RICE UNIVERSITY

ION-MOLECULE REACTIONS IN MIXTURES
OF METHANE AND CARBON DIOXIDE

by

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ABSTRACT

Using a quadrupole mass filter, ion-molecule reactions in mixtures of methane and carbon dioxide were investigated at pressures of 0.1-0.4 torr. Rate constants for several of the reactions were determined and it was found necessary to use ionic mobilities to calculate the appropriate residence times. Reaction rate constants for two of the reactions have been determined at low pressures and were lower than the values obtained in this work. One of the reactions goes to equilibrium and from the equilibrium constant a heat of reaction in close agreement with literature values was determined.
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I. INTRODUCTION

Chemical ionization mass spectrometry as defined by Munson and Field (1) is an analytical technique for determining the structures of compounds and identifying compounds and mixtures. Basically the technique utilizes a gas which produces a set of ions which are not very reactive with the gas itself but which can react with other gases of interest. The reaction gas most commonly employed is methane because its high pressure spectrum is simple and well characterized.

High pressure mass spectrometry and the kinetics of ion-molecule reactions have occupied a significant portion of the literature in the past decade, especially following the theoretical work of Field, Franklin, and Lampe (2) and Gioumousis and Stevenson (3).

The present investigation was proposed in order to apply the chemical ionization technique to a kinetic study of ion-molecule reactions in mixtures. The fundamental technique involved was to admit a fixed amount of some reaction gas to the ion source of the mass spectrometer and monitor the change in the relative ion intensities as a function of concentration of additive. If $X^+$ is an ion formed in the reaction gas and a small amount of $M$ is added to the system, the reaction

$$X^+ + M \rightarrow Y^+ + Z \quad (1-1)$$

can be observed in the mass spectrometer if it is non-
endothermic. From this it is possible to derive the pseudo first order rate expression (4),
\[
\ln \left( \frac{[X^+]_0}{[X^+]_t} \right) = k(M)t
\]
(1-2)
where \([X^+]_0\) is the concentration of \(X^+\) with no additive, \(M\). The reaction time, \(t\), is an instrumental parameter that is a constant for a given ion and set of conditions in low pressure work; see Sections II-a and III-c for calculations of this time. An analysis of the change in ion concentration as the concentration of additive is varied can be used to evaluate the reaction rate constant, \(k\). If \(Y^+\) reacts further with the additive additional rate expressions can be developed and evaluated.

The particular system of carbon dioxide and methane was chosen because of the relative simplicity of the individual high pressure spectra. Additionally, although the major product ions of methane are non-reactive with methane (5), the same does not hold for carbon dioxide (6). The individual relative ion intensities as functions of pressure are given in Figures (I-1) and (I-2). A small amount of work was also done on mixtures of carbon dioxide and deuterium.

There are no high pressure studies of carbon dioxide with either methane or deuterium available although low pressure investigations have been reported in two papers by Shannon and Harrison (7,8); these results were later revised by Harrison and Myher (9). They studied concurrent ion-mole-
FIGURE I-1

Ion distribution in methane.
FIGURE I-2

Ion distribution in carbon dioxide.
cule reactions which lead to the same product and determined rate constants. For the reactions

\[ \text{CO}_2^+ + \text{CD}_4 \rightarrow \text{CO}_2\text{D}^+ + \text{CD}_3 \]  

(1-3)

and

\[ \text{CD}_4^+ + \text{CO}_2 \rightarrow \text{CO}_2\text{D}^+ + \text{CD}_3 \]  

(1-4)

they obtained \(1.2 \times 10^{-9}\) and \(1.1 \times 10^{-9}\) cc \(\cdot\) molecule \(^{-1}\) \(\cdot\) sec \(^{-1}\) for the respective rate constants. In like manner, for the reactions

\[ \text{CO}_2^+ + \text{D}_2 \rightarrow \text{CO}_2\text{D}^+ + \text{D} \]  

(1-5)

and

\[ \text{D}_2^+ + \text{CO}_2 \rightarrow \text{CO}_2\text{D}^+ + \text{D} \]  

(1-6)

the rate constants were measured as \(0.62 \times 10^{-9}\) and \(7.0 \times 10^{-9}\) cc \(\cdot\) molecule \(^{-1}\) \(\cdot\) sec \(^{-1}\), respectively. These rate constants are in the range expected for transfer of a deuteron or abstraction of a deuterium atom except for reaction (1-6); the authors justify the high rate constant by assuming that the reaction

\[ \text{D}_2^* + \text{CO}_2 \rightarrow \text{CO}_2\text{D}^+ + \text{D} + e^- \]  

(1-7)

where \(\text{D}_2^*\) is an excited deuterium molecule contributes extensively near the ionization potential of deuterium. Under the conditions used for the present work it was not possible to study the analogue of reaction (1-4) in the carbon dioxide-methane system since there is no \(\text{CH}_4^+\) present at high methane pressures (see Figure I-1). The analogue of reaction (1-3) and also of reaction (1-5) were a part of the present investigation.
II. EXPERIMENTAL

a. Instrumentation

An electric quadrupole mass filter was used for the analysis of reaction products. The instrument was originally developed by Paul and Steinwedel (10); the instrument used in this work was designed and built in this laboratory by Ghosh et. al. It is well-suited to the study of ion-molecule reactions for a number of reasons:

i). the ion transmission efficiency between source and collector is high;

ii). it is possible to operate at relatively high source pressure because of the considerable pressure allowance capability of the analyzer due to the use of separate six inch diameter diffusion pumps on the source and on the flight sections;

iii). the resolution can be readily varied.

After leaving the reaction chamber the ions are accelerated uniformly through the a -10V potential before entering the 20 in. quadrupole mass filter. Mass scanning was accomplished by varying a DC voltage, \( U \), and the maximum of the superimposed radiofrequency component, \( V_o \), across the quadrupole rods in such a way that the ratio \( U/V_o \) remained constant. The ions which pass completely through the mass filter are finally accelerated through 3000 V
onto the first dynode of a fourteen stage copper-beryllium secondary electron multiplier which in turn is connected to a Kiethley Model 417 fast electrometer. The amplified current is then plotted against the quadrupole DC voltage on an Electro- Instruments Model 520 X-Y recorder.

The ion-molecule reaction source is similar to that described by Futrell et al. (11). Electrons are emitted from a heated tungsten filament and are accelerated from -150 V to ground potential. After being collimated they enter the reaction chamber which remains at approximately 340°K. Electron collimation within the source is aided by two permanent rod magnets which have a field of about 130 gauss at the center of the gap. An electron trap is maintained at +6 V to remove any electrons which pass completely through the 1 cm. wide chamber. Thus, the ionizing electron beam passes in a tight spiral through the center of the chamber and parallel to the ion-repeller grid and the ion exit orifice (0.03 cm. in diameter) plate which are 0.52 cm. apart. The ion-repeller backing plate has arms which extend into the chamber such that an ion formed in the electron beam is formed at a potential of one-half of that applied to the repeller grid (12). The repeller potential was maintained at $6.0 \pm 0.2$ V, which corresponds to a field of $11.5 \pm 0.4$ V/cm.

