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discrepancy could also be explained if our curves for transition pressure *vs* temperature were too steep (dP/dT too large). Both of these are possibilities, since the factors which influence the transition are largely unknown quantities.

These latent heats can be used to estimate the amount of the conversion which took place in the heat capacity work, where hysteresis was observed to be dependent on the rate of cooling, etc.[10] The specific heat anomaly which was found at 165°K contains an enthalpy of about 50 cal/mole, whereas one would expect a total latent heat of the order of 500 cal/mole to appear if the transition were complete. Thus, only about one-tenth of the sample could have transformed into the condensed cubic phase. Of course, one must be careful about applying thermodynamics to situations like this where large hysteresis occurs, and the state of the system is not uniquely defined by a temperature and a pressure.

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Note added in proof by the authors:—A recent paper on "The Phase Diagram for Cerium" by Likhter, Raybinin, and Vereshchagin [Zhur. Eksptl. i Teoret. Fiz. **33,** 610 (1957)], is quoted in Physics Abstr. (No. 1648, April, 1958) as giving a value of 43 kg/cm^2-deg for the slope of the transition line for cerium of 99.8% purity. A translation of this paper is not as yet available, but the above figure may be considered as in reasonable agreement with our experiments.

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Dissociation of Formic Acid and Deuteroformic Acids by Ion-Molecule Collision

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The dissociation of 5.1 kev $HCOOH^+$, $DCOOH^+$, and $HCOOD^+$ ions by ion-molecule collision with H_2, D_2, He, N_2, A, and Kr has been investigated in a mass spectrometer. Approximate values for the cross sections for the resultant fragment ions have been calculated. Positive ion fragments CHO^+ and CHO_2^+ are produced by loss of hydrogen from both of the possible positions. However, rupture of the C—H bond is a factor of two more probable than cleavage of the O—H bond in the formation of CHO_2^+. The CHO^+ ion fragment is formed mainly by removal of the hydroxyl group.

INTRODUCTION

ALTHOUGH dissociation of molecular ions by ion-molecule collision reactions has been studied by many investigators,[1–10] most of the work is qualitative and data on the structure and formation of the resultant fragment ions have not been reported. This paper gives data on the structure and source of fragment ions produced by ion-molecule collision reactions for 5.1 kev formic acid molecular ions in a number of common gases. Measurements were made on formic acid ions from both the ordinary and the deuterium substituted molecules. These results are complementary to those reported in a previous paper[11] giving data on the structure of formic acid ions produced by electron impact.

No quantitative theories have been advanced to describe the interaction of low-energy (kev) molecular ions and molecules resulting in dissociation. Salpeter[12] estimated the cross section for dissociation of H_2^+ ions in gases for ions of energies of 1–20 Mev. His calculations were verified recently by Damodaran[13] for H_2^+ ions with energies above 200 kev. However, the agree-

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* Operated by Union Carbide Company for the U. S. Atomic Energy Commission.

