# GAS-PHASE DECOMPOSITION OF FORMIC ACID IN CARBON COATED VESSELS

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THESIS

### ABSTRACT

## GAS-PHASE DECOMPOSITION OF FORMIC ACID IN CARBON-COATED VESSELS

by Sandra Wollert Watson

Formic acid decomposes thermally to form two sets of products,  $H_2 + CO_2$ , and  $H_2O + CO$ :

$$HCOOH \xrightarrow{\longrightarrow} CO_2 + H_2 \quad (1)$$
$$\xrightarrow{\longrightarrow} CO + H_2O \quad (2)$$

The decompositions (1) and (2) are subject to surface catalysis by a large number of substances, the exact product distribution depending on the relative selectivity of the catalyst for the two paths. Recent work has indicated that the surface decomposition proceeds through formate ion, rather than by a molecular or radical mechanism. The photolytic decomposition, on the other hand, proceeds by a radical mechanism.

The kinetics of the decomposition occurring in carbon coated vessels have been examined at 451, 478, and  $505^{\circ}C$ and good agreement with earlier work by Blake and Hinshelwood (BH) was obtained. On the basis of the kinetics and the invariability of the rate to an 8-fold increase in surface/volume ratio and to addition of modest amounts of radical inhibitors, BH proposed that the decomposition under these conditions was homogeneous and that reactions (1) and (2) are molecular.

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Considerable interest attaches to molecular processes, and in order to examine the molecular character of the decomposition, the product ratios  $CO/CO_2$  and  $H_2/CO_2$ , and the isotopic content of hydrogen produced from the decomposition of DCOOH and HCOOD, have been determined at  $505^{\circ}C$ . The results indicate that slightly less hydrogen is produced than  $CO_2$  which is inconsistent with a molecular split mechanism; however, hydrogen may be removed by side reactions with the coating or other materials under the conditions of the experiment, and this result taken alone is inconclusive. The  $H_2/CO_2$  product ratio was found to be insensitive to the initial formic acid pressure, whereas the  $CO/CO_2$  product ratio increases significantly with increasing initial formic acid pressure.

When DCOOH and HCOOD were decomposed under the same conditions, all three isotopic hydrogens  $H_2$ , HD,  $D_2$  were produced as shown by both gas chromatography and mass spectrometry. Under identical conditions, a mixture of  $H_2$ and  $D_2$  was found to be stable toward exchange, and the result indicates that processes other than the molecular decomposition (1) and (2) must be operative in the system. In all cases, the HD/H<sub>2</sub> and  $D_2/H_2$  ratios were nearly twice as large in the case of DCOOH than for HCOOD, whereas the decomposition rates were comparable at all pressures. The results with DCOOH are very similar to those observed in the photolytic decomposition of formic acid, suggesting similar mechanisms as operative. The present results are consistent with a radical mechanism in which the chain is carried mainly by the processes

Η・	+	HCOOH	>	$H_2$	+	•СООН
н•	+	нсоон	<del></del> >	H20	+	нсо•
•СООН			>	C0 <sub>2</sub>	+	н•
нсо	•		>	co	+	н•

Molecular processes may also be occurring in the system. The results are discussed with respect to the previous explanation. It is suggested that the experiments of BH are inconclusive but not inconsistent with a radical mechanism.

## GAS-PHASE DECOMPOSITION OF FORMIC ACID IN

CARBON COATED VESSELS

Ву

Sandra Wollert Watson

## A THESIS

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To my mother, father and Jim

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### I. INTRODUCTION

Theories relating reaction rates to molecular parameters have been developed for elementary unimolecular processes in the gas-phase.<sup>1</sup> Considerable interest attaches to these theories because of the assumptions concerning intermolecular and intramolecular energy exchange processes, vibrational anharmonicity, the "strong collision" assumption, etc. These assumptions are important in other areas and in particular for the understanding of other rate processes. The nature and validity of the assumptions are subject to direct investigation and test in unimolecular reactions by comparison of experimental results with those calculated from the various theories: only a limited number of unimolecular reactions are known for which detailed comparisons have been made, particularly over wide ranges of temperature and pressure. Most molecules which undergo unimolecular reaction in the gas-phase are large molecules of considerable complexity for which only the first-order region is accessible for study, and for which the calculations are onerous. Considerable more information can be obtained from the unimolecular reactions of small molecules, which can be studied in the secondorder and/or the fall-off region of pressure.

Formic acid decomposes under a variety of conditions in the gas-phase by paths (1) and (2):

	The
	and
1	the
	pro
	fol
	pro
	and
	bot
	of
	of
	sub
	cf
	C0-'
	for
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	Sur
	of.
	ard
	the
	-1.6
	2
	act;
	Ig Ce

$$\xrightarrow{} CO_2 + H_2$$
 (1)

$$HCOOH \longrightarrow CO + H_2O \qquad (2)$$

The decomposition can be carried out both photochemically and thermally. Recent photochemical studies<sup>2</sup> suggest that the reaction occurs almost exclusively via the primary process:

HCOOH +  $h\nu \longrightarrow$  HCO· + ·OH

followed by secondary chain processes leading to final products. Molecular processes such as represented by (1) and (2) are of negligible importance under these conditions.

In the thermal decomposition, it has been found that both paths (1) and (2) are subject to catalysis by a number of substances, and the decomposition has been the subject of many studies on selective catalysis.<sup>3-9</sup> However, most substances catalyze the dehydrogenation (Path 1), and most of the catalysis work has been on this path. Hirota and co-workers<sup>10-12</sup> have obtained evidence for the presence of formate ion on the catalyst surface, and they propose a mechanism involving a rather complex series of radical and surface reactions which explain all of the main features of the reaction, including the deuterium isotope effects and the distribution of isotopic hydrogen in the products in the decomposition of the various deuterated acids.

Recently, Blake and Hinshelwood<sup>13</sup> reported that in reaction vessels coated with a specially prepared carbon surface, the surface reactions and radical reactions were

inhibited, and that homogeneous components of both path (1) and (2) occur. They find that under these conditions, path (1) is first-order and path (2) very nearly secondorder (except at very low initial pressures of formic acid, where the observed order increases somewhat for both processes). They suggest that path (1) consists of a unimolecular decomposition of monomer HCOOH, whereas path (2) corresponds to a unimolecular decomposition of dimer  $(\text{HCOOH})_2$ . Their evidence concerning the molecular character of the decomposition consists of the observations that the rate was unaffected by added radical inhibitors (propylene, isobutene, NO) in modest amounts, and by an 8-fold increase in the surface/volume ratio. Also, the dependence of rate on initial formic acid pressure was much different than observed on uncoated vessels.

The kinetic parameters found for path (2) assuming a unimolecular decomposition of dimer,

 $\log_{10} k_{CO} (sec^{-1}) = 13.58 - 42600/2.303 RT$ 

are reasonable and support the assumption. However, those observed for path (1),

$$\log_{10} k_{CO_2} (sec^{-1}) = 4.8 - 30600/2.303 \text{ RT}$$

are very abnormal for a unimolecular reaction; in particular, the pre-exponential factor,  $10^4 \cdot 8$ , is much lower than the "typical" value of  $10^{13}$ , indicating an abnormally small entropy of activation. Blake and Hinshelwood suggest that a possible explanation for the low pre-exponential factor is that path (1) actually consists of the decarboxylation of ion pairs  $(HCOO^{-})(H^{+})$  present in minute concentration, but no supporting evidence is offered.

Since carbon and active charcoal were found to catalyze the decomposition, especially that of path (2), and since the evidence concerning the molecular character of the decomposition is indirect only, the interpretation of Blake and Hinshelwood is questionable. If either path (1) or (2) or both were found to be molecular under the conditions of Blake and Hinshelwood, they could serve as important new reasons for study, and it was felt worthwhile to investigate in more detail the molecular character of the decomposition.

