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Factors Influencing the Compensation Effect during Formic Acid Decomposition on Silver

A. LAWSON

From the Commonwealth Scientific and Industrial Research Organization, Division of Tribophysics, University of Melbourne, Australia

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A radiotracer technique is used to measure the desorption of $H^{14}COOH$ monolayers in vacuum, the exchange of gas phase $H^{12}COOH$ with $H^{14}COOH$ monolayers, and the catalytic decomposition of $H^{12}COOH$ gas in the presence of $H^{14}COOH$ monolayers, on silver films with a small area, which were either polycrystalline or (111) epitaxed films on mica substrates.

It is proposed that the number of labeled molecules removed from the surfaces during decomposition be equated with the number of active sites on the catalysts. From estimates of the proportions of (111) area in the two types of film, the concentration of active sites is calculated for the atomically smooth (111) plane and for the atomically rough surface. A compensation effect occurs which can largely be explained assuming that the entropy difference between the adsorbed state and the activated complex is different for the two types of film. Evidence is presented that the activated complex is formed from the interaction of a physically adsorbed formic acid molecule with a chemisorbed formate ion and the reasons for the different entropy changes are discussed on the basis of this model.

INTRODUCTION

The decomposition of formic acid on metals has been extensively studied and used as a test reaction in many cases. The effect of crystal orientation on the parameters of the reaction is pronounced and has been established by several workers. On copper single crystals Rienacker's work (*1*) in the zero order range showed that there is little difference in activation energies for the (111) and (100) surfaces, but Crocker and Robertson (*2*), who worked in the first order range, found that the activation energy decreases in the order (111), (110), (100). In the zero order range, Sosnovsky's work (*3*) on silver single crystals showed that there are variations in activation energy with orientation, and Bagg, Jaeger, and Sanders (*4*), and Jaeger (*5*), working with epitaxed silver films showed that the activation energy decreases in the order polycrystalline, (100), (111). Recently, Jaeger (*5*) explained the difference in order of activities on the basis that the activation energy was related to the strength of adsorption on the various crystal planes.

All of the above workers found that a compensation effect operated when the orientation of the surface was changed and, for zero order kinetics, the pre-exponential factor for the (111) surface was considerably less than that of a polycrystalline surface. Cremer (*6*) has pointed out that this could be due either to different numbers of active sites on planes of different orientation, or to the change in entropy on going from the adsorbed state to the activated complex being different for the two types of film.

This paper describes experiments which determine the number of active sites on (111) and polycrystalline surfaces during reaction. A method for doing this has been developed by Thomson and Wishlade (*7*) where a radioactive monolayer of the material is first adsorbed on the surface, and then catalytic reaction is carried out with non-radioactive material. The difference in count rate from the surface after reaction measures the fraction of the adsorbed layer involved in the reaction at a given temperature. Results are therefore described here for the desorption of $H^{14}COOH$ monolayers in vacuum, for the exchange of gas-phase $H^{12}COOH$ with $H^{14}COOH$ monolayers, and for the catalytic decomposition of $H^{12}COOH$ gas in the presence of $H^{14}COOH$ monolayers. The fraction of the adsorbed layer removed during catalysis can be observed for both polycrystalline and (111) epitaxed films of silver on mica. This should substantiate whether or not the (111) area is an active patch, and the proportions of the other rougher active patches involved in the reaction will also become apparent. The values of their respective coverages, i.e., the number of active sites on each patch, can then be applied to the Arrhenius equation together with the values of rates and activation energies obtained by Jaeger (*5*) from reaction on similar surfaces. The magnitude of any entropy change will then become apparent, and will have to be interpreted on the basis of the nature of the activated complex formed during reaction.

EXPERIMENTAL

The apparatus, catalyst preparation, and counting technique have already been described (*8*). $H^{12}COOH$ (A.R. 98%) was purified by vacuum distillation and stored over anhydrous magnesium sulfate. Prior to use, its container was always evacuated at −100°C to remove impurities. Carbon-14 formic acid was treated similarly, and had a specific activity of 21.8 mc/mM. Pressure measurement was made with a thermistor gauge and a capacitance diaphragm manometer. An air furnace was used to heat the catalyst vessel.

At the completion of a catalytic reaction or a desorption experiment, the count rate of the chemisorbed layer and the products were determined by observing changes in count rate and pressure when a cold finger was held at various temperatures. Table 1 shows how this was accomplished. The table has been split into a number of steps corresponding to each observation, and succeeding tables follow the same format.

Because of the tenacity with which formic acid is adsorbed on the apparatus, and an exchange reaction of the ^{12}C-formic acid with the ^{14}C-formic acid, it was necessary, at the conclusion of an experiment, to bake out the whole apparatus to 400°C to remove all traces of formic acid.

^{14}C-formic acid was adsorbed onto substrates of polycrystalline or (111) epitaxed films of silver on mica, and three calibration substrates, in the manner previously described (*8*). At the completion of an adsorption run, the gas-phase formic acid was condensed back into the formic acid

TABLE 1
METHOD OF PRODUCT ANALYSIS

Step	Operation	Count rate detects	Pressure indicates	Products	
				Δ Count rate measures	Δ Pressure measures
I	Trap cooled to −196°C	$C_L{}^a + {}^{14}CO^b$	$H_2 + CO$	^{14}CO	$H_2 + CO$
II	System evacuated with trap cooled to −196°C	C_L	Vacuum	$^{14}CO_2$	CO_2
III	System isolated and trap warmed to −100°C	$C_L + {}^{14}CO^b$	CO_2	$H^{14}COOH$	$HCOOH$
IV	Trap now warmed to room temperature	$C_L + {}^{14}CO_2{}^b + H^{14}COOH^b$	$CO_2 + HCOOH$		

[a] C_L, Count rate of chemisorbed layer present while system is evacuated.