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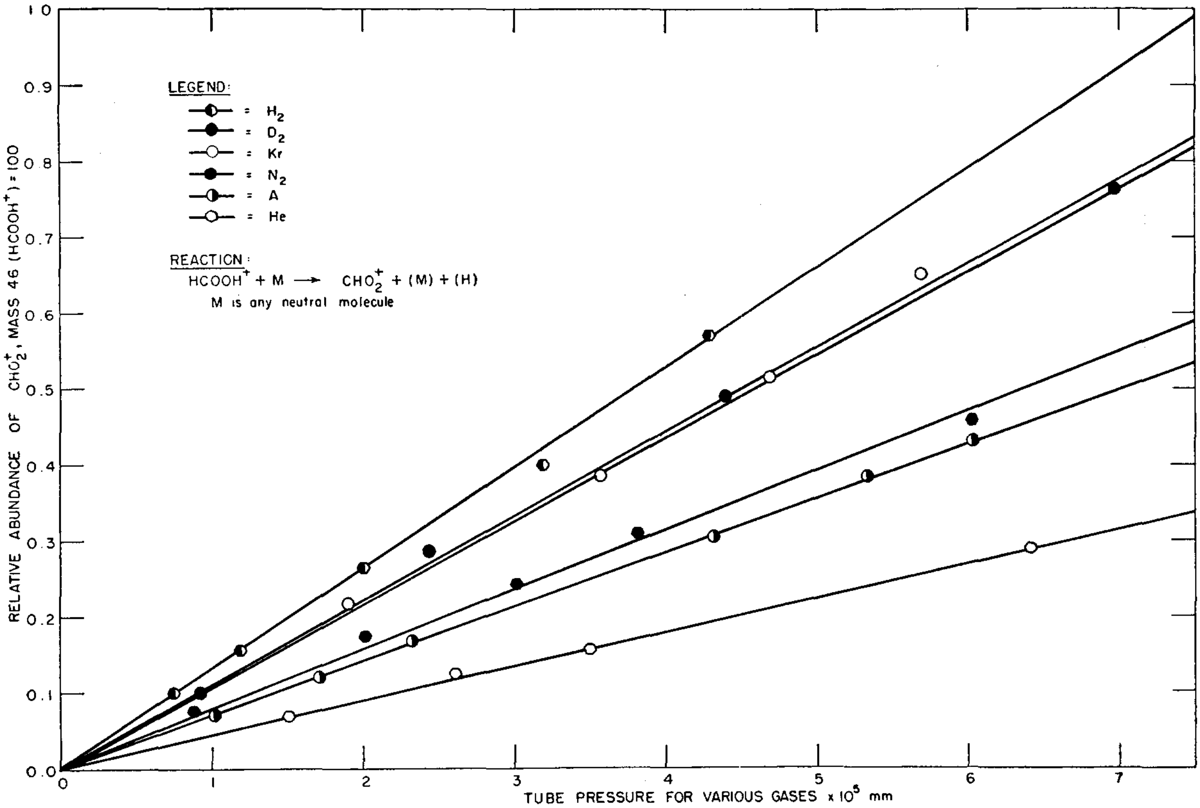

FIG. 1. Pressure dependence of the relative abundance of CHO_2^+ from $HCOOH^+$.

ment between theory and experiments is poor at energies below 200 kev.

It was thought that a study of the dissociation cross section in several molecules would be useful in helping to formulate a theory for the complicated collision reactions. Approximate values for these cross sections were obtained for 5.1 kev formic acid ions and several molecules.

METHOD

The technique was essentially the same as was previously described in the study of carbon monoxide,[14] including the evaluation of the apparent mass of the fragment ions. However, in this study the energy of the ionizing electrons was reduced from the usual 75 ev to 12.5 ev to assure a homogenous beam of parent $HCOOH^+$ ions. The abundance of the primary fragment ions was less than 1% of that for the parent ion. This technique of reducing the energy of the ionizing electrons to provide a monomolecular ion beam is somewhat simpler than the method of the double mass spectrometer used by Dukel'skii.[15–17] Unfortunately, it has a disadvantage in that the cross section for ion production is proportional to the energy of the ionizing electrons in this energy range. The method of sample preparation and purification was identical to that described in the previous paper[11] on formic acid.

RESULTS AND DISCUSSION

Data for the principal fragment ions resulting from ion-molecule collision reactions of 5.1 kev $HCOOH^+$ ions are summarized in Figs. 1–3. Relative abundance of the fragment ions normalized to the abundance of the parent $HCOOH^+$ ions equal to 100 is shown as a function of tube pressure for H_2, D_2, Kr, N_2, A, and He. The linear pressure dependence of the relative abundance for each of the resultant fragment ions shows that they are produced by a single collision.

