$$

and

$$\frac{\partial n_B}{\partial t}=\mathfrak{D}_B n_B+\alpha_{BA}n_A+\beta_B\ , \tag{3}$$

where

$$\mathfrak{D}_i=D_{Ti}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)+D_{Li}\,\frac{\partial^2}{\partial z^2}-v_{di}\,\frac{\partial}{\partial z}-\alpha_i\ ; \tag{4}$$

D_{Ti}, D_{Li}, v_{di}, and α_i represent, respectively, the transverse and longitudinal diffusion coefficients, the drift velocity, and the depleting reaction frequency of species i; and α_{ij} is the frequency of the reaction from species j to species i. The source-input term for species i is represented by β_i.

The source input is represented as an axially thin disk of radius r_0 formed at $t=0$:

$$\beta_i=f_i s S(r_0-r)\delta(z)\delta(t)\ , \tag{5}$$

where f_i is the fraction of ions of species i, s is the areal-source ion density, and $S(R)=1$ if R is positive, and zero otherwise. The coupled differential equations were solved[8] by successive applications of the Green's function representing depletion of a species n into species $(n+1)$. The full solution to these equations gives for the flux of ions passing through the exit aperture of the drift-tube mass spectrometer

$$\begin{aligned}\Phi_A(0,z,t)=as\int_0^t du\,\{&f_A[\delta(u)+\alpha_{AB}\alpha_{BA}(t-u)2I_1(\eta)/\eta]\\&+f_B\alpha_{AB}I_0(\eta)\}\{[2D_{LA}(z-r_d)/r_L^2]+v_{dA}\}\\&\times e^{-\gamma-(z-r_d)^2/r_L^2}(1-e^{-r_0^2/r_T^2})\,(\pi r_L^2)^{-1/2}\ ,\end{aligned} \tag{6}$$

$$\begin{aligned}\Phi_B(0,z,t)=as\int_0^t du\,\{&f_B[\delta(t-u)+\alpha_{AB}\alpha_{BA}(u)2I_1(\eta)/\eta]\\&+f_A\alpha_{BA}I_0(\eta)\}\{[2D_{LB}(z-r_d)/r_L^2]+v_{dB}\}\\&\times e^{-\gamma-(z-r_d)^2/r_L^2}(\pi r_L^2)^{-1/2}(1-e^{-r_0^2/r_T^2})\ ,\end{aligned} \tag{7}$$

where

$$r_T^2=4D_{TA}(t-u)+4D_{TB}u\ , \tag{8}$$

$$r_L^2=4D_{LA}(t-u)+4D_{LB}u\ , \tag{9}$$

$$r_d=v_{dA}(t-u)+v_{dB}u\ , \tag{10}$$

$$\gamma=\alpha_A(t-u)+\alpha_B u\ , \tag{11}$$

$$\eta^2=4\alpha_{AB}\alpha_{BA}u(t-u)\ , \tag{12}$$

u is the time the ion spends as species B, a is the area of the exit aperture, I_1 and I_0 are the first- and zero-order modified Bessel functions. Here A represents the CO^+ ions and B the $\mathrm{CO}^+\cdot\mathrm{CO}$ ions.

If we restrict our consideration to the case where the backward reaction makes a negligible contribution to the product-ion spectrum, as in the present experiments, then α_{AB} may be put equal to zero, and we have

$$\begin{aligned}\Phi_B(0,z,t)=as\int_0^t du\,[f_B\delta(t-u)+f_A\alpha_{BA}](\pi r_L^2)^{-1/2}\\\times\left(\frac{2D_{LB}(z-r_d)}{r_L^2}+v_{dB}\right)\exp\left(-\gamma-\frac{(z-r_d)^2}{r_L^2}\right)\\\times\left[1-\exp\left(-\frac{r_0^2}{r_T^2}\right)\right]\ .\end{aligned} \tag{13}$$