More direct evidence on the molecular character of the decomposition can be obtained by the use of deuterated acids. If path (1) and (2) represent the unimolecular decomposition of monomer and dimer, respectively, then in the decomposition of <u>d</u>-formic acid (DCOOH) and formic acid-<u>d</u> (HCOOD), HD and HDO would be the sole hydrogen-containing products, providing

(a) the water gas equilibrium

 $H_2O + CO \xrightarrow{} H_2 + CO_2$ 

was not mobile, and that the exchange processes

- (b)  $H_2 + D_2 \xrightarrow{} 2HD$  and
- (c)  $H_2O + D_2O \xrightarrow{} 2HDO$

did not occur, under the conditions of the experiment. It was established that neither (a) nor (b) occurred in the experiments, but that (c) did occur; therefore, the experiments directed toward establishing the molecular character of path (1) by determination of the isotopic content of the hydrogen produced in the decomposition of DCOOH and HCOOD. In addition, a complete product analysis was undertaken in order to establish that equivalent amounts of CO and  $H_2O$ and of CO<sub>2</sub> and  $H_2$  were produced, since these are demanded for molecular processes, but not necessarily for radical processes; discrepancies are noted, for instance, in the photochemical decomposition,<sup>2</sup> which has been shown to occur primarily by radical processes.

#### II. HISTORICAL BACKGROUND

The vapor-phase decomposition of formic acid has been studied extensively by photochemical and thermal methods.

Formic acid vapor decomposes by two simultaneous paths: (1) dehydrogenation and (2) dehydration:



Most of thermal studies have been concerned with the selective catalysis by various substances, by studying the ratio of rates for the two paths on a given substance, and by studying the rates of the individual paths (1) and (2) on various substances (most such studies have been made on path (1), the dehydrogenation). Metals, especially noble metals, such as Ag, Pt, Au, Rh, Pd, Cu, as well as some Oxides (i.e., ZnO;, see Table I), catalyze the dehydrogenation, path (1), predominantly, while many other substances show varying catalysis for both reactions. In fact, a whole spectrum of substances ranging from purely dehydrators through catalysts of varying selective activity, to purely dehydrogenators, has been defined by the work of many **Chemists.** The original suggestion by Sabatier<sup>14</sup>, that the selective catalytic activity was an intrinsic chemical **Property** of a substance requires modification by the findings • Adkins<sup>15</sup> and others that especially for substances ex**hibiting selective** catalytic activity for paths (1) and (2),

the relative selectivity depends also upon the mode of preparation of the catalyst; and that materials with large pores tend to catalyze the dehydrogenation, and those with fine pores tend to catalyze dehydration. Schwab and Schwab-Agallidis<sup>6</sup> also have found that factors such as increasing crystal size and surface shrinkage, as effected by precipitating and aging at elevated temperatures (which would also tend to decrease crystal imperfection, holes, cracks, and small pores) tend to favor dehydrogenation over dehydration, an effect attributed to a more significant decrease in the partial surface active for dehydration. For example, Table I indicates that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared at 970°C produced 95-100% dehydration, whereas  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> prepared at 1100°C produced only 16-30% dehydration. Other examples of such effects are also obvious from Table I.

The explanation of the above effects offered by Schwab<sup>6</sup> and others is a molecular decomposition by a highly distorted monomer molecule on the surface of a catalyst to split off hydrogen (Figure 1a), or by a concerted decomposition to split off CO and  $H_2O$  in the submicroscopic imperfections of the crystal (Figure 1b).

The apparent activation energies for production of  $CO_2$ ( $E_{CO_2}$ , path 1) and of  $CO(E_{CO}$ , path 2) are also listed in Table I. The values of  $E_{CO_2}$  range from 22-37 Kcal/mole, most of the values being close to 35 Kcal/mole, whereas values of  $E_{CO}$  range from 20-30 Kcal/mole, most being close to 24 Kcal/mole. There is some apparent variability with

Table 1.

Data for decomposition of formic acid on various surfaces.

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Table	I
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Catalyst	% CO2	Temper- ature <sup>0</sup> C	ECO (Kcal)	ECO2 (Kcal)	Refer- ence
	0	138_185	20.3		5
110 <sub>2</sub>	0		29.0	 (AE)	G
$\gamma - A_{12}O_3$	0-5	317-341	27.0	(45)	0
$S10_2$ (cold)	0-5	289-324	23.0	35.0	6
С	15-30	430-560	28.5	30.6	13
$\gamma-Al_2O_3$	17-33	307-343	24.0	34.0	6
$\gamma-Al_2O_3(inversed)$	30-64	355-358	25.5	41.0	6
Cr <sub>2</sub> O <sub>3</sub> (20 <sup>0</sup> C)	32.43	304-330	27.0	34.0	6
C (active)	40-72	300-315	19.2	35.5	6
glass	40-90	<b>240-3</b> 50	16.0	28.0	3
α-Al <sub>2</sub> O <sub>3</sub> (1100 <sup>0</sup> C)	7 <b>0</b> -84	392-414	24.0	36.0	6
Cr <sub>2</sub> O <sub>3</sub> (ppt.)	79-83	320-333	38.0	34.0	6
ZnO	92-96	304-372	23.5	30.0	6
CaF <sub>2</sub>	93-100	284-364	21.0	39.0	6
SiO <sub>2</sub> (1100 <sup>0</sup> C)	96-98	<b>3</b> 71-391	22.0	30.0	6
Pt	100	141-234		22.2	4
Cu (powder)	100	46-81		29.3	9
Ag	100	180-250		29.0	8
Ag	100	141-250		31.3	4
Ag (reduced)	100	100		22.6	7
Au	100	140-185		23.5	5
Au (fillings)	100	50-90		20.9	9
Au (foil)	100	120-170		24.3	9
Rh	100	156-182		25.0	5
Pd (fillings)	100	80-110		32.9	9
Pd (foil)	100	100-140		32.8	9

Figure 1.

Surface Catalyzed Decomposition of Formic Acid



PATH (2)



PATH (1)

method of preparation, but the values are remarkably consistent on very different catalysts. Hinshelwood and Topley<sup>5</sup> have suggested that these apparent activation energies represent energy requirements only for the absorbed molecule, and that the true activation energy for the decomposition would have to include the heat of absorption, and that suitable correction would bring the values on all catalysts into agreement. However, it seems unlikely that the heats of absorption of formic acid on such widely varying substances as glass, Cu (powder), Ag, Carbon and Zinc would be the same, as would seem to be indicated for the path (1) since the apparent activation energies are very nearly identical in these cases. If critical energies alone were responsible for selective catalysis, path (2) should predominate on all substances. Schwab and Schwab-Agallidis<sup>6</sup> have suggested that the selective catalytic behavior is almost entirely due to differences in the preexponential Arrhenius factors for the two reactions and they propose explanations based on critical molecular configurations and catalyst surface characteristics, based on the molecular mechanisms discussed previously.

Many early workers searched for evidence of radicals in the catalytic decomposition of formic acid vapor, but their results proved to be negative. However, recent studies by Sachtler<sup>16-19</sup> and others have shown the presence of formate ion on the catalyst surface and these workers have proposed a rate determining step (a)

(a) HCOOH (surface) ----> HCOO<sup>-</sup> (ads) + H<sup>+</sup> (ads)
for metals with unstable formates and a rate determining
step (b)

(b)  $HCOO^{-}(ads) \longrightarrow CO_{2} + H(ads) + e^{-}$ for metals with stable formates. This mechanism is not consistent with all of the available data, and has more recently been largely disproved by Schwab and Watson<sup>9</sup> using deuterated formic acids. The isotope effect (here defined as the ratio of rate constants for reactions of **is**otopic molecules) gives directly information concerned with the rate determining step. It is easy to show that the deuterium isotope effect in the decomposition of d**f**ormic acid (DCOOH) should be primary for a reaction (b) and secondary for reaction (a) i.e., k(HCOOH)/k(DCOOH) >> 1 for (b) and  $\simeq$  for (a). Conversely, for formic acid-d (HCOOD), one expects k(HCOOH)/k(HCOOD) >> 1 for (a) and  $\simeq 1$  for (b). Schwab and Watson found that  $k_H^{-}/k_D^{-}$  was considerably greater than unity for all of the deuterated acids **HCOOD**, **DCOOH** and **DCOOD** on all catalysts investigated, some of which had stable formates and some of which did not.