The HCO_2^+ ions, (Fig. 1) corresponding to the loss of a hydrogen atom from $HCOOH^+$ were more abundant than any of the other collision induced ions. There are several reactions similar to those for dissociation by electron impact which will produce HCO_2^+. The two most probable reactions are:

$$HCOOH^+ + M \rightarrow HCOO^+(M) + (H), \qquad (1)$$

corresponding to rupture of the O—H bond, and

$$HCOOH^+ + M \rightarrow COOH^+ + (M) + (H), \qquad (2)$$

corresponding to cleavage of the C—H bond, where M is any neutral molecule and parentheses indicate that

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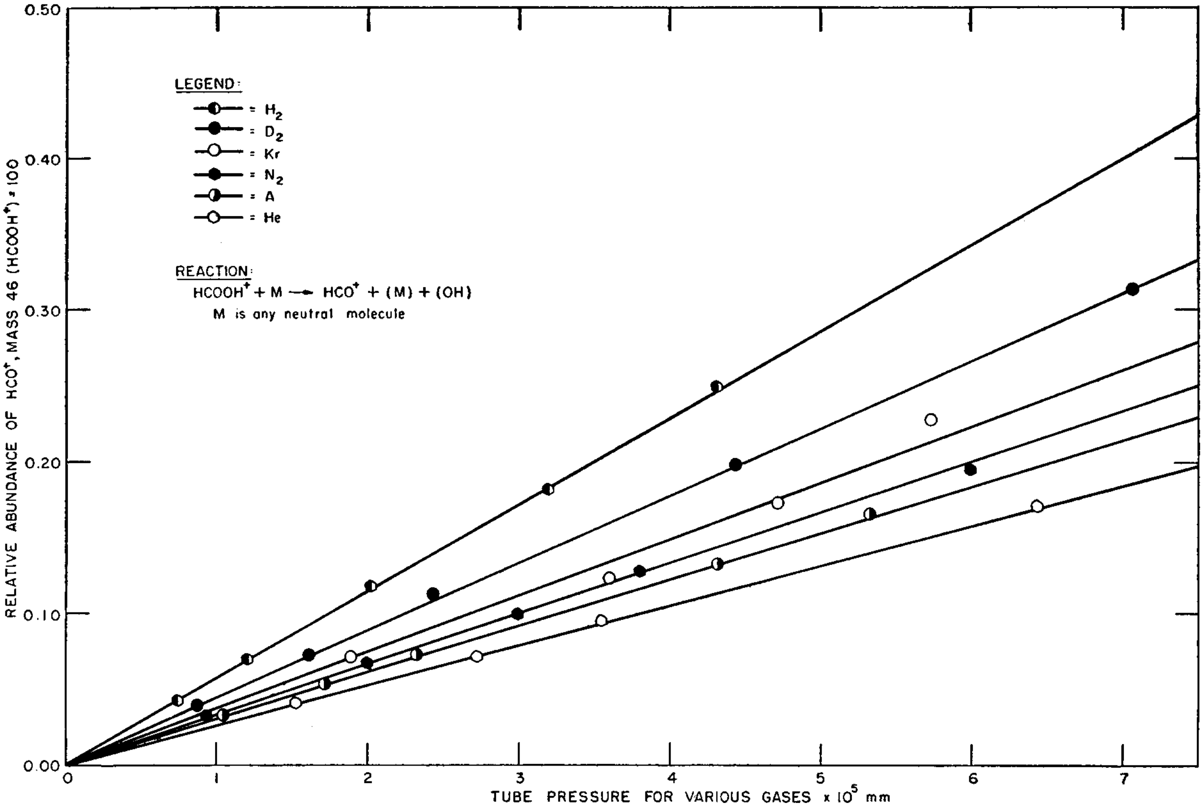

FIG. 2. Pressure dependence of the relative abundance of HCO^+ from $HCOOH^+$.