It is the ion-repeller potential which determines the residence time of a primary ion in the reaction chamber at
low pressures. The force imparted to the ion by the repeller potential is given by (13)
\[ ma = eE = m \frac{d}{dt} \left( \frac{dz}{dt} \right) \] (2-1)
which after integration yields
\[ t = (2md/eE)^{\frac{1}{2}} \] (2-2)
where \( m \) is the mass of the ion of interest, \( d \) is the average distance it travels (0.26 cm.), and \( E \) is the field strength. For example, if \( \text{CO}_2^+ \) is considered,
\[ t = \frac{(2)(44/6.02 \times 10^{23})(0.26)}{(4.80 \times 10^{-10})(11.5/300)} = 1.44 \times 10^{-6} \text{ sec.} \] (2-3)
(Note that the equation for the residence is also frequently given by
\[ t = 2d(m/eV)^{\frac{1}{2}} \] (2-4)
by use of the relation \( E = V/2d \)).

b. Procedure

Matheson research grade \( \text{CO}_2 \), \( \text{CH}_4 \), and \( \text{D}_2 \) were used for all experiments; it was found that "Bone Dry" \( \text{CO}_2 \) still contained too much water to be of use since it obscured ions at \( m/e = 17 \) and also participated in some of the reactions. The methane and carbon dioxide were passed through liquid nitrogen traps so that they could be more consistently regulated at the very lowest partial pressures by use of variable leaks. The total pressure in the reaction chamber was monitored by means of an MKS "Baratron" capac-
itance manometer located in the inlet line close to the chamber.

The mass filter was routinely operated at a low resolution of about one in forty to prevent mass discrimination. In this way ionic concentration values were proportional to recorded peak heights; this was calibrated by comparing the spectra obtained from butane and 1-bromobutane with standard spectra (14). In those cases where some overlap of adjacent peaks occurred a second spectrum would be taken at a resolution which was high enough to isolate the contributions of the overlapping peaks.

In order to check the overall operation of the apparatus the standard procedure was to check the rate constants of the well-characterized reactions,

\[
\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3 \quad (2-5)
\]

and

\[
\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \quad (2-6)
\]

in methane. Measured rate constants were within 10% of the values of \(10.3 \times 10^{-10}\) and \(8.2 \times 10^{-10}\) cc·molecule\(^{-1}\)·sec\(^{-1}\), respectively, obtained by Field, Franklin, and Munson (5).
III. RESULTS AND DISCUSSION

a. Methane with added carbon dioxide

Since methane at high pressures (0.3 - 0.4 torr) produces ions which are not further reactive with methane, it was decided that the first experiment should be the addition of carbon dioxide to a fixed amount of methane. Radical changes in the ion distribution were sought as evidence of the reaction of the ions from methane with carbon dioxide. At a partial pressure of approximately 0.1% carbon dioxide the experiment is equivalent to the chemical ionization technique (1). Figure III-1 presents the variation in ion distribution as a function of added carbon dioxide at a methane pressure of 0.35 torr. (At the reaction chamber temperature of 340°K, one torr is equivalent to $2.8 \times 10^{16}$ molecules/cc.). The most apparent feature of the figure is the lack of change in ion distribution.

Since the ionization cross sections for methane and carbon dioxide are virtually equal (15), the intensity of the ions due to carbon dioxide should be proportional to the fraction of it in the system if the two ion systems were completely independent. This expected distribution is superimposed on the figure.

This dilution effect with the addition of carbon dioxide would be expected because at the methane pressures under investigation virtually all of the entering electrons...
Typical curves of ion intensities in 0.35 torr of methane with added carbon dioxide.

1). mole fraction of carbon dioxide
2). m/e = 17
3). m/e = 29
4). m/e = 41
5). m/e = 45
undergo ionizing collisions. The fraction of electrons which pass completely through the chamber is given by

\[ \frac{i}{i_0} = \exp(-Qnd) \]  

(3-1)

where \( Q \) is the total ionization cross section in cm\(^2\), \( n \) is the gas concentration in molecules/cc, and \( d \) is the distance in cm through which the electrons pass in the reaction chamber. The total ionization cross section of methane for 150eV electrons is not known but it has been measured by a number of workers (16) for 70eV electrons. An average value of \( 4 \times 10^{-16} \text{cm}^2 \) obtained from these measurements is adequate for the argument at hand although it is not strictly accurate. Using 1 cm as the electron path length, the fraction of electrons which pass through the chamber at various methane concentrations is given in Table III-1. From the table it is evident that above 0.3 torr virtually all of the entering electrons undergo ionizing collisions.

Figure III-1 seemingly indicates that there is little or no reaction with carbon dioxide of the ions (\( \text{CH}_4^+ \), \( \text{C}_2\text{H}_5^+ \), and \( \text{C}_3\text{H}_5^+ \)) that are characteristic of high pressure methane systems (5). However, a reaction which does occur may not be observed because the product reacts further. For example, the reaction

\[ \text{CH}_4^+ + \text{CO}_2 \rightarrow \text{HCO}_2^+ + \text{CH}_3 \]  

(3-2)

is energetically feasible and has been observed using deuterated methane (9); its heat of reaction (See the Appendix for a tabulation of heats of formation), \( \Delta H_r \), is 3 kcal/mole.
TABLE III-1

Fraction of electrons which do not undergo ionizing collisions

<table>
<thead>
<tr>
<th>$P(CH_4)$, torr</th>
<th>$i/i_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.33</td>
</tr>
<tr>
<td>0.15</td>
<td>0.20</td>
</tr>
<tr>
<td>0.20</td>
<td>0.105</td>
</tr>
<tr>
<td>0.25</td>
<td>0.06</td>
</tr>
<tr>
<td>0.30</td>
<td>0.035</td>
</tr>
<tr>
<td>0.35</td>
<td>0.02</td>
</tr>
<tr>
<td>0.40</td>
<td>0.01</td>
</tr>
</tbody>
</table>
(A positive $\Delta H_r$ is considered as exothermic). The $\text{HCO}_2^+$ so produced reacts readily with methane (see following Section) and would not be observed. Although it cannot be determined to what extent the ions from methane are reacting with carbon dioxide, it is apparent that the ions formed in carbon dioxide are reacting with the methane. This follows from the near constancy of relative ion intensities of the ions at m/e of 17 and 29. A mass-to-charge ratio of 17 can be either $\text{CH}_3^+$ or $\text{OH}^+$; $\text{C}_2\text{H}_5^+$ and $\text{CHO}^+$ occur at m/e = 29. Also, it should be noted that the ion whose intensity increases as carbon dioxide is added occurs at m/e = 45 and not 44 as would have been expected.

The ion at m/e = 17 is $\text{CH}_3^+$ since any $\text{OH}^+$ present would react rapidly with methane. Additionally, there are no non-endothermic reactions which can give $\text{OH}^+$ as a product in the system under investigation. The fact that the relative intensity of this ion remains practically constant also indicates that it is being formed by a reaction of some ion of carbon dioxide with methane. If this were not the case, the ion intensity should decrease in direct proportion to the decrease in partial pressure of methane brought about by the addition of carbon dioxide since virtually all of the entering electrons undergo ionizing collisions.

At high concentrations of methane $\text{C}_2\text{H}_5^+$ is one of the predominant ions but it also cannot react exothermally
with carbon dioxide. The ion intensity should decrease by dilution of the system with carbon dioxide but this decrease is partially offset by slow formation of HCO⁺.

These qualitative and tentative conclusions will be discussed in greater detail in the following Sections.

b. Carbon dioxide with added methane

In order to confirm that the ions from carbon dioxide were in fact reacting with methane a fixed amount of carbon dioxide was admitted to the ion source and small increments of methane were added. Figures III-2a and III-2b show the variation in ion distribution as a function of added methane; the carbon dioxide pressure (0.36 torr) is approximately the same as that of methane in Figure III-1. The shapes of the curves are markedly different from those of Figure III-1; they show that the ions characteristic of carbon dioxide are reacting rapidly with the added methane.

Experiments were also carried out with emphasis on the very low range (less than 5%) of partial pressure of methane in order to clarify the reactions which were occurring. Figure III-3 shows the results for a carbon dioxide pressure (0.35 torr) approximately the same as that in Figure III-2. Since the reactions appeared to be so fast the same experiment was carried out over the range of 0.025-0.4 torr of carbon dioxide. The results were qualitatively similar but there were fairly large quantitative differ-
FIGURE III-2

(a) and (b). Typical curves of ion intensities as a function of added methane in 0.36 torr of carbon dioxide.