Other evidence against a Sachtler-type mechanism is **af** forded by the work of Hirota and co-workers<sup>20</sup> who studied **the** decomposition of formic acid on several catalysts in **the** presence of  $D_2$  and observed no HD in the products. Since **adsorbed** H atoms are involved, one would expect exchange **under** the condition of the experiments. Strong evidence against the simple molecular mechanism (Figure 1) was obtained by Hirota, Kuwata and Nakai<sup>11</sup> who observed that the dehydrogenation produced less H<sub>2</sub> than CO<sub>2</sub> on all dehydrogenating catalysts studied. These workers also argue that the distortion of the absorbed monomer molecule required in a molecular mechanism as shown in Figure 1 is inconsistent with the rather low activation energy observed. Further work by Hirota and co-workers<sup>12</sup> and by Otaki<sup>7</sup>, particularly on infrared studies, product analysis, isotopic content of hydrogen produced by the decomposition of deuterated formic acids, and deuterium isotope effects have led to a mechanism consistent with nearly all of the observed facts for the dehydrogenation of formic acid:

It seems that it is fairly well established that the Catalytic dehydrogenation of formic acid does not occur by a simple molecular process, but by a rather more compli-Cated series of surface reactions involving formate ion and Perhaps other absorbed species.

Much less is known about the catalytic dehydration, but the available evidence<sup>21-22</sup> suggests this may also proceed by a complex mechanism.

Even less is known about the detailed mechanism of the decomposition of formic acid on surfaces which catalyze both the dehydrogenation and the dehydration. One such catalyst of particular importance for this study is active charcoal (C-active), Table I. This very porous, mostly divided substance shows a selective catalytic behavior which is very dependent upon the method of preparation.

There has also been a considerable number of studies, involving the photolysis of formic acid.<sup>2</sup>,<sup>23,26</sup> This reaction tends to be more complex, the sole products being again  $H_2$ , CO, CO<sub>2</sub>,  $H_2O$ , but the product yields being very dependent on wavelength, temperature, and rate of photolysis. Most of the photolysis work was done at wavelengths corresponding to an excitation energy of 50 Kcal/mole, considerably above that available in the thermal reactions, with an increased probability of the presence of radicals in the reaction. Since most of the studies were carried out near room temperature, and at pressures at which formic acid vapor is known to associate considerably<sup>27</sup>, hence the presence of the dimer is also an important factor in photolysis experiments. In an early paper Taylor and Gorin<sup>24</sup> photolyzed formic acid under optimum conditions for dimerization, and suggested that the dimer decomposed molecularly to form exclusively CO<sub>2</sub> and H<sub>2</sub>. They reported no evidence for the presence of radicals when the photolysis was performed in the presence of para-rich hydrogen; no ortho-para conversion was detectable by thermal conductivity measurements.

Burton<sup>25</sup> also obtained no evidence for atoms or radicals when he photolyzed formic acid in the presence of an antimony mirror. However, Terenin<sup>28</sup> observed an emission spectrum of the OH radical in photolysis experiments, and on this basis Burton<sup>25</sup> proposed that the primary process was

HCOOH +  $h\nu \longrightarrow$  HCOOH\*  $\longrightarrow$  HCO· + ·OH

Gordon and Ausloss<sup>2</sup> were the first researchers to establish the importance of radicals in the direct and mercury photosensitized photolysis of formic acid (HCOOH and DCOOH). They found that the yield of H<sub>2</sub> was in all cases smaller than the yield of  $CO_2$ , and that the production of H<sub>2</sub> was markedly reduced in the presence of efficient H-atom scavengers ( $C_2H_4$  and  $O_2$ ). Thus it is clearly indicated that processes other than direct molecular-split mechanisms were involved in the photolysis. The possible primary processes proposed were:

нсоон	+	hν	>	C02	+	H <sub>2</sub>	(1)
			>	CO	+	H <sub>2</sub> O	(2)
			>	нсо•	+	•ОН	<b>(3</b> )
			>	Н	+	•СООН	(4)
			>	HCOO ·	+	н	(5)

The low yields of  $H_2$  relative to  $CO_2$  indicate that process (1) cannot account for more than 5% of the overall yield. Moreover, the fact that the yield of  $H_2$  is greatly reduced in the presence of H-atom scavengers, whereas that of  $CO_2$  is not affected, indicates that processes other than (1)

are more important for the production of  $H_2$  and  $CO_2$ . Many other observations suggest that, other than a small contribution from the molecular reactions (1) and (2), the important primary process is process (3), the production of formyl and hydroxyl radicals.

Secondary processes involving H abstraction from HCOOH by OH to form  $H_2O$  and either .COOH or HCOO. (both of which are presumed to yield H and  $CO_2$  in subsequent steps, especially at high temperatures), decomposition of excited formyl radical to yield CO and H, and an abstraction reaction of H with HCOOH to form  $H_2O$  and HCO. account for most of the results observed by Ausloss and Gordon at ordinary and moderate temperatures. Termination is assumed to occur by hydrogen atom recombination. At higher temperatures, a sharp rise in rates of production of  $H_2$  and  $CO_2$  indicates the importance of chain reactions involving H atom abstraction from formic acid by H to form  $H_2$  and COOH or HCOO which form  $CO_2$  and H.

More recent work<sup>7</sup> is consistent with the proposed radical reactions. It thus seems that the photolytic decomposition of formic acid vapor occurs almost exclusively by radical and radical-chain processes, and that molecular mechanisms for dehydration and/or dehydrogenation are relatively unimportant at higher energies.

Blake and Hinshelwood<sup>13</sup> have recently suggested that the heterogeneous surface and/or radical paths for dehydrogenation and dehydration of formic acid vapor are suppressed when formic acid is decomposed thermally in reaction

vessels which had been especially coated with carbon, and that under these conditions, the decomposition of either process consists of the molecular components. They further propose that the reaction to produce  $CO_2$  and  $H_2$  is a unimolecular decomposition of monomer formic acid, and that the reaction to form  $H_2O$  and CO proceeds by a unimolecular decomposition of dimer molecules. This seems an unlikely possibility, since carbon generally shows varying selective catalytic effects for both reactions. However, the surface obtained by Blake and Hinshelwood by cracking isobutylene at 600°C followed by a baking at 700°C would more likely form a synthetic carbon surface with greatly reduced area and porosity than active charcoal, then by analogy with the behavior of other substances upon similar treatments, the catalytic effect expected would be one of increased dehydrogenation; the opposite effect is observed; at nearly all pressures, the dominant reaction was the formation of CO. It thus seems likely that either carbon is anomolous in its behavior, or the reaction in the Blake-Hinshelwood reactor is indeed of a different character. If the molecular components of either the dehydration or dehydrogenation of formic acid could be isolated for study, such studies would be very important, for formic acid is a relatively simple molecule for which detailed theoretical rate calculations are feasible. Hence an example of a reaction which could be compared with theory in detail may

be afforded. This research was undertaken to examine in some detail the molecular character of the decomposition reactions of formic acid vapor in carbon-coated vessels. Before outlining the experiments undertaken, a review of the evidence presented by Blake and Hinshelwood to support the assumption of molecular reactions seems appropriate.

The Blake-Hinshelwood reaction vessel consisted of a silica vessel coated with carbon from the decomposition of six charges of isobutylene at 600°C followed by a final baking at 700°C. After careful pump-out and seasoning with a small amount of formic acid for several hours followed by a final evacuation, formic acid vapor was decomposed at temperatures of 436 to 532°C The rate of the decomposition was followed by measuring the total pressure of the system. The pressure increase was extrapolated to obtain initial rates based formally on a first-order rate equation.