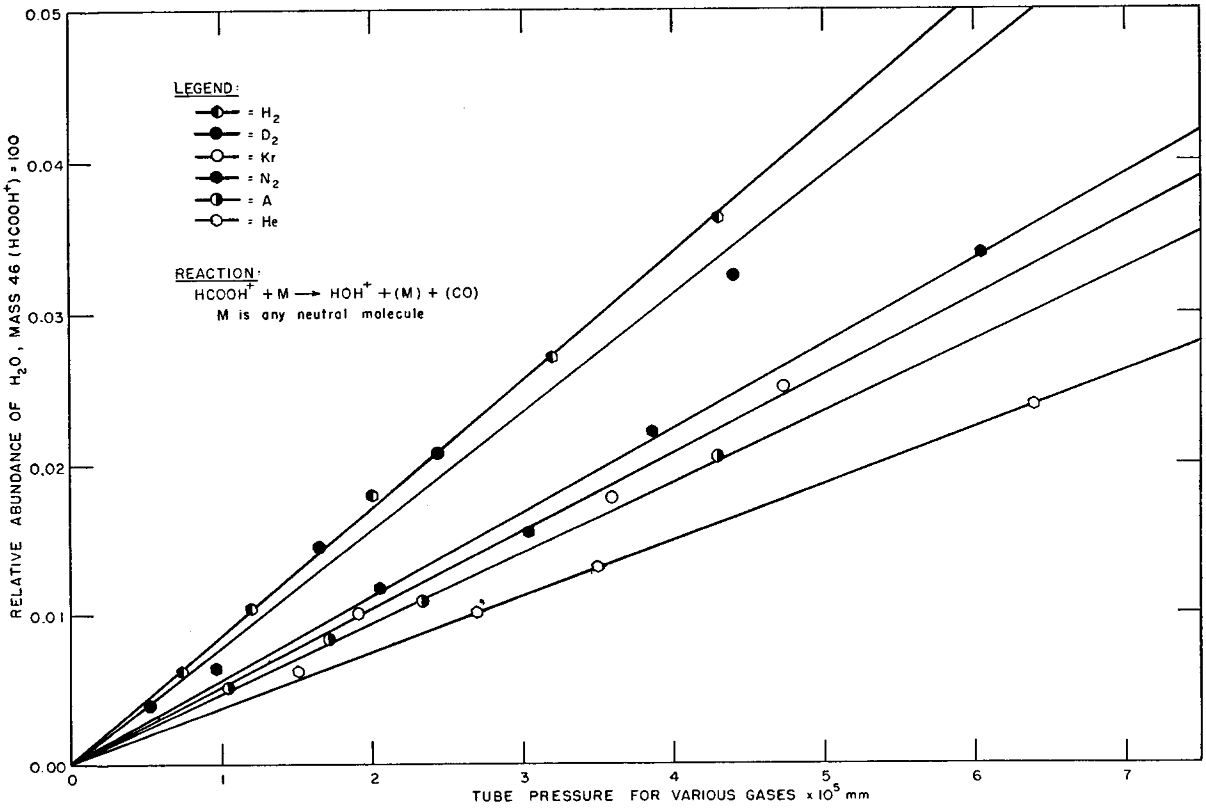

FIG. 3. Pressure dependence of the relative abundance of H_2O^+ from $HCOOH^+$.