III-2a:
1). m/e = 44
2). m/e = 45
3). m/e = 17
4). m/e = 29

III-2b:
1). m/e = 88
2). m/e = 89
FIGURE III-3

Ion distribution in 0.35 torr of carbon dioxide with low partial pressures of added methane.

1). m/e = 44
2). m/e = 88
3). m/e = 45
4). m/e = 89
5). m/e = 29
6). m/e = 17
ences which are discussed more fully in the following Section.

From the shapes of curves such as those in Figures III-2 and III-3, and from consideration of the heats of reaction (the observed reactions must be non-endothermic and without appreciable activation energy (17)), the following reaction scheme has been devised:

\[
\begin{align*}
\text{CO}_2^+ + \text{CH}_4 &\rightarrow \text{HCO}_2^+ + \text{CH}_3 & (3-3) \\
\text{HCO}_2^+ + \text{CH}_4 &\rightarrow \text{CH}_5^+ + \text{CO}_2 & (3-4) \\
\text{CO}_2^+ + \text{CH}_4 &\rightarrow \text{HCO}_2^+ + \text{CH}_3\text{O} \ (\text{or} \ \text{HCO} + \text{H}_2) & (3-5) \\
\text{C}_2\text{O}_4^+ + \text{CH}_4 &\rightarrow \text{HC}_2\text{O}_4^+ + \text{CH}_3 & (3-6) \\
\text{HC}_2\text{O}_4^+ + \text{CH}_4 &\rightarrow \text{CH}_5^+ + 2\text{CO}_2 & (3-7) \\
\text{CO}_2^+ + \text{mCO}_2 &\rightarrow \text{C}_2\text{O}_4^+ + (\text{m-1})\text{CO}_2 & (3-8)
\end{align*}
\]

The heats of formation (see Appendix) of the species involved in reactions (3-3), (3-4), and (3-5) are known, and the heats of reaction are 27, 0, and 7 kcal/mole, respectively. The criterion that the heat of reaction be non-endothermic allows an estimate to be made of the upper limits of the heats of formation of \(\text{C}_2\text{O}_4^+\) and \(\text{HC}_2\text{O}_4^+\) from reactions (3-8) and (3-7), respectively. This yields \(\Delta H_f^\circ(\text{C}_2\text{O}_4^+) \leq 129 \text{ kcal/mole} \) and \(\Delta H_f^\circ(\text{HC}_2\text{O}_4^+) \leq 78 \text{ kcal/mole}\).

A question may arise as to the effect on the above reaction scheme of the ions (mainly \(\text{CH}_3^+\) and \(\text{CH}_4^+\)) formed by the direct ionization of methane. It is not energetically feasible for \(\text{CH}_3^+\) to react with carbon dioxide and 18
so it would not enter into the scheme. In Section I it was stated that \( \text{CD}_4^+ \) reacts rapidly with carbon dioxide. The same would be expected of \( \text{CH}_4^+ \) and it should contribute to the total ion abundance of \( \text{HCO}_2^+ \). The kinetics work involved was done at very low partial pressures of methane and the amount of \( \text{CH}_4^+ \) formed would be extremely small in this range.

Reaction (3-8) has been proposed by Schildcrout and Franklin (6) in their work on the ion chemistry of carbon dioxide in this laboratory. There was some question as to the identity of the species at \( m/e = 17(\text{CH}_5^+) \) and 29(\( \text{HCO}^+ \)). An experiment was therefore run with deuterated methane added to carbon dioxide and the products occurred at \( m/e = 22(\text{CD}_5^+) \) and 30(\( \text{DCO}^+ \)); there was no ion at \( m/e = 18(\text{D}^+) \), and only a very minor peak at \( m/e = 34(\text{C}_2\text{D}_5^+) \).

c. Kinetics

With reactions (3-3) through (3-7)

\[
\begin{align*}
\text{CO}_2^+ + \text{CH}_4 & \rightarrow \text{HCO}_2^+ + \text{CH}_3 \quad (3-3) \\
\text{HCO}_2^+ + \text{CH}_4 & \rightarrow \text{CH}_5^+ + \text{CO}_2 \quad (3-4) \\
\text{CO}_2^+ + \text{CH}_4 & \rightarrow \text{HCO}_^+ + \text{CH}_3\text{O} \quad (3-5) \\
\text{C}_2\text{O}_4^+ + \text{CH}_4 & \rightarrow \text{HC}_2\text{O}_4^+ + \text{CH}_3 \quad (3-6) \\
\text{HC}_2\text{O}_4^+ + \text{CH}_4 & \rightarrow \text{CH}_5^+ + 2\text{CO}_2 \quad (3-7)
\end{align*}
\]

it is possible to investigate the kinetics of the reacting systems.
The relationship for the disappearance of $\text{CO}_2^+$ in this scheme is given by

$$\frac{d(\text{CO}_2^+)}{dt} = -(k_3 + k_5)(\text{CH}_4)(\text{CO}_2^+)$$  \hspace{1cm} (3-9)

which is integrated directly to yield

$$\ln \left[ \frac{(\text{CO}_2^+)/{(\text{CO}_2^+)_0}} \right] = -(k_3 + k_5)(\text{CH}_4)t$$  \hspace{1cm} (3-10)

Similarly, the variation in $\text{HCO}_2^+$ is given by

$$\frac{d(\text{HCO}_2^+)}{dt} = k_3(\text{CH}_4)(\text{CO}_2^+) - k_4(\text{CH}_4)(\text{HCO}_2^+)$$  \hspace{1cm} (3-11)

Substituting for $(\text{CO}_2^+)$ from equation (3-10) gives

$$\frac{d(\text{HCO}_2^+)}{dt} = k_3(\text{CH}_4)(\text{CO}_2^+)_0 \left[ e^{-(k_3 + k_5)(\text{CH}_4)t} \right] - k_4(\text{CH}_4)(\text{HCO}_2^+)$$  \hspace{1cm} (3-12)

which integrates to

$$\frac{(\text{HCO}_2^+)}{(\text{CO}_2^+)_0} = \frac{k_3}{k_4 - k_3 - k_5} \left[ e^{-(k_3 + k_5)(\text{CH}_4)t} \right. - \left. e^{-k_4(\text{CH}_4)t} \right]$$  \hspace{1cm} (3-13)

since $(\text{HCO}_2^+)_0 = 0$. In general

$$e^{-x} \approx 1 - x$$  \hspace{1cm} (3-14)

as $x$ approaches zero. Therefore at low partial pressures of methane such that equation (3-14) is valid, equation (3-13) reduces to the approximation

$$\frac{(\text{HCO}_2^+)}{(\text{CO}_2^+)_0} \approx k_3(\text{CH}_4)t$$  \hspace{1cm} (3-15)

and from this equation an approximation to $k_3$ may be determined.