The homogeneity of the reaction was established by the fact that the rate was only slightly affected (in fact, the rate was slightly decreased) in a reaction vessel packed with small glass chips so that an eight-fold increase in surface volume ratio was effected.

In several experiments, modest amounts (maximum ratio inhibitor :HCOOH = 2:1) of radical-chain inhibitors (isobutene, propene, NO) were added, with no noticeable decrease in rate. In fact, a small increase in the case of added NO was noted, and attributed to the reaction of NO with the carbon surface to expose the silica surface. The

rate was established to be much faster on the uncoated silica vessel. The product composition (CO/CO<sub>2</sub> ratio) was also substantially unchanged by addition of propylene. These results were interpreted by Blake and Hinshelwood as making it very improbable that radical-chain processes contribute significantly to the reaction under these conditions. However, experiments in which much larger amounts of inhibitors were added would be needed to definitely rule out a radical process. The results in the presence of modest amounts of inhibitors probably indicate only that long chains are not involved in the reaction. Short chain radical processes, such as those proposed for the photolytic reaction, may not be seriously affected by small amount of inhibitors.

Product analysis was limited to determining the  $CO/CO_2$ ratio as the reaction proceeded. In separate experiments it was shown that the water gas equilibrium  $CO + H_2O \xrightarrow{}$  $H_2 + CO_2$  was not mobile under the conditions of the experiments, so that the  $CO/CO_2$  ratio may be used to partition the overall observed rate constant k into that describing the dehydration,  $k_{CO}$ , and that for dehydrogenation,  $k_{CO_2}$ .

The initial decomposition rate was found to have a dependence on initial formic acid pressure represented by an average order slightly less than 2 over the pressure range 1-650 mm pressure, although the order is slightly higher than 2 below about 50 mm. The individual rate constants  $k_{\rm CO}$  and  $k_{\rm CO_2}$  obtained by partitioning the rate

constant by the observed product ratio  $CO/CO_2$ , were found to have very different dependences on initial formic acid pressure:  $k_{CO_2}$  is, within experimental error first-order at all pressures, whereas  $k_{CO}$  is slightly less than 2nd order above 50 mm, and very nearly 2nd order below 50 mm. At all pressures above 10 mm, the reaction forming CO (dehydration) is dominant. At lower pressure, dehydrogenation becomes dominant, but at high pressure this reaction is negligible. It is thus possible by studying the temperature dependence in the high and low pressure region, to obtain apparent activation energies for the two processes; these were found to be  $E_{CO} = 28.5$  and  $E_{CO_2} = 30.6$  Kcal/mole. The product distribution,  $CO/CO_2$ , is thus nearly independent of temperature.

On an uncoated silica vessel, the reaction rate was approximately one-half order in initial formic acid pressure, and the product ratio CO/CO<sub>2</sub> was >> 1 at all pressures, even below 10 mm. The reaction is thus very different in the coated vessel, and Blake and Hinshelwood conclude that both reactions are homogeneous, molecular processes under the conditions of the experiments.

The reaction forming CO is nearly second-order in initial formic acid pressure, and if the small deviation is neglected, the results expressed as a bimolecular rate Constant,  $k'_{CO}$ , it is found that

 $k_{CO} = 3 \times 10^7 \exp(28500/RT) - 1 \text{ mole}^{-1} \sec^{-1}$ ,

implying a steric factor of  $\sim 10^{-4}$ , somewhat lower than would be expected. The interpretation proposed is that the second-order reaction forming CO is really a unimolecular decomposition of dimer molecules present in the system. Correcting for the concentration of dimer molecules and for the heat of dimerization one obtains an apparent first-order rate constant for unimolecular decomposition of dimer molecules:

$$k_{CO}^{dimer} = 4 \times 10^{13} \exp(-42600/RT) \sec^{-1}$$
,

and the Arrhenius parameters are in the proper range for an unimolecular process.

The slight deviation from second-order behavior is presumed due to a small contribution from a first-order decomposition of monomer to form CO and  $H_2O$ .

The reaction forming  $CO_2$  is first-order at all pressures, and assumed to be molecular, with a rate expression of

$$k_{CO_2} = 10^4 \cdot 8 \exp(-30600/RT) \sec^{-1}$$
.

The pre-exponential factor differs so significantly from the usual value of  $10^{13} \text{ sec}^{-1}$ , that a unimolecular decomposition of monomer seems unlikely. Indeed, it is difficult to reconcile two different unimolecular decompositions of the monomer--one to form CO as assumed to account for the deviation of  $k_{CO}$  from second-order, and one forming CO<sub>2</sub> and H<sub>2</sub> with a very different rate. A very speculative explanation is offered, that the reaction forming CO<sub>2</sub> actually consists of a rate determining decarboxylation of ion pairs  $(HCOO^{-}, H^{+})$  present in minute concentration.

The evidence of the molecular character of the decomposition of formic acid vapor in carbon-coated vessels consists mainly of (1) the apparent homogeneity of the decomposition, (2) the lack of evidence for radical-chain processes, and (3) the lack of suitable alternative mechanisms to account for the kinetics and product composition. Also Blake and Hinshelwood report only results on the initial rates, and no mention is made of detailed study of the kinetics over the extent of the reaction; therefore, a more detailed kinetic study is desirable.

It has already been noted that in many of the catalytic and photolytic studies, an excess of  $CO_2$  over  $H_2$  was observed, thus arguing against a molecular-split mechanism for this mode of decomposition of formic acid. Blake and Hinshelwood apparently did not investigate the  $H_2/CO_2$  product ratio for the reaction in carbon-coated vessels, although such information could be very important for their conclusions. The product composition  $H_2:CO:CO_2$  was one of the goals of the present investigation.

In the catalytic studies, the deuterium isotope effects and especially the isotopic distribution of hydrogens formed from decomposition of HCOOD and/or DCOOH have been among the most important facts leading to an understanding of the nature of the reaction. Such studies are equally if not more important for establishing the molecular character of

the decomposition of HCOOH in carbon-coated vessels. It was established during this study that the exchange reaction  $H_2 + D_2 \xrightarrow{\longrightarrow} HD$  does not occur under the conditions of the experiments, so that if the reaction forming CO<sub>2</sub> and H<sub>2</sub> is molecular (whether the actual process is a unimolecular decomposition of monomer molecules or decarboxylation of ion pairs in the gas phase), the only isotopic hydrogen which should be produced in the decomposition of either HCOOD or DCOOH is HD. In addition, the kinetics are easily studied, so that deuterium kinetic isotope effects between HCOOH and all three deuterated acids are readily measured by comparative rate methods (competitive rate methods would be possible only between HCOOH and DCOOH, since the carboxylic hydrogen exchanges readily), and could offer valuable information concerning the rate-determining step of the reactions.
#### III. EXPERIMENTAL

## A. <u>Materials</u>

Formic acid (99%) obtained from K & K Chemical Laboratories was purified by at least four trap-to-trap vacuum distillations shortly before use in a run. After this procedure, the purity was checked by gas chromatography on a 6 ft. x 1/4 in. column of 100-120 mesh Porapak Q (Waters Associates, Framingham, Mass.). No impurities other than water were detected, and the vacuum purification was repeated until no water was detectable (estimated  $\pm 1$  mole % max., impurities).

Formic acid-d (HCOOD) and d-formic acid (DCOOH) of 99+% purity were obtained from Merck, Sharp, and Dohme, Ltd., Montreal, Canada. No further purification was required for the labeled acids.

Isobutylene (C.P. grade 99.0 minimum % purity) was obtained from Matheson Co., and used without further purification.

Copper oxide wire, Fisher Certified Reagent, was sifted through a coarse cloth to remove dust, and used to fill the combustion tubes. A plug of copper gauze (Cenco), washed with hot ethanol and acetone to remove the lacquer and oxidized in an oxidizing flame, was used as a stop at each end of the combustion tube. The combustion tube was re-oxidized with tank oxygen for at least one hour at 700°C before use.