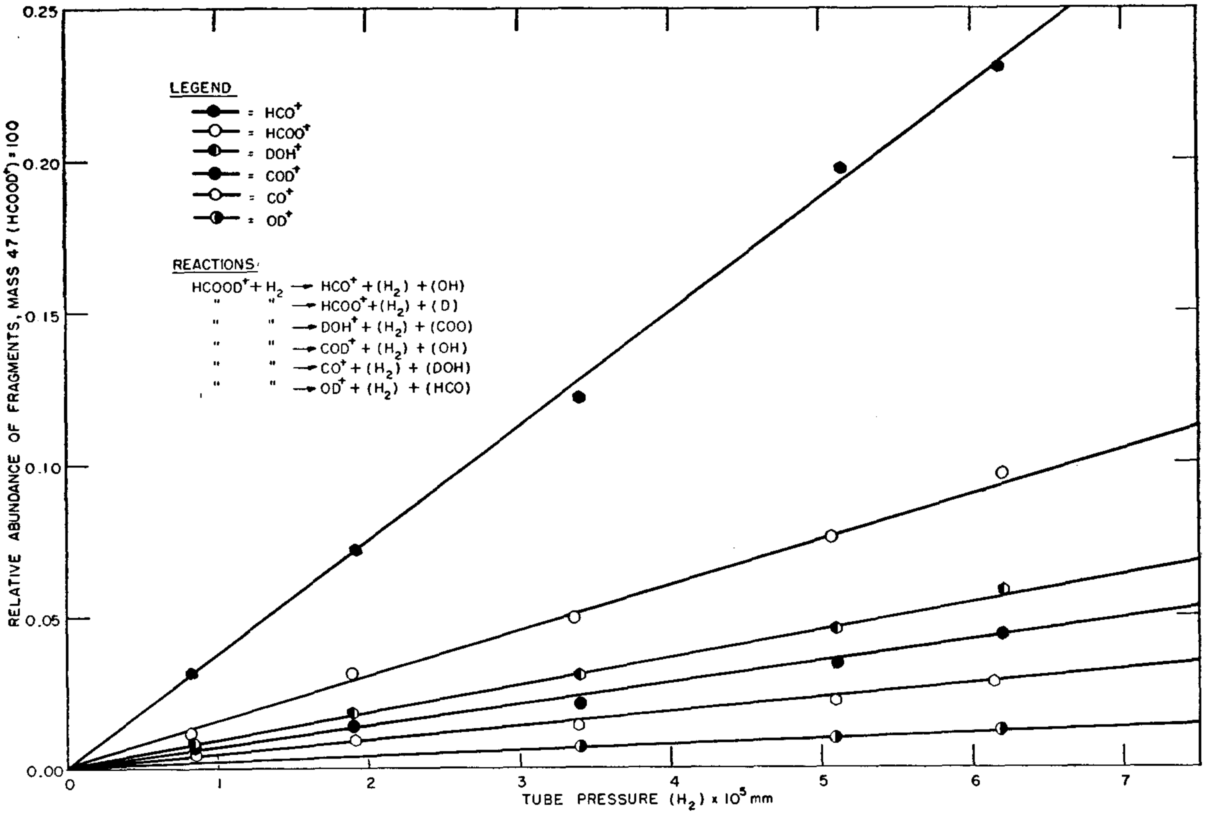

FIG. 4. Pressure dependence of ion-molecule collision reactions for $HCOOD^+$ and H_2.