III. PROCEDURE

The basic experimental data that were used to calculate the reaction-rate coefficients were the arrival-time profiles of the reaction-produced ions. The arrival-time profiles were matched to the analytical expression (13) that was presented in Sec. II. If the difference in drift distances, $(v_{dA}t - v_{dB}t)$, traveled by the two ion species in a time t is large compared to the square root of the sum of the diffusion areas, $(4D_{LA}t + 4D_{LB}t)^{1/2}$, for the same time t, then several simplifying approximations can be made. As shown in Ref. 8, these approximations lead to an expression relating the slope of the logarithm of the product-ion current versus time to the reaction frequency and transverse-diffusion coefficient. If the drift velocities of the parent- and product-ion species are sufficiently different, the use of this expression is convenient. If the drift velocities are different, but not greatly so, the best way to analyze the data is to use the full analytical expression (13) for the product-ion flux as a function of time and to fit the experimental arrival-time spectra to it. This was the scheme used in this research. In the curve-fitting procedure, the feature of the arrival-time spectrum that is most carefully matched is the broad sloping shoulder representing the transition from the situation where the ions spend almost all of their drift time as the parent-ion species to the situation where the ions spend none of their time in the parent form.

The first step in the analysis is the determination of values of the drift velocities and longitudinal-diffusion coefficients for use in the analytical expressions. For certain values of E/N we were able to obtain these values by the methods outlined in Paper I. However, in many cases we needed values where they could not be measured by the normal methods because of the influence of the ion-molecule reaction. In these regions, the difference in the drift velocities of the parent and product ions was estimated by measuring the width of the reaction-influenced product-ion arrival-time spectra; then by using the knowledge of one of the drift velocities, we could estimate the drift velocity of the other ion. In the case of the longitudinal-diffusion coefficients, only estimates of their values were needed because they enter into the analytical expression very weakly.

Once the drift velocities are determined, and estimates for the longitudinal-diffusion coefficients are found, the transverse-diffusion coefficients and the reaction frequency are determined. Both D_T and α determine the slope of the main shoulder of the product-ion spectra. To separate the effects of transverse diffusion and reaction, the differing effects of changes in pressure on these two quantities are used. The transverse-diffusion coefficient varies inversely with pressure, whereas the reaction frequency varies directly as the square of the pressure for a three-body clustering reaction. At low pressure, the slope of the product-ion spectrum is influenced more strongly by diffusion than at high pressure. The effect of the reaction frequency is just opposite, being more influential at high pressure. The best values of transverse-diffusion coefficients are arrived at by iteration. At low pressure, a guess is made for the value of the reaction frequency, and the transverse-diffusion coefficients are varied to get a close fit between the experimental data taken at this pressure and the analytical profiles. Either or both of the transverse-diffusion coefficients can be varied to arrive at the proper fit, for they have the same pressure dependence and their separate effects cannot be distinguished. Once satisfactory values of transverse-diffusion coefficients have been determined, the high-pressure experimental spectra are examined. The previously determined D_T's are used, and the value of the reaction frequency is varied to arrive at a good fit. The process is repeated until stationary values for both transverse-diffusion coefficients and reaction frequency are found. The agreement at various pressures indicates that the proper value of the reaction rate has been determined.

Figures 1 and 2 demonstrate the resolution of the curve-fitting procedure. The values of the reduced mobility (K_0) and ND_L for each species were determined as described earlier. The value of ND_T for $CO^+ \cdot CO$ was determined from the Wannier expression[9] and was not found experimentally. By using the curve-fitting procedure, the value of the reaction rate at an E/N of 75 Td was determined to be 1.35×10^{-28} cm^6/sec, with ND_T for CO^+ set equal to 17.1×10^{17} cm sec^{-1}. The reaction-rate coefficient was then varied by ±10%, and in each case, the value of ND_T for CO^+ was adjusted so that at 0.133 Torr the theoretical profiles again agreed with the experimental data. These three identical curves are plotted as the dashed line in Fig. 1.