$\text{HCO}^+$ is formed in reaction (3-5). Substituting from
equation (3-10) in

\[
d(HCO^+)/dt = k_5(CH_4)(CO_2^+)
\]  

(3-16)

and integrating with \((HCO^+)_0 = 0\) gives

\[
\frac{(HCO^+)}{(CO_2^+)_0} = \frac{k_5}{k_3 + k_5} \left[ 1 - e^{-(k_3 + k_5)(CH_4)t} \right]
\]

(3-17)

At low methane pressures this reduces to the approximation

\[
(HCO^+)/CO_2^+ \approx k_5(CH_4)t
\]

(3-18)

The disappearance of \(C_2O_4^+\) is given by equation (3-6) which leads to the relation

\[
d(C_2O_4^+)/dt = -k_6(CH_4)(C_2O_4^+)
\]

(3-19)

and is integrated directly to

\[
\ln \left( \frac{(C_2O_4^+)}{(C_2O_4^+)_0} \right) = -k_6(CH_4)t
\]

(3-20)

The relationship for \((HC_2O_4^+)\) is given by

\[
d(HC_2O_4^+)/dt = k_6(CH_4)(C_2O_4^+) - k_7(CH_4)(HC_2O_4^+)
\]

(3-21)

Equation (3-20) is used for \((C_2O_4^+)\) and with \((HC_2O_4^+) = 0\), integration yields

\[
\frac{(HC_2O_4^+)}{(C_2O_4^+)_0} = \frac{k_6}{k_7 - k_6} \left[ e^{-k_6(CH_4)t} - e^{-k_7(CH_4)t} \right]
\]

(3-22)

Again at low methane pressures such that equation (3-14) is valid, equation (3-22) reduces to the approximation

\[
(HC_2O_4^+)/C_2O_4^+ \approx k_6(CH_4)t
\]

(3-23)

From equation (3-10) it can be seen that the semilog
plot of the decrease of $(\text{CO}_2^+)$ as a function of added methane should have a slope equal to $(k_3 + k_5)t$. Figure III-4 shows the plots for various carbon dioxide pressures and Table III-2 lists the values of $(k_3 + k_5)t$ found at the various pressures. Also tabulated are values for $k_3 + k_5$ calculated by use of the constant residence time of $1.44 \times 10^{-6}$ sec, determined by the repeller potential and ionic mass (Section II-a). The constant calculated in this manner shows a wide variation, increasing approximately linearly with carbon dioxide pressure.

In view of a situation in which a rate constant apparently varies with pressure mobility considerations (18) were applied. The drift velocity of an ion through a gas is proportional to the electric field intensity

$$v_d = \mu E \quad (3-24)$$

where the proportionality constant, $\mu$, is defined as the ionic mobility. A value of $1.03 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ has been found by Saporoschenko and Wisner (19) for the zero-field reduced mobility, $\mu_0$, of $\text{CO}_2^+$ in carbon dioxide. The reduced mobility is simply the mobility at the standard conditions of $273^\circ \text{K}$ and 760 torr and it is related to the mobility by

$$\mu = \mu_0 \left( \frac{760}{P} \right) \left( \frac{T}{273} \right) \quad (3-25)$$

At the source temperature of $340^\circ \text{K}$, the mobility is

$$\mu = 1.03 \left( \frac{760}{P} \right) \left( \frac{340}{273} \right) = 975/P \text{ cm}^2 \cdot \text{torr} / \text{V} \cdot \text{sec} \quad (3-26)$$

22
FIGURE III-4

Semilog plot of decay in intensity of CO$_2^+$ with added methane at 1). 0.29 torr, 2). 0.33 torr, 3). 0.35 torr, 4). 0.38 torr, 5). 0.42 torr of carbon dioxide.
**TABLE III-2**

Determinations of rate constant for decay of CO\(_2^+\), \(k_3 + k_5\)

<table>
<thead>
<tr>
<th>(P(\text{CO}_2)), torr</th>
<th>(10^{14}kt)</th>
<th>(10^9k)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Constant</td>
<td>Mobility</td>
</tr>
<tr>
<td>.10</td>
<td>0.60</td>
<td>4.2</td>
</tr>
<tr>
<td>.15</td>
<td>0.80</td>
<td>5.6</td>
</tr>
<tr>
<td>.20</td>
<td>1.0</td>
<td>7.0</td>
</tr>
<tr>
<td>.295</td>
<td>1.45</td>
<td>10.0</td>
</tr>
<tr>
<td>.30</td>
<td>1.5</td>
<td>10.5</td>
</tr>
<tr>
<td>.33</td>
<td>1.5</td>
<td>10.5</td>
</tr>
<tr>
<td>.35</td>
<td>1.8</td>
<td>12.5</td>
</tr>
<tr>
<td>.375</td>
<td>2.0</td>
<td>14.0</td>
</tr>
<tr>
<td>.38</td>
<td>2.1</td>
<td>14.5</td>
</tr>
<tr>
<td>.38</td>
<td>2.0</td>
<td>14.0</td>
</tr>
<tr>
<td>.39</td>
<td>1.9</td>
<td>13.2</td>
</tr>
<tr>
<td>.42</td>
<td>2.2</td>
<td>15.0</td>
</tr>
</tbody>
</table>
If equation (3-25) is substituted into (3-24) with an electric field of 11.5 V/cm,

\[ \nu = \frac{975}{P} (11.5) \]

\[ = \frac{11,200}{P} \text{ cm·torr/sec} = \frac{d}{t} \]  \hspace{1cm} (3-27)

it is possible to solve for the residence time,

\[ t = \frac{0.26P}{11,200} = 2.3 \times 10^{-5} \text{ P sec} \]  \hspace{1cm} (3-28)

Equation (3-28) combined with the values of \((k_3 + k_5)\) from Table III-2 permit the calculation of the rate constant which is given in the last column of the table. At the lowest pressures of carbon dioxide enough methane has been added to make a significant difference in the mobility of \(\text{CO}_2^+\). Thus, if the value at 0.10 torr is neglected, one obtains the average value for the combined rate constant, \(k_3 + k_5\), of \(2.2 \times 10^{-9} \text{ cc·molecule}^{-1} \text{·sec}^{-1}\).

Evidently the source pressure is high enough that the residence times are being controlled by the mobilities of the ions in carbon dioxide. Although most of the ionic mobilities have not been measured they may be estimated from the equation of Hasted (20),

\[ K_0 = 13.45 / (a \mu)^{1/2} \]  \hspace{1cm} (3-29)

where \(K_0\) is the reduced mobility, \(a\) is the polarizability of the gas in \(\AA^3\), and \(\mu\) is the reduced mass in atomic weight units. Hasted's notation is being maintained in order to distinguish calculated mobilities from the experimental value of \(\text{CO}_2^+\) in carbon dioxide used previously. Table III-3 lists \(K_0\) for the ions of interest calculated by the
### TABLE III-3

Reduced mobilities for ions in carbon dioxide

<table>
<thead>
<tr>
<th>Ion</th>
<th>$K_0$, cm²·V⁻¹·sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HCO}_2^+$</td>
<td>1.77</td>
</tr>
<tr>
<td>$\text{HCO}^+$</td>
<td>2.00</td>
</tr>
<tr>
<td>$\text{C}_2\text{O}_4^+$</td>
<td>1.54</td>
</tr>
<tr>
<td>$\text{HC}_2\text{O}_4^+$</td>
<td>1.54</td>
</tr>
</tbody>
</table>
use of $2.59 \text{Å}^3$ for the polarizability of carbon dioxide (21). Following a development parallel to equations (3-24) through (3-28), one obtains

$$t = 2.39 \times 10^{-5} \frac{P}{K_0}$$

(3-30)

which can be used to calculate residence times.

Figure III-5 shows plots of $\frac{(\text{HCO}^+)/(\text{CO}_2^+)_0}{(\text{CO}_2^+)}$ as a function of added methane at 0.35 and 0.37 torr of carbon dioxide. From the slopes of the linear portions of the curves and the reaction time determined from equation (3-28), one obtains an estimate of $1.4 \times 10^{-11} \text{ cc molecule}^{-1} \text{ sec}^{-1}$ for $k_5$; therefore, $k_3$ is approximately $2.2 \times 10^{-9} \text{ cc molecule}^{-1} \text{ sec}^{-1}$. The slight curvature in Figure III-5 near the origin is believed to be due to the approach to the lower measurement limit rather than to formation of $\text{C}_2\text{H}_5^+$ particularly in view of the very small amounts of methane present.