No detectable impurities were added to the gas mixture from the combustion furnace.

The Activated Alumina (Grade F-1, Mesh 40-80) was purchased from the Aluminum Company of America.

The Ferric Chloride (Reagent A.C.S. lumps of 99% purity) was obtained from Matheson, Coleman and Bell.

The Ammonium Hydroxide was Reagent Grade 99+% purity from Fisher Scientific Company.

B. Apparatus

1. <u>The Reaction Vessel</u> consisted of a quartz cylinder, 23 cm long and 2.8 cm i.d., joined by a Vycor-Pyrex seal to a short length of 2 mm Pyrex capillary tubing, and a 2 mm capillary vacuum stopcock to the introduction and vacuum system. In addition, a side arm from the neck of the reaction vessel connected with a mercury manometer for measuring pressures. (Figure 4,p. 32.)

2. <u>The Furnace</u> used for heating the reaction vessel was a single tube furnace heavy insulating type 13559 (Central Scientific Company) closed at one end with a 1-inch plug of asbestos. The space remaining at the other end was closed by wrapping 1-inch asbestos tape about the neck of the reaction vessel so that a good fit was obtained when the reaction vessel was inserted into the furnace. A 7.5 amp manually-controlled variac was used to power the furnace. 3. <u>The Vacuum System</u> consisted of three sections: the manifold and trapping section, the sample introduction system, and the gas-analysis and product handling system. The design was conventional, consisting of Pyrex tubing, high-vacuum stopcocks, U-traps, and a Toepler pump for handling non-condensable gases. Details will be given under the section on experimental procedure (Figure 2).

4. The Toepler Pump was automatic of conventional design, purchased from Delmar Scientific Co.. However, it was found that the relay control supplied by the manufacturer caused arcing across the leads in the pump, which is very undesirable, especially when pumping combustible gases such as hydrogen, so that the pump was operated by a relay control circuit shown in Figure 3. The control circuit operates as follows: the lower chamber of the Toepler pump is fitted with a stopcock which was connected to a Y connector, one connection going to a vacuum pump (Cenco Hyvac-2), the other connection to one end of Hoke needle valve. The other end of the needle valve is arranged so that it is firmly closed by an arm connected to the power relay PR of the circuit with that relay in the closed position; otherwise it was open to the atmosphere, and the valve served as a variable-rate leak valve. When connection is made between the common and the upper lead of the Toepler pump by mercury (Figure 3), the relay PR is activated; the leak is closed, and the 110 outlet to the pump is activated; the lower

Figure 2

The Vacuum System



Figure 3.

Relay Control Circuit and Toepler Pump



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Figure 4.

The Reaction Vessel and Introduction System



chamber evacuates, and the mercury level in the pump lowers until the mercury makes contact between the <u>common</u> and and <u>lower</u> leads, at which point the relay PR is de-activated, the pump is shut off, and the leak to atmosphere is open, forcing the mercury up in the pump until contact is again made with the <u>upper</u> lead, and the cycle is repeated. The circuit employs a 22.5 V potential through 10<sup>6</sup> ohms across the contacts in the pump, which will not cause arcing.

5. The Gas Chromatographic System consisted of an Aerograph Model 90-P manually programmed chromatograph, modified so that a gas inlet system could be interposed in the He inlet line, and so that an external column (with an empty dummy column substituted in the chromatograph) could be used for the isotopic hydrogen analysis, where immersion of the column in liquid nitrogen was necessary.

The temperature of the injector, column; and detector were always the same (200°C for the analysis of the formic acids, or 150°C for the analysis of the isotopic hydrogens), and a flow rate of 80-100 ml/min of He were used in all cases.

#### C. Experimental Procedure

1. <u>The Sample Introduction</u> was effected by expansion of a known amount of formic acid from bulb-Bl, (Figure 4) maintained near  $100^{\circ}$ C by boiling water in a Dewar flask, and by nichrome heating wire wrapped around the section between stopcocks S-1 and S-2, through stopcock S1 directly

into the preheated reaction vessel. Fifteen seconds were allowed for equilibration, and S1 was closed.

Formic acid was contained in a storage bulb B2. Prior to a run, equilibration of formic acid vapor from B2 into the expansion bulb B3 (various size bulbs were used as expansion bulbs B3 in different runs) was effected at room temperature. The vapor trapped in B3 was then transferred to bulb B1 by vacuum distillation for later expansion into the reaction vessel.

2. The Kinetics of the Decomposition were followed by measuring the total pressure in the reaction vessel as the reaction proceeded. For this purpose, one arm of a capillary manometer was connected to the neck of the reaction vessel as shown in Figure 4. The mercury level in the manometer was adjustable by means of a leveling bulb and was adjusted prior to a run so that the mercury was very close to the neck of the reaction vessel, so as to expose as small an area of uncoated glass as possible. The other arm of this null manometer NM was connected to a measuring manometer, MM, as shown in Figure 4. The 200 cc ballast bulb B4 on top of the high pressure arm of MM could be connected by stopcock S4 to vacuum or, by means of a very fine capillary, to air. During a run, the expected initial pressure of HCOOH was calculated from the amount transferred to bulb B1 and the temperature of the furnace, and this pressure of air was leaked into B4 and MM by S4. After expanding the

HCOOH into the reaction vessel and closing stopcock S1, the timer was started, and stopcock S3 connecting NM and MM opened, and the level in NM brought back to its null position by adjusting the pressure in MM by S4. The pressure in MM and the time were recorded. Similarly, measurements of P were made by this null technique at various times t during the reaction.

3. Product Analysis was made usually only after the reaction had proceeded to completion. The reaction was quenched by opening stopcocks S1, S2, S5, S6, (See Figure 2) and allowing the reaction mixture to expand into traps T1 (room temp.) and T2 cooled in dry-ice--i-propanol bath  $(-70^{\circ}C)$ . The volume of traps T1 and T2 were each about 50 cc. The toepler pump was started immediately, and the entire contents of the reaction vessel were pumped through the traps. Water and any unreacted HCOOH were retained in T2, and the remaining gases noncondensable at  $-70^{\circ}C$  (CO<sub>2</sub>,  $CO, H_2$ ), were pumped into the volume C1 and connecting volumes. After all of the gas had been transferred, stopcock S8 was closed. The volume C1 was constructed of a 100 ml graduated cylinder, and was attached at the lower end to a leveling bulb of Hg, so that the Hg level in C1 could be adjusted to any level (h) and read. The volume of C1 and the connecting tubing to the capillary closed-end manometer M2 was calibrated as a function of level h in C1 and pressure P measured on M2, so that the absolute quantity of gas contained in the volume could be determined

at any level h of C1. Generally, the Hg level in C1 was raised until a pressure P on M2 convenient for measurement with a small error, was obtained. The quantity of gas was then determined. Initially this corresponds to  $n_{CO} + n_{CO_2} + n_{H_2}$ , where n represents moles of gas.

Subsequently, T1 was cooled to  $-196^{\circ}$ C by liquid nitrogen, and the gas was cycled from C1 via S11, S12, bypassing the furnace, through S13 and S14, and finally through T1 (where CO<sub>2</sub> is retained) and T2 back to C1. After a sufficient time for cycling, S12 was closed and the remaining gas (CO and H<sub>2</sub>) transferred back into C1 and remeasured, yielding  $n_{CO} + n_{H_2}$ . Finally, the CO and H<sub>2</sub> were cycled through the CuO combustion furnace at 500°C (where they were burned to CO<sub>2</sub> and H<sub>2</sub>O) through T2 (H<sub>2</sub>O retained), back to C1, and finally remeasured, yielding  $n_{CO}$  (measured as CO<sub>2</sub> at this point).

The quantities of each of the three products CO,  $CO_2$ , H<sub>2</sub> were thus obtained by direct measurement, and, if desired, the quantity of H<sub>2</sub>O could be obtained by difference, CO, H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub> were determined to be the sole products.