Keeping the reaction-rate coefficients and values of ND_T constant for these three curves, the reaction frequencies and values of D_T were then computed for a pressure of 0.080 Torr. These values were used to compute the analytical curves displayed as the dashed curves in Fig. 2. Because the reaction frequency varies as N^2 and the diffusion coefficients vary as $1/N$, the three analyttical curves are no longer identical, and the match with the experimental arrival-time spectrum indicates the correctness of the determined rate constant. The values of ND_T for CO^+ that are

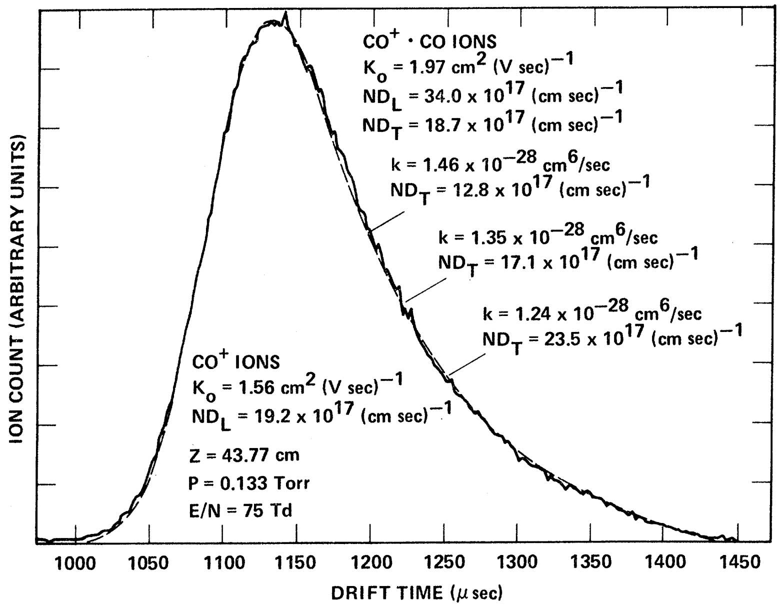

FIG. 1. A product-ion arrival-time spectrum obtained at high pressure (0.133 Torr). The solid line represents experimental results. The dashed line is obtained by the curve-fitting procedure explained in the text.

determined along with the reaction rate must be used with caution. The value of ND_T for CO$^+\cdot$CO predicted by the Wannier expression is assumed to be correct. Any error in this value will produce corresponding errors in the value of ND_T for CO$^+$, since both transverse-diffusion coefficients have the same pressure dependence.

IV. RESULTS

Reaction-rate coefficients were obtained over an E/N range of 75 to 150 Td. At each value of E/N where the reaction rate was measured, experimental data were taken at three or four pressures, from 0.078 to 0.159 Torr. Using reasonable values for the transverse-diffusion coefficients, the value of the reaction frequency α was clearly dependent on the number density to the second power, indicating that the reaction was definitely three body. The measured values of the reaction-rate coefficient varied from a high of 1.35×10^{-28} cm^6/sec at an E/N of 75 Td to 1.1×10^{-28} cm^6/sec for values of E/N between 110 and 150 Td, and are listed in Table I.