In order to check the value obtained for $k_3$ the ratio of $\frac{(\text{HCO}_2^+)/((\text{CO}_2^+)_0)}{(\text{CO}_2^+)}$ can be plotted as a function of methane concentration according to equation (3-15). These curves are shown in Figure III-6 for various carbon dioxide pressures, and Table III-4 lists the values of $k_t$ obtained from the initial slopes. The reaction time is again determined from equation (3-28) and leads to the average value $k_3 = 2.4 \times 10^{-9} \text{ cc molecule}^{-1} \text{ sec}^{-1}$ which is within the range of experimental error for the value of $2.2 \times 10^{-9} \text{ cc molecule}^{-1} \text{ sec}^{-1}$ calculated by the use of equation (3-10).
FIGURE III-5

+ Intensity of HCO as a function of added methane at 1). 0.35 and 2). 0.37 torr of carbon dioxide.
\[ P(CH_4) \times 10^3 \text{, TORR} \]
Intensity of $\text{HCO}_2^+$ as a function of added methane at 1). 0.20, 2). 0.35, and 3). 0.40 torr of carbon dioxide.
$P(\text{CH}_4) \times 10^3 \text{ TORR}$
**TABLE III-4**

Determination of rate constant for reaction (3-3)

<table>
<thead>
<tr>
<th>$P(CO_2)$, torr</th>
<th>$10^{14}kt$</th>
<th>$10^6t$</th>
<th>$10^9k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1.20</td>
<td>4.6</td>
<td>2.6</td>
</tr>
<tr>
<td>0.33</td>
<td>2.00</td>
<td>7.6</td>
<td>2.6</td>
</tr>
<tr>
<td>0.35</td>
<td>1.67</td>
<td>8.0</td>
<td>2.1</td>
</tr>
<tr>
<td>0.42</td>
<td>2.50</td>
<td>9.7</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The rate constant for reaction (3-3) has also been determined by Harrison and Myher (9); they used deuterated methane rather than methane and obtained a value of $1.2 \times 10^{-9}$ cc.mole$^{-1}$.sec$^{-1}$. This is approximately one-half the average value obtained in this experiment.

In Figure III-2a the concentration of HCO$_2^+$ decays slowly as methane is added above 0.01 torr. This decay is much less pronounced than that of CO$_2^+$ in the same figure which means that $k_4$ is much smaller than $k_3 + k_5$. Therefore, at methane pressures above 0.01 torr $\exp {-(k_3 + k_5)(CH_4)t}$ is approximately zero, and the equation reduces to

$$\frac{(HCO_2^+)}{(CO_2^+)_0} \approx \frac{k_3}{k_4 - k_3 - k_5} \left[ -e^{-k_4(\text{CH}_4)t} \right] \quad (3-31)$$

or,

$$\ln \left[ \frac{(HCO_2^+)}{(CO_2^+)_0} \right] \approx k_4(\text{CH}_4)t + C \quad (3-32)$$

above 0.01 torr of methane. These curves are shown in Figure III-7 and the calculations are summarized in Table III-5. Also given in the table are rate constants calculated on the basis of reaction time calculated from equation (3-30). Using the value $K_0 = 1.77$ cm$^2$.V$^{-1}$.sec$^{-1}$ one obtains

$$t_H = 1.35 \times 10^{-5} \text{p} \quad (3-33)$$

Using this "Hasted time" the average value of the rate constant, $k_4$, is $1.3 \times 10^{-10}$ cc.mole$^{-1}$.sec$^{-1}$.

The rate constant for reaction (3-6) can be determined from equation (3-20). Semilog plots of
Semilog plots of intensity of $\text{HCO}_2^+$ as a function of added methane at 1). 0.35, 2). 0.36, 3). 0.37, and 4). 0.40 torr of carbon dioxide.
\[ P(\text{CH}_4), \text{Torr} \]

\[ \log [\text{CO}_2^+/\text{HCO}_2^+] / [\text{HCO}_2^+] \]

Lines 1, 2, 3, and 4 plotted on the graph.
TABLE III-5

Determination of rate constant for reaction (3-4)

<table>
<thead>
<tr>
<th>$P(\text{CO}_2)$, torr</th>
<th>$10^{16}k_t$</th>
<th>$10^6t_H$</th>
<th>$10^{10}k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>6.0</td>
<td>4.7</td>
<td>1.3</td>
</tr>
<tr>
<td>0.36</td>
<td>6.4</td>
<td>4.85</td>
<td>1.3</td>
</tr>
<tr>
<td>0.37</td>
<td>6.65</td>
<td>5.0</td>
<td>1.3</td>
</tr>
<tr>
<td>0.37</td>
<td>6.65</td>
<td>5.0</td>
<td>1.3</td>
</tr>
<tr>
<td>0.40</td>
<td>6.65</td>
<td>5.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>
\( \frac{(C_2O_4^+) / (C_2O_4^+)}{0} \) as a function of added methane for various carbon dioxide concentrations are shown in Figure III-8. A summary of the data is given in Table III-6 which shows an average value for \( k_6 \) of \( 3.5 \times 10^{-9} \text{cc\cdot molecule}^{-1}\cdot \text{sec}^{-1} \) based on reaction times calculated from equation (3-30).

The rate constant for reaction (3-6) may also be estimated from equation (3-19) at very low concentrations of added methane. The relevant data are summarized in Figure III-9 and Table III-7 and lead to an average rate constant of \( 3.0 \times 10^{-9} \text{cc\cdot molecule}^{-1}\cdot \text{sec}^{-1} \).

If the methane concentration is high enough the first exponential term in equation (3-22) may be neglected. This leads to the approximation

\[
\ln \left[ \frac{(HC_2O_4^+) / (C_2O_4^+)}{0} \right] \approx k_7(CH_4)t \quad (3-34)
\]

since \( k_6 \) is significantly greater than \( k_7 \) as can be seen in Figure III-2b. Equation (3-34) is plotted in Figure III-10 for various carbon dioxide pressures and the data summarized in Table III-8. Using the reaction time calculated from equation (3-30) gives an average rate constant, \( k_7' \), of \( 1.1 \times 10^{-10} \text{cc\cdot molecule}^{-1}\cdot \text{sec}^{-1} \).

A summary of the rate constants which have been determined is given in Table III-9. Only \( k_3 \) and \( k_5 \) have been determined by use of the experimentally determined mobility (19) of \( CO_2^+ \) in carbon dioxide to calculate reaction times. The reaction times used for the calculation of the rest of the rate constants have been estimated on the
FIGURE III-8

Semilog plots of decay in intensity of $C_2O_4^+$ with added methane at 1). 0.33, 2). 0.35, 3). 0.37, and 4). 0.42 torr of carbon dioxide.
**TABLE III-6**

Determination of rate constant for reaction (3-6)

<table>
<thead>
<tr>
<th>P(CO₂), torr</th>
<th>10^{14}kt</th>
<th>10^6t</th>
<th>10^9k</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>1.85</td>
<td>5.1</td>
<td>3.6</td>
</tr>
<tr>
<td>0.35</td>
<td>1.95</td>
<td>5.4</td>
<td>3.6</td>
</tr>
<tr>
<td>0.37</td>
<td>1.64</td>
<td>5.7</td>
<td>2.9</td>
</tr>
<tr>
<td>0.42</td>
<td>2.35</td>
<td>6.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Intensity of $\text{HC}_2\text{O}_4^+$ as a function of added methane at 1). 0.33, 2). 0.35, 3). 0.37, and 4). 0.42 torr of carbon dioxide.
Estimation of $k_6$ from equation (3-19)