4. Isotopic Content of the Hydrogen produced in the decompositions of the deuterated acids HCOOD and DCOOH was determined by gas chromatography. The products noncondensable at  $-196^{\circ}C$  (CO and H<sub>2</sub>) were removed through the port at S11 in a small storage bulb and removed for chromatographic analysis.

The  $H_2$ -CO was introduced through the gas-inlet port on the chromatographic system shown in Figure 5. Helium carrier gas from a cylinder C swept the sample in the specially prepared Fe-Alumina column maintained at -196°C by immersion in liquid nitrogen. The CO was retained and separation of  $H_2$ , HD, and  $D_2$  were effected. The isotopic hydrogens were then burned to the corresponding isotopic water by passage through a CuO combustion tube at 500°C, and finally were analyzed by thermal conductivity in the detector of the chromatograph.

The column was prepared from 8 ft. x 1/4 in. Cu tubing packed with the prepared packing material. The packing was prepared according to the method described by G. F. Shipman.<sup>29</sup> Alcoa Alumina F-1, mesh 40-80, was ignited in air at 500°C for 16 hours. To 80 ml of this alumina were added in small increments 40 ml of 1.8 <u>M</u> FeCl<sub>3</sub>, followed by addition of 100 ml H<sub>2</sub>O. The mixture was then titrated with 6<u>M</u> NH<sub>4</sub>OH to pH 7 (Beckmann pH meter). The resulting mixture was decanted, filtered, and washed with H<sub>2</sub>O until the washings were pH 6 (pHydrion paper). The resulting packing material was dried in air at 120°C for 24 hours and packed in the column.

The column was conditioned for 12 hours with  $CO_2$  and for 24 hours with He at room temperature prior to use. Reconditioning with  $CO_2$  was accomplished periodically, especially if the system were shut off for a period of time. After several samples of  $H_2$ -CO were run, the column was allowed

Figure 5.

The Gas Chromatographic System



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to warm to room temperature in order to liberate the trapped CO.

The temperature of the column is difficult to maintain exactly at  $-196^{\circ}$ C because of rapid evaporation of N<sub>2</sub> when He is flowing through the column. The peak shapes and retention times were markedly sensitive to the temperature of the column. The best overall results were obtained by maintaining the dewar in which the column was immersed three-fourths full of liquid N<sub>2</sub>. The average temperature of the column was not known under these conditions, but a temperature of -175 to  $-190^{\circ}$ C seems likely. The retention times under these conditions were 24 min (H<sub>2</sub>), 27.5 min (HD), 34 min (D<sub>2</sub>). There was a small overlap of the H<sub>2</sub>-HD peaks, and no overlap of the HD-D<sub>2</sub> peaks. The peaks tailed only slightly under these conditions.

The equilibrium  $H_2/D_2/HD$  mixture for checking the chromatographic column was prepared from  $H_2$  (Prepurified Grade 99.95 min. % purity) and  $D_2$  (C.P. Grade 99.5 min. % purity) by the method described by P. P. Hunt and H. H. Smith<sup>30</sup>. The  $H_2$  and  $D_2$  were placed in a bulb with a nichrome wire connected to tungsten leads sealed in separated wells on the bulb as shown in Figure 6; the tungsten leads were then connected to a Variac and the nichrome wire heated to dull red for 12 hours. The equilibrium constant  $K = (HD)^1/(H_2)(D_2)$  was determined by mass spectrometry as K = 3.55, which corresponds to a temperature<sup>32</sup> of about  $450^{\circ}C$ , which is very reasonable.

Figure 6.

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Apparatus for Equilibration of  ${\rm H_2}$  and  ${\rm D_2}$ 

#### IV. RESULTS AND DISCUSSION

## A. <u>Kinetics</u>

The rate of decomposition of formic acid in the specially coated carbon vessel was followed at 451°C, 478°C and 505°C, by measuring the increase of pressure with a manometer communicating with the reactor, as described in the last chapter. In order to facilitate comparison of the results with those of Blake and Hinshelwood<sup>13</sup>, the data was treated formally by a first-order rate expression The first-order rate constant was determined by two methods; in the first method, the integrated first-order rate expression

$$k_1 = -1/t \ln (l - f)$$
,

where f is the fraction of reaction obtained at time t, was used to calculate first-order rate constants corresponding to each pressure-time data point. A plot of  $k_1^{-1/2}$  <u>vs</u>. t was then constructed and extrapolated to t = 0 to obtain the initial first-order rate constants. The fraction f of reaction was calculated from the relation<sup>31</sup>

$$f = P - P_0 / P_{op} - P_0$$

where P is the total pressure,  $P_0$  the initial pressure of formic acid (obtained by extrapolation of a plot of P <u>vs</u>. t to t = 0),  $P_{\infty}$  is the final pressure Generally, the pressure was followed for only one or two half-lives, and hence  $P_{\infty}$  was not measured. Since the only products

are  $H_2$ ,  $CO_2$ ,  $H_2O$  and CO, the final pressure should be  $P_{\infty} = 2P_0$  under the conditions of the experiments. In those runs in which a final pressure reading was established, a value close to  $2P_0$  was obtained. In the second method,  $P_0$  was obtained from extrapolation of a plot of  $P \underline{vs}$ . t to t = 0, and values of the pressure increase  $\Delta P = P - P_0$ was calculated at each time. The initial rate  $R_0$  is obtained as the limiting slope of a plot of  $\Delta P \underline{vs}$ . t near t = 0. The first-order rate constant is then given by

$$k_1 = R_0 / P_0$$
 .

Rate constants determined by the two methods always agreed very closely, but the second method proved somewhat more reliable.

For comparison, second-order rate constants were also determined as follows: The integrated rate expression assuming second-order dependence on formic acid (represented as A) is:

$$1/A - 1/A_0 = kt$$
,

multiplying by  $A_0$ , substituting  $1 - f = A/A_0$ , and simplifying yields

$$f/1 - f = A_0kt$$

assuming  $P_{\infty} = 2P_0$  ,

$$f = P - P_0/P_0 = \triangle P/P_0$$

and using pressure units for the initial concentration of formic acid, one obtained the second-order rate constant

$$k_2 = \frac{1}{P_0 t} \quad \frac{\Delta P / P_0}{1 - \frac{\Delta P}{P_0}}$$

Figure 7 shows typical pressure  $\underline{vs}$ . time curves obtained at each of the three temperatures. Table 2 is a summary of the initial first-order rate constants  $k_1$  as a function of initial pressure at each temperature. Figures 8, 9, and 10 show plots of  $k_1 \underline{vs}$ . P<sub>0</sub> at 451, 478, and 505°C, respectively. Included for comparison on Figures 9 and 10 are data obtained by Blake and Hinshelwood (BH)<sup>13</sup> at 476.8 and 500°C, respectively. The agreement is excellent, and shows conclusively that the experimental conditions of BH were reproduced in this study. The rate constant  $k_1$  is extremely sensitive to the condition of the coating, especially at low pressure, as found by BH and verified in this study.

Table 3 shows raw data from two runs, one at  $451^{\circ}C$  and one at  $505^{\circ}C$ , as well as values of  $k_1$  and  $k_2$ . The overall reaction order can be seen to be very nearly second order. Detailed examination of all of the data indicate an order slightly less than two, in agreement with the results of BH.

# B. Product Analysis

The relative amounts of  $H_2$ , CO, CO<sub>2</sub> produced in several runs at 505<sup>o</sup>C were determined by the method described in Chapter III. The results are shown in Table 4 There is



Figure 7.