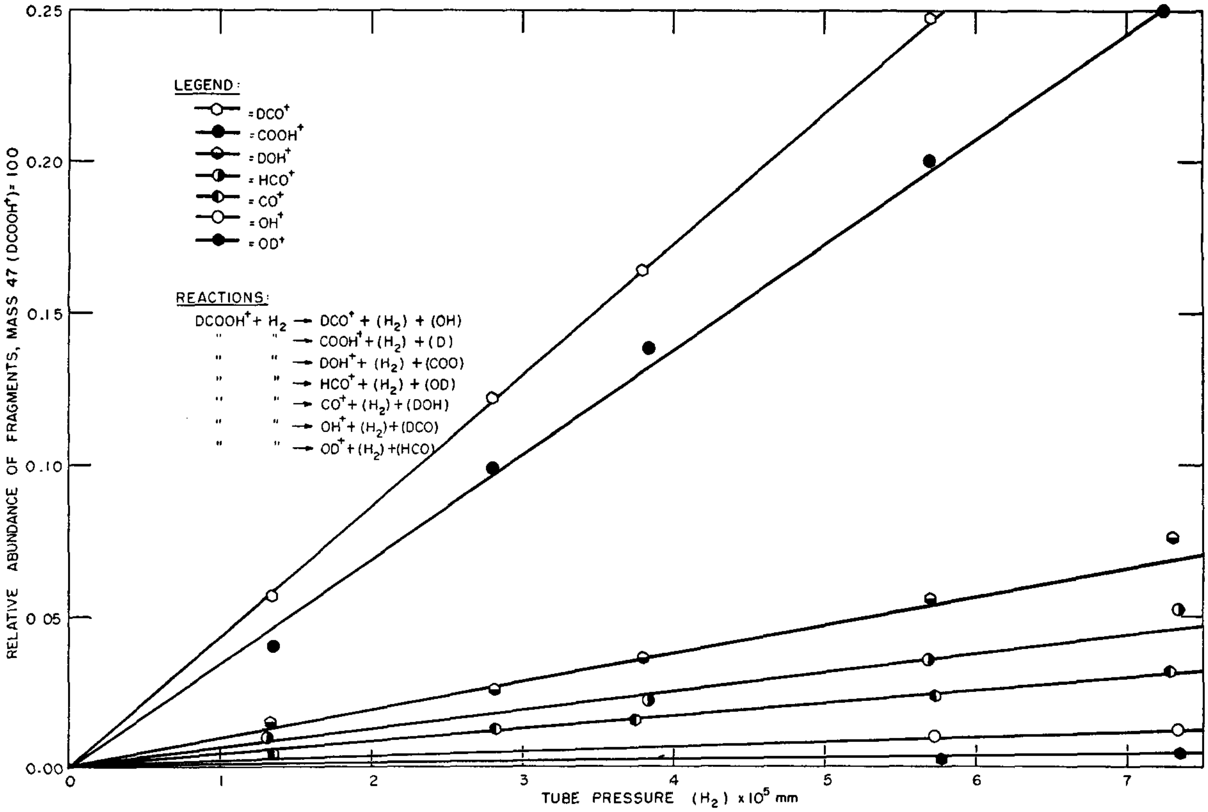

FIG. 5. Pressure dependence of ion-molecule collision reactions for $DCOOH^+$ and H_2.

the state, i.e., neutrals, free radicals, or ions, is not known. Assuming the mode of dissociation for the deuteroformic acids to be qualitatively the same as for the normal formic acids, a study of the dissociation products shown in Figs. 4 and 5 from the deuterated acids should indicate the predominant reaction for the formation of CHO_2^+. These figures give the pressure dependence for the relative abundance of the principal fragment ions observed. Relative abundances for other fragment ions could not be determined with sufficient precision due to their low intensity or to interference from more abundant ions. The relative abundance of $HCOO^+$ produced by reaction (1) from $HCOOD^+$, shown in Fig. 4, is about a factor of two less than that for $COOH^+$ produced by reaction (2) from $DCOOH^+$, shown in Fig. 5. If one assumes negligible isotopic effect, this would indicate that cleavage of the C—H bond has a higher probability, but that dissociation by both reactions occurs.

By using a similar argument to discuss the CHO^+ ion shown in Fig. 2 and comparing the results with those appearing in Figs. 4 and 5, it can be shown that formation of CHO^+ by loss of the hydroxl group according to the reaction

$$HCOOH^+ + M \rightarrow HCO^+ + (OH) + (M) \qquad (3)$$

is a factor of six more probable than formation by other reactions. The results of Figs. 4 and 5 indicate that some of the ions are formed by the reaction,

$$HCOOH^+ + M \rightarrow COH^+ + (OH) + (M). \qquad (4)$$

Here the structure of the CHO^+ ion is not known. One possibility would be the migration of the hydrogen atom to form $H—C=O^+$. However, it is more probable that the ion has a structure of $C=OH^+$. Similar results were observed for dissociation by electron impact in the previous study.[11]

A tabulation of the relative cross sections for dissociation of $HCOOH^+$ by ion-molecule collisions appears in Table I. These values are normalized to the value of the cross section for dissociation of $HCOOH^+$ into CHO_2^+ by ion-molecule collision with H_2. The relative cross sections for dissociation of $HCOOH^+$ by collision with H_2 or D_2 are identical within experimental error, reproducible to ±10%. The cross sections for collision-induced dissociations are approximately in direct proportion to the mass and/or size of the neutral gas molecules with the exception of H_2 which exhibits an exceptionally large cross section. This large cross section for H_2 might be attributed to a chemical interaction The same abnormality was exhibited by H_2 in similar studies[14,18] using CO^+ ions and N_2^+ ions, but the cross sections for the rare gases in these cases were approximately inversely proportional to the mass. The difference in the mass effect in these studies might be related to the fact that the energy required for dissociation of CO^+ and N_2^+ is much higher than that for $HCOOH^+$. Consequently, the ionization potential of the neutral gas might be a more important factor in determining the cross sections for dissociation of CO^+ and N_2^+ through the competition of a possible charge exchange process with the observed dissociation reaction.

TABLE I. Relative cross sections for dissociation of 5.1 kev $HCOOH^+$ ions by ion-molecule reaction.