<table>
<thead>
<tr>
<th>$P(CO_2)$, torr</th>
<th>$10^{14}k_t$</th>
<th>$10^6t_H$</th>
<th>$10^9k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>2.0</td>
<td>6.5</td>
<td>3.1</td>
</tr>
<tr>
<td>0.37</td>
<td>1.8</td>
<td>5.7</td>
<td>3.2</td>
</tr>
<tr>
<td>0.35</td>
<td>1.5</td>
<td>5.4</td>
<td>2.8</td>
</tr>
<tr>
<td>0.33</td>
<td>1.6</td>
<td>5.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Semilog plots of intensity of $\text{HCO}_4^+$ with added methane at 1). 0.36, 2). 0.37, and 3). 0.42 torr of carbon dioxide.
### TABLE III-8

Determination of rate constant for reaction (3-7)

<table>
<thead>
<tr>
<th>$P(CO_2)$, torr</th>
<th>$10^{16}k_t$</th>
<th>$10^6t$</th>
<th>$10^{10}k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36</td>
<td>6.0</td>
<td>5.6</td>
<td>1.1</td>
</tr>
<tr>
<td>0.37</td>
<td>6.4</td>
<td>5.7</td>
<td>1.1</td>
</tr>
<tr>
<td>0.42</td>
<td>7.9</td>
<td>6.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>
### TABLE III-9

Summary of rate constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$10^{10}$ k. cc.molecule⁻¹.sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2^+ + \text{CH}_4 \rightarrow \text{HCO}_2^+ + \text{CH}_3$</td>
<td>22</td>
</tr>
<tr>
<td>$\text{HCO}_2^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CO}_2$</td>
<td>1.3</td>
</tr>
<tr>
<td>$\text{CO}_2^+ + \text{CH}_4 \rightarrow \text{HCO}^+ + \text{CH}_3\text{O}$</td>
<td>0.14</td>
</tr>
<tr>
<td>$\text{C}_2\text{O}_4^+ + \text{CH}_4 \rightarrow \text{HC}_2\text{O}_4^+ + \text{CH}_3$</td>
<td>30</td>
</tr>
<tr>
<td>$\text{HC}_2\text{O}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + 2\text{CO}_2$</td>
<td>1.1</td>
</tr>
</tbody>
</table>
basis of mobilities obtained from the Hasted equation (20). These times seem somewhat low, especially that for HCO$_2$; it would not normally be expected that the residence time of HCO$_2$ would be only 60% of that of CO$_2$ under the same conditions. The corresponding rate constants are therefore probably high and should be taken only as estimates.

An interesting exercise would be to use the rate constants determined in this work to compute the relative intensity of CH$_5$ and compare this with measured values. From the reaction scheme,

$$\frac{d(\text{CH}_5^+)}{dt} = k_4(\text{CH}_4)(\text{HCO}_2) + k_7(\text{CH}_4)(\text{HC}_2\text{O}_4) \tag{3-35}$$

equations (3-13) and (3-22) can be substituted for (HCO$_2$) and (HC$_2$O$_4$), respectively, to give

$$\frac{d(\text{CH}_5^+)}{dt} = \frac{k_3k_4(\text{CH}_4)(\text{CO}_2^+)}{k_4-k_3-k_5} \left[ e^{-(k_3+k_5)(\text{CH}_4)t} - e^{-k_4(\text{CH}_4)t} \right]$$

$$+ \frac{k_6k_7(\text{CH}_4)(\text{C}_2\text{O}_4^+)}{k_7-k_6} \left[ e^{-k_6(\text{CH}_4)t} - e^{-k_7(\text{CH}_4)t} \right] \tag{3-36}$$

If the approximation that the residence time for CO$_2$ and C$_2$O$_4$ is the same, which it is not, integration and rearrangement yields
\[
\frac{(\text{CH}_5^+)}{(\text{CO}_2^+)_0} = \frac{k_3 k_4}{k_4 - k_3 - k_5} \left\{ \frac{1 - e^{-(k_3 + k_5)(\text{CH}_4)t}}{k_3 + k_5} \right. \\
- \frac{1 - e^{-k_4(\text{CH}_4)t}}{k_4} \right\} \\
+ \frac{k_6 k_7 (\text{C}_2\text{O}_4^+)_0}{(k_7 - k_6)} \left\{ \frac{1 - e^{-k_6(\text{CH}_4)t}}{k_6} - \frac{1 - e^{-k_7(\text{CH}_4)t}}{k_7} \right\}
\]

If the carbon dioxide pressure is 0.35 torr (see Figure III-3) the residence time of \( \text{CO}_2^+ \) is \( 8 \times 10^{-6} \) sec and that of \( \text{C}_2\text{O}_4^+ \) is \( 5.4 \times 10^{-6} \) sec from equations (3-28) and (3-30), respectively. The ratio of \( (\text{CH}_5^+)/\text{(CO}_2^+)_0 \) can then be calculated from equation (3-37) for various additions of methane. These calculated values along with the derived relative ion intensities are summarized in Table III-10 along with the corresponding observed values. The agreement is quite good in view of the fact that the calculations incorporate all of the approximations and errors introduced in computing reaction times and rate constants.

d. Thermodynamics

In Figure III-2 it appears that some of the reactions approach equilibrium; therefore, it should be possible to calculate equilibrium constants for them and also deduce thermodynamic data of interest.

The equilibrium constant, \( K_{eq} \), for reaction (3-4),
TABLE III-10

Calculated and observed values for the relative intensity of \( \text{CH}_5^+ \).

<table>
<thead>
<tr>
<th>( P(\text{CH}_4) ), torr x 10^3</th>
<th>( I_r(\text{CH}_5^+) ), calc.</th>
<th>( I_r(\text{CH}_5^+) ), obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.008</td>
<td>0.012</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>0.032</td>
</tr>
<tr>
<td>4</td>
<td>0.054</td>
<td>0.093</td>
</tr>
<tr>
<td>6</td>
<td>0.096</td>
<td>0.145</td>
</tr>
<tr>
<td>8</td>
<td>0.131</td>
<td>0.177</td>
</tr>
<tr>
<td>10</td>
<td>0.175</td>
<td>0.205</td>
</tr>
<tr>
<td>15</td>
<td>0.275</td>
<td>0.275</td>
</tr>
<tr>
<td>20</td>
<td>0.350</td>
<td>0.345</td>
</tr>
</tbody>
</table>
\[ \text{HCO}_2^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CO}_2 \] (3-4)

is given by

\[ K_{eq} = \frac{(\text{CO}_2)(\text{CH}_5^+)}{(\text{CH}_4)(\text{HCO}_2^+)} \] (3-38)

This is equivalent to

\[ K_{eq} = \frac{P(\text{CO}_2) \times I_r(\text{CH}_5^+)}{P(\text{CH}_4) \times I_r(\text{HCO}_2^+)} \] (3-39)

where \( P \) is the partial pressure of the appropriate gaseous species and \( I_r \) is the relative ion intensity. Figures III-11a-c present the ion distribution curves of \( \text{HCO}_2^+ \) and \( \text{CH}_5^+ \) as a function of added methane for various carbon dioxide concentrations. Equilibrium constants calculated from equation (3-39) are summarized in Table III-11. Above 0.2 torr of methane the reaction is at equilibrium with an average value of the constant of 7.5. From this value for the equilibrium constant one can then calculate the free energy change for the reaction from

\[ F = -RT \ln(K_{eq}) \] (3-40)

With \( T = 340^\circ K \) one obtains \( F = 1.35 \) kcal/mole. Since the reaction involves only a proton transfer it is unlikely that there will be a significant entropy change. Therefore, the heat of reaction \( \Delta H_r \), will approximately equal the negative free energy change, or \( \Delta H_r = 1.35 \) kcal/mole.