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Typical Kinetic Runs

▲ 451°C
▲ 478°C

о 505<sup>0</sup>с



Run #	Initial Pressure(m	m) 1st-Order Rate Constants(sec <sup>-1</sup>
	Tempe	rature = 451 <sup>0</sup> C
36	37.8	$1.1 \times 10^{-4}$
37	104.4	$2.0 \times 10^{-4}$
38	132.6	$2.6 \times 10^{-4}$
40	149.4	$3.4 \times 10^{-4}$
39	183.4	$4.1 \times 10^{-4}$
	Tempe	rature = 478°C
12	26.6	$2.8 \times 10^{-4}$
15	49.3	$2.4 \times 10^{-4}$
3	56.8	$2.8 \times 10^{-4}$
14	64.4	$3.8 \times 10^{-4}$
8	76.4	$4.1 \times 10^{-4}$
16	93.6	$4.9 \times 10^{-4}$
21	101.4	$4.8 \times 10^{-4}$
5	106.8	$4.0 \times 10^{-4}$
22	118.5	$5.7 \times 10^{-4}$
31	160.7	$7.3 \times 10^{-4}$
23	164.0	$6.5 \times 10^{-4}$
6	205.0	$8.0 \times 10^{-4}$
	Tempe	rature = 505°C
44	39.5	$4.1 \times 10^{-4}$
49	54.7	$5.3 \times 10^{-4}$
42	58.6	$4.8 \times 10^{-4}$
45	<b>95.3</b>	$7.6 \times 10^{-4}$
46	110.2	$8.5 \times 10^{-4}$
47	137.2	$10.9 \times 10^{-4}$
48	140.2	$10.2 \times 10^{-4}$

Table 2. Initial first-order rate constants as a function of pressure at the three temperatures.

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Figure 8.

Initial First-order Rate Constants as a function of Initial Pressure at  $451^{\circ}C$ .

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Figure 9.

Initial First-Order Rate Constants as a Function of Initial Pressure at 478°C.

- A Reference 13 at 476.8°C
- $\odot$  This research at  $478^{\circ}$ C



Figure 10.

2

Initial First-order Rate Constants as a Function of Initial Pressure at 505°C.

- ▲ Reference 13 at 500°C
- **Q** This research at 505°C



Time (sec	)	<b>P</b> ( cm )	<b>∆P</b> ( <b>c</b> m)	$k_1(sec^{-1})$ x 10 <sup>-4</sup>	$\begin{array}{r} & k_2 \\ & k_2 \\ (cm^{-1} sec^{-1}) \\ & x \ 10^{-5} \end{array}$
			Run#38(4	51 <sup>0</sup> C)	
0		13.26			
55		13.40	0.14	1.93	1.46
140		13.70	0.44	2.41	1.85
240		14.00	0.74	2.39	1.86
340		14.30	1.04	2.40	1.89
430		14.60	1.34	2.48	1.97
560		15.10	1.84	2.67	2.17
750		15.50	2.24	2.47	2.04
940		15.90	2.64	2.36	1.99
1230		16.50	3.24	2.28	1.98
1560		16.95	3.69	2.09	1.86
1940		17.45	4.19	1.96	1.80
2410		18.00	4.74	1.84	1.74
	<b>k</b> 1	(Method 1,	extrapolatio	on) = 2.8 x 10	-4 sec <sup>-1</sup>
	k <sub>1</sub>	(Method $2$ ,	initial rate	e) = 2.6 x 10	-4 sec <sup>-1</sup>
	k <sub>1</sub>	(Ref. 13, s	smoothed resu	ults) =	
			Run # <b>48</b>	(505°C)	
0		14.02			
70		15.10	1.08	11.45	9.71
90		15.50	1.48	12.40	9.35
115		15.90	1.88	12.52	9.60
145		16.40	2.38	12.83	10.16

Table 3.	The first and second-order rate constants a	as	a
	function of time for two typical runs.		

Time (sec	)	<b>P</b> (cm)	<b>△P</b> ( cm )	k <sub>1</sub> (sec <sup>-1</sup> ) x 10 <sup>-4</sup>	$k_2$ (cm <sup>-1</sup> sec <sup>-1</sup> ) x 10 <sup>-5</sup>
175		16.70	2.68	12.12	9.63
220		17.20	3.18	11.69	9.51
270		17.70	3.68	11.28	9.40
304		18.10	4.08	11.28	9.60
370		18.60	4.58	10.69	9 <b>.3</b> 5
435		19.10	5.08	10.34	9.32
495		19.50	5.48	10.01	9.25
555		19.90	5.88	9.80	9.28
<b>63</b> 5		20.30	6.28	9.36	9.11
730		10.70	6.68	8.86	8.89
810		21.10	7.08	8.68	8.98
975		21.70	7.68	8.14	8.86
1110		22.10	8.08	7.74	7.92
1290		22.50	8.48	7.20	8.46
	k <sub>1</sub>	(Method 1,	extrapola	tion) = 14.40 x 1	.0 <sup>-4</sup> sec <sup>-1</sup>
	k <sub>1</sub>	(Method 2)	initial r	ate) = 10.20 x 1	.0 <sup>-4</sup> sec <sup>-1</sup>
	<b>k</b> 1	(Ref. 13,	smoothed r	esults) = 10.60 x	$10^{-4} \text{ sec}^{-1}$

Table 3 (Continued)

Run #	<b>P</b> <sub>0</sub> (mm)	co/co <sub>2</sub>		H <sub>2</sub> /CO <sub>2</sub>
		This Work	Ref. 13	•
54	35.4	3.1	2.2	0.84
56	37.0	3.6	2.3	0.98
51	53.5	2.0	3.1	0.76
53	55.9	3.7	3.2	1.07
59	59.0	5.0	3.3	0.96
55	80.6	2.2	4.2	0.74
58	83.0	3.9	4.3	0.90
57	100.7	4.4	5.0	0.90
52	135.1	4.4	6.1	0.72

Table 4. Product analysis of formic acid

considerable error in the results, and the agreement with the results of BH (ref. 13) for the  $CO/CO_2$  ratio is only fair. Therefore, no firm conclusions regarding the molecular character of the dehydrogenation reaction can be drawn from these results, even though in 6 out of 9 runs, values considerably less than unity for the  $H_2/CO_2$  ratio were observed. Many more data would be required in order to establish whether there is actually less hydrogen than CO<sub>2</sub> produced. Even if the results are optimistically viewed as reflecting a discrepancy in the amount of  $H_2$  found, any interpretation is still questionable since under the conditions of the experiment it is not unlikely that H<sub>2</sub> could react with stopcock grease, or even with the carbon coating itself, with the result that low  $H_2/CO_2$  ratios would be observed. In the photolysis work of Gordon and Ausloss<sup>2</sup>, a  $H_2/CO_2$  ratio of less than unity was observed, but the photolysis reaction was carried out at room temperature, and the results are more meaningful in that case. Any argment concerning the molecular character of the thermal reactions of formic acid must be based upon information in addition to, or other than, product analysis alone.

#### C. Studies Using DCOOH and HCOOD

The isotopic content of the hydrogen produced in the decomposition of DCOOH and/or HCOOD provide much more direct evidence concerning the molecular character of the dehydrogenation of formic acid. In a separate control experiment, it
was shown that no exchange between  $H_2$  and  $D_2$  to form HD takes place under the conditions of the experiments. In that case, a molecular mechanism for the dehydrogenation of either DCOOH or HCOOD could only produce HD.

The runs with DCOOH and HCOOD were carried out in the same manner as described for regular formic acid HCOOH. The first-order rate constants were calculated in order to obtain the kinetic isotope effect  $k_H/k_D$  for each acid. However, only a few runs were made for each acid since the main interest was in the isotopic content of the hydrogen produced, and as there is considerable scatter in the kinetic results (see Figures 8, 9, 10), a value of  $k_H/k_D$  at a given pressure determined from  $k_H$  obtained from smoothed results (Figure 10) and a single value of  $k_D$  determined at that pressure is subject to considerable uncertainty. The kinetic isotope effects are intended to give order-ofmagnitude only. The results are given in Table 5.