Neutral molecule	Fragment CHO_2^+	Fragment HCO^+	Fragment HOH^+
H_2	100	40	6
D_2	90	40	6
Kr	90	30	4
N_2	60	30	4
A	50	20	3
He	30	20	3

TABLE II. Absolute cross sections for dissociation of 5.1 kev $HCOOH^+$ ion by ion-molecule collision.

Reaction	Cross section in units of 10^{-16} cm^2
$HCOOH^+ + H_2 \rightarrow CHO_2^+ + (H_2) + (H)$	1.4
$\rightarrow HCO^+ + (H_2) + (OH)$	0.6
$\rightarrow HOH^+ + (H_2) + (CO)$	0.09
$\rightarrow CO^+ + (H_2) + (HOH)$	0.08
$\rightarrow OH^+ + (H_2) + (HCO)$	0.03

Approximate values for the absolute cross section for dissociation are given in Table II. These results were obtained by making the following assumptions: (a) The ionization gauge, which was calibrated for linearity and sensitivity to various gases by means of the external gas expansion volume, micromanometer, and mercury manometer, is taken to indicate the true pressure in the tube, and (b) the collection efficiencies for primary ions which pass through the field free region, and for secondary ions formed in this region by collision reactions are equal. Assumption (b) is made simply because no better data are available and is probably not strictly valid.

The reaction involving hydrogen loss from the parent molecule gave the largest value for the absolute cross section. It is interesting to note that the cross section for the reaction giving CO_2^+ was too small to be reliably determined, which is in contrast to the high cross section for the formation of CO_2^+ obtained from dissociation by electron impact. The observation that the relative abundance for the fragment ions produced by electron impact-induced dissociation is qualitatively the same as that for collision-induced dissociation with the exception of CO_2^+ suggests that the CO_2^+ observed for electron impact-induced dissociation is probably a result of thermal decomposition of the molecule on a surface. This is further supported by

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TABLE III. Absolute cross sections for dissociation of 5.1 kev $HCOOD^+$ and $DCOOH^+$ ions by ion-molecule collision.

Reaction	Cross section in units of 10^{-17} cm^2	Reaction	Cross section in units of 10^{-17} cm^2
$HCOOD^+ + H_2 \rightarrow HCO^+ + (H_2) + (OD)$	4.0	$DCOOH^+ + H_2 \rightarrow DCO^+ + (H_2) + (OH)$	5.0
$\rightarrow HCOO^+ + (H_2) + (D)$	2.0	$\rightarrow DCOO^+ + (H_2) + (H)$	[a]
$\rightarrow COOD^+ + (H_2) + (H)$	[a]	$\rightarrow COOH^+ + (H_2) + (D)$	4.0
$\rightarrow COD^+ + (H_2) + (OH)$	0.7	$\rightarrow COH^+ + (H_2) + (OD)$	0.7
$\rightarrow CO^+ + (H_2) + (HOD)$	0.5	$\rightarrow CO^+ + (H_2) + (HOD)$	0.5
$\rightarrow OD^+ + (H_2) + (HCO)$	0.2	$\rightarrow OH^+ + (H_2) + (DCO)$	0.2

[a] Not evaluated because of coincidence of masses with other ions.

the large discrepancies reported[19-21] for the relative abundance of CO_2^+ produced from HCOOH by electron impact.

Values for the absolute cross sections for the dissociation reactions studied in deuteroformic acids are tabulated in Table III. These cross sections indicate that formation of HCO^+ from $HCOOD^+$ by removal of the hydroxyl group is about an order of magnitude greater than that for formation of COD^+ by rupture of the CH bond and removal of an oxygen atom. This observation is further supported by the cross sections for the formation of DCO^+ and COH^+ from $DCOOH^+$. Similar results were observed for dissociation of formic acids and deuteroformic acids by electron impact.[11]

Charge permutation[22] of the type,

$$HCOO^- + Kr \rightarrow HCOO^+ + (Kr) + 2e,$$

resulting from ion-molecule collision was observed for both positive and negative ions from formic acid. The cross section for these reactions was about an order of magnitude smaller than that for dissociation into fragment ions of like charge.

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