In Section III-2b this reaction was found to be athermal on the basis of heats of formation of the species involved; this is good agreement with the value calculated here.
(a), (b), and (c). Ion intensities of CH$_5^+$ and HCO$_2^+$ with added methane at 1). HCO$_2^+$ and 2). CH$_5^+$ at (a) 0.36, (b) 0.37, and (c) 0.40 torr of carbon dioxide.
TABLE III-11

Determination of equilibrium constant for reaction (3-4)

<table>
<thead>
<tr>
<th>P(CH₄), torr</th>
<th>Kₑq</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>10.5</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>0.200</td>
<td>7.3</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td>0.225</td>
<td>7.2</td>
<td>7.5</td>
<td>7.6</td>
</tr>
<tr>
<td>0.250</td>
<td>7.3</td>
<td>7.4</td>
<td>7.4</td>
</tr>
</tbody>
</table>

a). 0.36 torr carbon dioxide
b). 0.37 torr carbon dioxide
c). 0.40 torr carbon dioxide
The fact that reaction (3-4) is very nearly athermal and quickly comes to equilibrium explains the observation of \( \text{HCO}_2^+ \) in Figure III-1. One would have expected that virtually all of it would have been converted to \( \text{CH}_5^+ \). If equation (3-39) is used to calculate the equilibrium constant from the curves in Figure III-1 an average value of 7.1 is obtained. This is in good agreement with that determined above.

Reaction (3-3),

\[
\text{CO}_2^+ + \text{CH}_4 \rightarrow \text{HCO}_2^+ + \text{CH}_3
\]

(3-3)

also appears to go to equilibrium, but an absolute value of the equilibrium constant,

\[
K_{eq} = \frac{(\text{CH}_3)(\text{HCO}_2^+)}{(\text{CH}_4)(\text{CO}_2^+)}
\]

(3-41)

cannot be obtained because the methyl radical concentration cannot be determined. A rough estimate of the concentration can be made by assuming that it is proportional to the amount of \( \text{CO}_2^+ \) which has reacted:

\[
(\text{CH}_3) = a \left[ (\text{CO}_2^+)_0 - (\text{CO}_2^+) \right]
\]

(3-42)

where \( a \) is an undetermined constant. Figures III-12a-b show the ion distributions of \( \text{CO}_2^+ \) and \( \text{HCO}_2^+ \) as a function of added methane at two carbon dioxide concentrations. Table III-12 summarizes the calculations from

48
(a) and (b). Ion intensities of $\text{CO}_2^+$ and $\text{HCO}_2^+$ with added methane at 1). $\text{CO}_2^+$ and 2). $\text{HCO}_2^+$ at (a) 0.35 and (b) 0.37 torr of carbon dioxide.
TABLE III-12

Determination of pseudo-equilibrium constant for reaction (3-3) from equation (3-43)

<table>
<thead>
<tr>
<th>P(CH₄), 10³ torr</th>
<th>10³Kₑq/a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>6</td>
<td>0.68</td>
</tr>
<tr>
<td>8</td>
<td>0.80</td>
</tr>
<tr>
<td>10</td>
<td>0.81</td>
</tr>
<tr>
<td>12</td>
<td>0.82</td>
</tr>
<tr>
<td>16</td>
<td>0.80</td>
</tr>
<tr>
<td>20</td>
<td>0.87</td>
</tr>
</tbody>
</table>

a). 0.35 torr carbon dioxide
b). 0.37 torr carbon dioxide
\[ K_{eq/\alpha} = \frac{[(CO_2^+) - (CO_2^+)]}{(CH_4)(CO_2^+)} \] (3-43)

where the ion concentrations are measured as relative intensities and the methane concentration as torr. It can be seen that above about 0.008 torr of methane the reaction seems to be at equilibrium. If this is indeed the case it would then be possible to obtain an estimate of the methyl radical concentration by again assuming that there is no significant change in entropy. By combining equations (3-40) and (3-41) one obtains

\[ F = -RT \ln \left[ \frac{P(CH_3) \times I_r(HCO_2^+)}{P(CH_4) \times I_r(CO_2^+)} \right] \] (3-44)

Using the heat of reaction of 27 kcal/mole and taking the ion intensities at 0.018 torr of methane from Figure III-12, one obtains \( P(CH_3) = 1.5 \times 10^{14} \) torr which indicates that the reaction does not actually attain equilibrium.

In Figure III-2 it appears that reaction (3-7)

\[ HC_2O_4^+ + CH_4 \rightarrow CH_5^+ + 2CO_2 \] (3-7)

is also approaching equilibrium at 0.25 torr of methane; Figure III-13 shows the distributions of \( CH_5^+ \) and \( HC_2O_4^+ \) to 0.3 torr of methane and it does not come to equilibrium.

de. Carbon dioxide with added deuterium

In the process of using deuterium to determine the product of the reaction of \( CO_2^+ \) with \( X(X = CH_4 \text{ or } D_2) \) a
FIGURE III-13

Ion intensities of 1). $\text{HC}_2\text{O}_4^+$ and 2). $\text{CH}_5^+$ in 0.37 torr of carbon dioxide with added methane.
\[ P(\text{CH}_4), \text{TORR} \]

Relative Intensity
kinetic study of the reaction

\[ \text{CO}_2^+ + \text{D}_2 \rightarrow \text{CO}_2\text{D}^+ + \text{D} \quad (3-45) \]

was performed. This was the only reaction occurring when deuterium was added to carbon dioxide. The disappearance of \( \text{CO}_2^+ \) is given by

\[ \frac{d(\text{CO}_2^+)}{dt} = -k_{45}(\text{CO}_2^+)(\text{D}_2) \quad (3-46) \]

which upon integration yields

\[ \ln \left[ \frac{(\text{CO}_2^+)}{(\text{CO}_2^+)_0} \right] = -k_{45}(\text{D}_2)t \quad (3-47) \]

The reaction times are again determined from equation (3-28). Figure III-14 shows the plots of equation (3-47) at various carbon dioxide concentrations, and the data are summarized in Table III-13. This reaction has also been studied by Harrison and Myher (9); they determined a value of \( 0.62 \times 10^{-9} \text{ cc\cdot molecule}^{-1}\cdot\text{sec}^{-1} \). They also state that the value calculated from the ion-induced-dipole model of Gioumousis and Stevenson (3) is \( 1.1 \times 10^{-9} \text{ cc\cdot molecule}^{-1}\cdot\text{sec}^{-1} \) which is in very good agreement with the average rate constant of \( 1.2 \times 10^{-9} \text{ cc\cdot molecule}^{-1}\cdot\text{sec}^{-1} \) obtained from this experiment.

For reaction (3-45) the formation of \( \text{CO}_2\text{D}^+ \) is given by

\[ \frac{d(\text{CO}_2\text{D}^+)}{dt} = k_{45}(\text{CO}_2^+)_0(\text{D}_2)e^{-k_{45}(\text{D}_2)t} \quad (3-48) \]

which integrates to
Semilog plots of decay of $\text{CO}_2^+$ as a function of added deuterium at 1). 0.12, 2). 0.24, 3). 0.29, and 4). 0.37 torr of carbon dioxide.
TABLE III-13

Determination of $k_{45}$ from equation (3-47).