No theoretical equation appears to be available

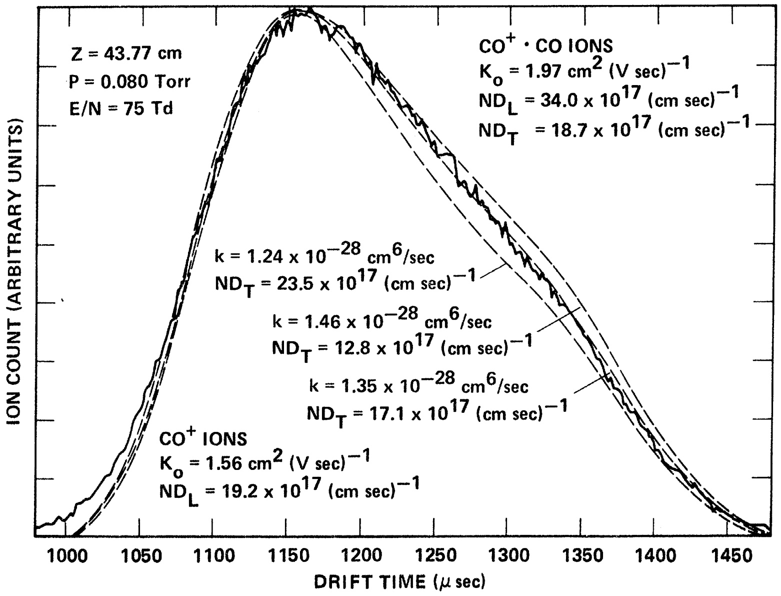

FIG. 2. A product-ion arrival-time spectrum obtained at low pressure (0.080 Torr). The solid line represents experimental data. The dashed lines are obtained by the curve-fitting procedure explained in the text.

TABLE I. Reaction-rate coefficient results for the reaction $CO^+ + 2CO \rightarrow CO^+ \cdot CO + CO$.

E/N (Td)	Rate coefficient (cm^6/sec)	Pressure range (Torr)	CO^+ mobility (cm^2/V sec)	$CO^+ \cdot CO$ mobility (cm^2/V sec)
75.0	1.35×10^{-28}	0.078–0.132	1.56	1.97
87.5	1.18×10^{-28}	0.078–0.159	1.52	2.00
100.0	1.21×10^{-28}	0.078–0.159	1.48	2.06
112.5	1.05×10^{-28}	0.078–0.159	1.45	2.11
125.0	1.05×10^{-28}	0.078–0.159	1.43	2.16
137.5	1.12×10^{-28}	0.053–0.132	1.40	2.27
150.0	1.12×10^{-28}	0.078–0.132	1.37	2.33

for an accurate calculation of the average energy of the reacting CO^+ ions in the intermediate range of E/N explored here. However, Fahr and Müller[10] have developed a theory applicable to the high E/N regime for the case where resonant charge-transfer collisions dominate the transport behavior of the ions, as is the case here. Their analysis gives the average energy of the ions derived from the electric field in excess of the thermal values as $\frac{1}{4}\pi m v_d^2$, where m is the mass of the ions.[11] In the absence of a more appropriate expression, we have used it to estimate the average "field energy" of the reacting CO^+ ions above the thermal value in our intermediate range of E/N. The results are that the average field energy is estimated to be 60% of the thermal value at an E/N of 75 Td and 184% of the thermal value at an E/N of 150 Td.

A careful study of the breakup reaction

$$CO^+ \cdot CO + CO \rightarrow CO^+ + 2CO \qquad (14)$$

was made, not by using an equilibrium constant which can contain serious errors owing to mass discrimination effects, but by examination of the CO^+ arrival-time spectrum for ions whose drift times indicated that they had spent part of their drift as $CO^+ \cdot CO$. The reaction was observed, but it occurred much more slowly than reported by Chong and Franklin.[1] No accurate numerical determination of the rate coefficient could be made, because of the slowness of the reaction at the pressures used in this research and the fact that the reaction

$$C^+ + CO \rightarrow CO^+ + C \qquad (15)$$

also produced CO^+ ions with drift time similar to those affected by the clustering reaction. An upper bound of about 10^{-14} cm^3/sec was placed on the breakup-reaction-rate coefficient, and the error introduced by neglecting this reaction was estimated to be less than 1%.

Errors due to inaccurate values of v_d, D_L, and D_T for the two species are estimated to be less than 5%. From comparisons such as those demonstrated in the figures, the curve-fitting procedure is estimated to be accurate to better than 10%. Combining these independent errors, an over-all error bound of ± 12% is assigned to the rate coefficient of the clustering reaction (1).

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