The isotopic analysis of the hydrogen was done by gas chromatography as described in Chapter III for all the pressures (Table 6) for both acids. In all cases,  $H_2$ , HD, and  $D_2$  were observed, but it appeared as though much less  $D_2$  than HD or  $H_2$  were being formed. However, the sensitivity of the column is different for the various isotopic hydrogens, and varies with time and temperature of the column, which is difficult to control. Therefore, it was decided to examine the relative amount of isotopic hydrogens produced by mass spectrometry on a Consolidated Model 21-103C instrument.

Run #	Initial Pressure	(mm)	Isotope Effect $(k_{H}^{}/k_{D}^{})$
	0.5 . 0	DCOOH	1.0
60	35.6		1.0
64	69.5	1.3	
61	87.2	1.4	
62	124.8	2.7	
65	189.8		4.9
		HCOOD	
69	40.6		1.1
66	57.4		1.3
67	125.0		2.7
68	173.0		1.6

Table 5. The kinetic isotope effect of the deuterated formic acids.

Run #	Initial Pressure	( mm )	HD/H <sub>2</sub>	$D_2/H_2$
		DCOC	<u>)H</u>	
70	36.0		1.14 ± 0.01	0.418 ± 0.005
65	189.9		1.24 ± 0.01	$0.493 \pm 0.005$
		HCOC	<u>D</u>	
69	40.6		$0.63 \pm 0.02$	0.17 ± 0.01
67	125.0		0.83 ± 0.01	0.22 ± 0.01
68	173.0		$0.82 \pm 0.01$	0.22 ± 0.01

Table 6. Isotopic hydrogen analysis

The equilibrated mixture of  $H_2/D_2/HD$  (Chapter III) and pure samples of  $H_2$  and  $D_2$  were used as standards, and it was found that at an ionizing voltage of 70 v and ionizing current of 15 ma, the relative peak heights at m/e 2, 3, 4 could be used to obtain accurate ratios of isotopic hydrogens. The results are shown in Table 6. The results show that under the conditions of the experiment, much more deuterium ends up in the hydrogen product for DCOOH than for HCOOD.

The results show conclusively that the first-order dehydrogenation of formic acid under the conditions of this study does not proceed entirely by a simple molecular process as suggested by Blake and Hinshelwood. The fact that  $H_2$  and  $D_2$  as well as HD were observed in the decomposition of DCOOH and HCOOD requires that other processes than a direct molecular split either surface reactions or free radical reactions be invoked to explain the results. The results are similar in many respects to the photolysis results of Ausloss and Gordon,<sup>2</sup> and an attractive explanation involves radical processes. A radical reaction can explain the difference in isotopic hydrogens produced from DCOOH and HCOOD. For, if the initiating reaction produced H. radicals which react by abstracting either a hydrogen from carbon to form  $H_2$  and  $\cdot COOH$ , (which later decomposes to  $CO_2 + H$ ) or an OH to form  $H_2O$  and  $HCO \cdot$  (which subsequently form  $CO + H \cdot$ ), then purely from a statistical argument, the deuterium will end up in the hydrogen product in the case of DCOOH and in the water product in the case of HCOOD.

Clearly the abstraction of H from the carboxyl end of formic acid to form  $H_2$  and  $HCOO \cdot$ , which later decomposes to  $CO_2 + H$  must also be involved to explain all features of the isotopic hydrogen results. It seems possible that the following processes are involved in the reaction:

Initiation HCOOH 
$$\longrightarrow$$
 H· + ·COOH (1a)  
HCO· + ·OH (1b)  
HCO· + H· (1c)

followed by unimolecular radical decompositions:

$$\cdot$$
 COOH  $\longrightarrow$  CO +  $\cdot$  OH (2a)

$$HCO \cdot \longrightarrow CO + H \cdot (3a)$$

$$|\text{HCOO}\cdot -| \longrightarrow CO_2 + H \cdot (4a)$$

$$| \longrightarrow 0. + HCO. \rightarrow CO_2 + H. \quad (4b)$$

and the several abstraction reactions:

$$H \cdot + HCOOH \longrightarrow H_2 + HCOO \cdot (5b)$$

$$| \longrightarrow H_2O + HCO \cdot (5c)$$

$$\cdot OH + HCOOH - | \longrightarrow H_2O + \cdot COOH$$
 (6a)

$$H_2O + HCOO \cdot$$
 (6b)

and possible termination reactions:

$$H \cdot + H \cdot \longrightarrow H_2$$
 (7a)

$$H \cdot + \cdot OH \longrightarrow H_2O$$
 (7b)

It seems unlikely that reaction (4b) contributes significantly to the reaction, since BH observed that even a small addition of oxygen to the system caused a very large acceleration of the rate. The other reactions correspond to a radical population in the reacting system which contains a large fraction of H atoms. The reaction is propagated, then, very largely by the abstraction reactions 5, and the product distribution will reflect this fact. If it is assumed that the abstraction by H from the carboxyl end of the molecule occurs preferentially by -OH abstraction, i.e., reaction 5c more important than 5b, then the mechanism is consistent with the isotopic distribution of hydrogens observed for DCOOH and HCOOD. The corresponding abstraction reactions important for the two isotopic acids are then for DCOOH:

 $H \cdot + DCOOH \longrightarrow HD + COOH$  $D \cdot + DCOOH \longrightarrow D_2 + COOH$  $HOD + DCOO \cdot$ 

and for <u>HCOOD</u>:



and it is seen that in the case of DCOOH, the deuterium

preferentially ends up in the hydrogen product, so that relatively larger values for the  $HD/H_2$  and  $D_2/HD$  product ratios should be observed than in the case of HCOOD, where the deuterium ends up preferentially in the water product. Table 6 shows that this is precisely what is observed.

At high pressures, the abstraction reactions will be relatively more important than the decomposition reactions 2 and 3 for determining product composition than at lower pressures. It has already been assumed that 5b is less probable than 5c. If, in addition, 5a and 5c are of comparable importance, then since 3a occurs subsequent to 5c to produce CO, and reaction(s) 2b (and 2a) occur subsequent to 5a to produce  $CO_2$  (and CO), it is possible for the  $CO/CO_2$  product ratio to increase slightly with pressure as observed (Table 4). The  $H_2/CO_2$  product ratio at low pressures (where reactions 2, 3, 4, and 7 are relatively more important) would be expected to be comparable to that at high pressures (where reactions 2, 3, 5a, 5c, are relatively more important). A value for  $H_2/CO_2$  close to unity as observed (Table 4) is not inconsistent with the mechanism. In addition, molecular split mechanisms or bimolecular mechanisms may also be of some importance in the reaction, and may help explain some of the results. In particular, a bimolecular reaction of formic acid (or a unimolecular decomposition of dimer) to produce CO and  $H_2O$  products would also lead to an increased  $CO/CO_2$  product ratio with increased pressure.

The kinetic isotope effects are difficult to interpret on the proposed mechanism, but are rather small and about the same for both acids. Both of these results are consistent with the radical mechanism. The isotope effect, if associated with abstraction, would be expected to be  $\sim \sqrt{2}$  due to the mass effect on breaking the H- residue bond.

One has still to explain why BH observed no noticeable surface/volume effect and no significant effect when radical inhibitors were added to the system, if a radical mechanism is assumed. However, these results do not, we believe, rule out the possibility of a radical reaction. The change in surface/volume ratio of BH was quite small, and did result in a small decrease in rate, which could occur if the radical terminated at the wall, which is not inconceivable on a carbon surface. The modest amounts of inhibitors used by BH would lead to a significant change in rate only if long chains were involved. For the present mechanism, only a small change in rate for this level of inhibitors would be expected, but the yield of hydrogen would probably be significantly reduced in the presence of a radical scavenger, as observed by Gordon and Ausloos<sup>2</sup> in the photolytic decomposition of formic acid.

A more detailed and extensive study of the product distribution, isotope effects, isotopic content of hydrogen, yield of hydrogen in scavenger experiments, and a more exhaustive study of the kinetics over larger extents of reaction would be useful for a more complete characterization of the reaction mechanism.

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