<table>
<thead>
<tr>
<th>$P(CO_2)$, torr</th>
<th>$10^{16}kt$</th>
<th>$10^6t$</th>
<th>$10^9k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37</td>
<td>96</td>
<td>8.5</td>
<td>1.1</td>
</tr>
<tr>
<td>0.29</td>
<td>87</td>
<td>6.8</td>
<td>1.3</td>
</tr>
<tr>
<td>0.24</td>
<td>68.5</td>
<td>5.5</td>
<td>1.2</td>
</tr>
<tr>
<td>0.12</td>
<td>41</td>
<td>2.75</td>
<td>1.5</td>
</tr>
</tbody>
</table>
\[
\frac{(CO_2^+D)}{(CO_2^+)_0} = 1 - e^{-k_{45}(D_2)t} \quad (3-49)
\]

Since \((CO_2D^+)_0 = 0\). Equation (3-49) reduces at low pressures to

\[
\frac{(CO_2D^+)}{(CO_2^+)_0} = k_{45}(D_2)t \quad (3-50)
\]

This function is plotted in Figure III-15 and the data summarized in Table III-14. An average value of 1.1 \times 10^{-9} \text{ cc} \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1} was obtained for the rate constant using equation (3-27) to calculate the reaction time. This value is the same as that obtained above.

Only the rate constants of reactions (3-3) and (3-45) compared to experimental values obtained at low pressures and in both cases the constants obtained in this work are a factor of two higher than the low pressure values. The values obtained here for \(k_t\) are self-consistent and reproducible, but the rate constants so determined are dependent on the computed residence times. The mobility of \(CO_2^+\) in carbon dioxide was used in the determination of the residence time in both cases and this value has been well established (19). If the rate constants were actually smaller, then the residence times would be larger than those calculated here. This would be the case if the average ionic path length inside the ion source were larger than the perpendicular distance from the electron beam to the ion exit slit used in the calculations. Also, the field
FIGURE III-15

Semilog plots of intensity of $\text{DCO}_2^+$ as a function of added deuterium at 1). 0.29, 2). 0.37, 3). 0.38, and 4). 0.39 torr of carbon dioxide.
TABLE III-14

Determination of $k_{45}$ from equation (3-50).

<table>
<thead>
<tr>
<th>$P(CO_2)$, torr</th>
<th>$10^{15}kt$</th>
<th>$10^6k$</th>
<th>$10^9k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.29</td>
<td>8.3</td>
<td>6.8</td>
<td>1.2</td>
</tr>
<tr>
<td>0.37</td>
<td>8.8</td>
<td>8.5</td>
<td>1.0</td>
</tr>
<tr>
<td>0.38</td>
<td>10.0</td>
<td>8.7</td>
<td>1.2</td>
</tr>
<tr>
<td>0.39</td>
<td>9.0</td>
<td>9.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
strength used in determining the residence times might be affected by space-charging due to the concentration of ions in the source. These ideas are merely speculative and there will be no way of confirming them until there are sufficient independent studies of some high pressure reaction rates to permit some standardization in much the same way that the reactions in methane (see reactions 2-5 and 2-6) are used as a standard for low pressure work.
IV. SUMMARY

This work has employed the basic chemical ionization techniques in an attempt to characterize ion-molecule reactions and study their kinetics. It was found that the reactions involved in adding carbon dioxide to a substantial amount of methane could not be studied: the reactions of ions from carbon dioxide have rate constants on the order of $10^{-9}$ cc.molecule$^{-1}$.sec$^{-1}$ and the major products, CH$_5^+$ and HCO$^+$, occur at the same mass-to-charge ratios as the products CH$_5^+$ and C$_2$H$_5^+$, respectively, from the high pressure spectrum of methane. If methane is added to carbon dioxide the situation is markedly different. The following scheme was derived:

\[
\begin{align*}
\text{CO}_2^+ + m\text{CO}_2 &\rightarrow \text{C}_2\text{O}_4^+ + (m-1)\text{CO}_2 \\
\text{CO}_2^+ + \text{CH}_4 &\rightarrow \text{HCO}_2^+ + \text{CH}_3 \\
\text{HCO}_2^+ + \text{CH}_4 &\rightarrow \text{CH}_5^+ + \text{CO}_2 \\
\text{CO}_2^+ + \text{CH}_4 &\rightarrow \text{HCO}^+ + \text{CH}_3\text{O} \text{ (or HCO + H}_2\text{) } \\
\text{C}_2\text{O}_4^+ + \text{CH}_4 &\rightarrow \text{HC}_2\text{O}_4^+ + \text{CH}_3 \\
\text{HC}_2\text{O}_4^+ + \text{CH}_4 &\rightarrow \text{CH}_5^+ + 2\text{CO}_2
\end{align*}
\]

From this it was determined that $\Delta H_f(C_2O_4^+) \leq 129$ kcal/mole and $\Delta H_f(HC_2O_4^+) \leq 78$ kcal/mole.

At the pressures involved ionic residence times were under the control of mobility considerations. With a value
of 1.03 cm²·V⁻¹·sec⁻¹ for the zero-field reduced mobility of CO₂⁺ in carbon dioxide values of 2.2 x 10⁻⁹ cc·molecule⁻¹·sec⁻¹ and 1.4 x 10⁻¹¹ cc·molecule⁻¹·sec⁻¹ were obtained for reactions (4-2) and (4-4), respectively. The Hasted equation was used to estimate the mobilities of HCO₂⁺, C₂O₂⁺, and HC₂O₂⁺ in carbon dioxide. Using residence times calculated from these mobilities, values of 1.3 x 10⁻¹⁰, 3.5 x 10⁻⁹, and 1.1 x 10⁻¹⁰ cc·molecule⁻¹·sec⁻¹ were obtained for the rate constants of reactions (4-3), (4-5), and (4-6), respectively. An experiment was also run with deuterium added to carbon dioxide and a rate constant of 1.2 x 10⁻⁹ cc·molecule⁻¹·sec⁻¹ obtained for the reaction

\[ \text{CO}_2^+ + \text{D}_2 \rightarrow \text{CO}_2\text{D}^+ + \text{D} \quad \text{(4-7)} \]

This is close to the theoretical value of 1.1 x 10⁻⁹ cc·molecule⁻¹·sec⁻¹.

An average value for the equilibrium constant for reaction (4-3) of 7.5 was determined. This corresponds to a heat of reaction of 1.35 kcal/mole which is close to the zero kcal/mole calculated from heats of formation.

Therefore, the general method is useful if each gas of the mixture is used in turn as the reactant component. The important stipulation is that mobility data be available for any reacting ions because it is mobility criteria which determine ionic residence times at the pressures of interest.
V. BIBLIOGRAPHY


12. T.O. Tiernan, private communication.


VI. APPENDIX

Heats of Formation (a)

<table>
<thead>
<tr>
<th>Species</th>
<th>$H_f, \text{kcal/mole}$</th>
<th>Species</th>
<th>$H_f, \text{kcal/mole}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>33</td>
<td>HCO$_2$</td>
<td>-58</td>
</tr>
<tr>
<td>CH$_4^+$</td>
<td>260</td>
<td>HCO$_2^+$</td>
<td>145(b)</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-17.9</td>
<td>HCO$^+$</td>
<td>8</td>
</tr>
<tr>
<td>CH$_5^+$</td>
<td>275</td>
<td>H$_2$O</td>
<td>-57.8</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>25</td>
<td>H$_2$O$^+$</td>
<td>233</td>
</tr>
<tr>
<td>C$_2$H$_5^+$</td>
<td>219</td>
<td>H$_3$O$^+$</td>
<td>143(c)</td>
</tr>
<tr>
<td>CO$_2$</td>
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<td>OH</td>
<td>9.3</td>
</tr>
<tr>
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<td>223</td>
<td>OH$^+$</td>
<td>327</td>
</tr>
<tr>
<td>CO</td>
<td>-26</td>
<td>O$_2^+$</td>
<td>278</td>
</tr>
<tr>
<td>CO$^+$</td>
<td>297</td>
<td>H</td>
<td>52</td>
</tr>
<tr>
<td>CH$_3$O</td>
<td>0(b)</td>
<td>H$^+$</td>
<td>365</td>
</tr>
</tbody>
</table>

(a) All values except those noted taken from ref. (22);
(b) ref. (23); (c) ref. (24).