[b] These may contain contributions from both adsorbed and gaseous states.

reservoir, and the adsorption vessel was evacuated, thereby removing a weakly adsorbed portion of the adsorbed layer and leaving a strongly adsorbed portion. The concentration of this strongly adsorbed portion, expressed as counts/sec (cps) is shown in Table 2 for various silver substrates and is compared with the monolayer values calculated from their Langmuir plots. Generally the agreement between the value for the strongly adsorbed portion and the monolayer value was quite good. The strongly adsorbed layers on the substrates were then either (i) heated in vacuum to desorb the $H^{14}COOH$, or (ii) exchanged with $H^{12}COOH$ in the vapor phase at room temperature, 200°C, and 270°C. At the latter two temperatures it was difficult to distinguish between the exchange reaction and the decomposition of the $H^{14}COOH$.

TABLE 2
VALUES FOR THE STRONGLY ADSORBED PORTION OF THE HCOOH LAYER NOT REMOVED BY EVACUATION AT ROOM TEMPERATURE

	Film No.	Count Rate (cps)	Langmuir Monolayer value (cps)
Polycrystalline Ag	1	200	204
	2	175	195
Epitaxed Ag	3	132	119
	4	118	124
	5	138	*a*
	6	90	*a*

[a] Langmuir monolayer values not determined for these films.

In all the experiments, the count rates of the gaseous products were higher than those expected for desorption or reaction on the silver substrates alone, and were therefore made up from reaction or desorption from the glass vessel as well as from the silver substrate.

The correction due to adsorption on the counter window has, however, been subtracted from all the count rates so that under vacuum the substrate count is that of the silver surface alone.

RESULTS

1. Desorption of $H^{14}COOH$ from epitaxed silver films on mica. (a) The substrate and its adsorbed layer were heated to 200°C, where formic acid decomposes, for a period of 1 hr with the cold finger at room temperature. The substrate was then cooled to room temperature, the cold finger was cooled to −196°C, and the desorption products analyzed.

Table 3 shows that a quarter of the initially adsorbed layer was desorbed from the surface during the 1-hr period of heating. The major components of the products were $^{14}CO_2$ and H_2 and the remainder was

TABLE 3
ANALYSIS OF PRODUCTS DESORBED FROM ADSORBED LAYER ON EPITAXED SILVER AT 200°C IN 1 HR

				Products	
Step	Operation	Count rate (cps) detects	Pressure (torr) indicates	Δ Count rate (cps) measures	Δ Pressure (torr) measures
	Initial count rate of adsorbed layer	Initial $C_L = 118$	10^{-5}		
I	Trap cooled to −196°C after desorption	88	1×10^{-3}	$^{14}CO = 0$	$H_2 + CO = 1 \times 10^{-3}$
II	System evacuated with trap at −196°C	After desorption $C_L = 88$	10^{-5}	$^{14}CO_2 = 26$	$CO_2 = 0.7 \times 10^{-3}$
III	System isolated and trap warmed to −100°C	114	0.7×10^{-3}		

TABLE 4

ANALYSIS OF PRODUCTS DESORBED FROM ADSORBED LAYER ON EPITAXED SILVER AT 200°C IN 1 HR WITH TRAP AT −196°C

				Products	
Step	Operation	Count rate (cps) detects	Pressure (torr) indicates	Δ Count rate (cps) measures	Δ Pressure (torr) measures
	Initial count rate of adsorbed layer	Initial $C_L = 90$	10^{-5}		
I	Trap at −196°C after desorption	76	10^{-5}	$^{14}CO = 0$	$H_2 + CO = 0$
II	System evacuated with trap at −196°C	After desorption $C_L = 74$	10^{-5}	$^{14}CO_2 = 0$	$CO_2 = 0$
III	System isolated and trap warmed to −100°C	75	10^{-5}	$H^{14}COOH = 10$	Pressure just measurable then decreased
IV	Trap warmed to room temperature	88 → 85	Pressure just measureable then decreased		

$H^{14}COOH$. Pressure measurements in this case were made at the limit of resolution of the gauge and are not accurate, but there is no evidence for the presence of CO.

(b) The cold finger was cooled to −196°C and the substrate and its adsorbed layer were heated to 200°C for 1 hr, after which the substrate was cooled to room temperature and the products analyzed. Again, a quarter of the initially adsorbed layer was removed by the heating, but the only desorption product was $H^{14}COOH$ (Table 4). No H_2, CO_2, and CO were detected. It is to be concluded that where gas-phase formic acid is present, decomposition can occur, but when gas-phase formic acid is excluded by condensation at −196°C, then the only desorption product is formic acid. The desorption rate is slow, and in order to desorb all of the formic acid at 200°C some 8 hr heating would be required.

2. Exchange and reaction of adsorbed $H^{14}COOH$ with gas-phase $H^{12}COOH$. A furnace at 200°C was placed around the substrate with its adsorbed layer and immediately 10 torr of $H^{12}COOH$ was admitted to the system for a few minutes. The residual gases were then condensed into the cold finger at −196°C, the substrate cooled to room temperature, and the products analyzed. The count rate due to the adsorbed layer alone was found to be less than that before the decomposition experiment. The substrate was again heated to the same temperature, more $H^{12}COOH$ at 10 torr admitted, and the experiments were continued in this way until no further change in count rate due to the adsorbed layer alone was observed. The results for an epitaxed silver film at 200°C are plotted in Fig. 1. Clearly the change in count rate from the adsorbed layer has occurred in a short period of time, and only 91% of the adsorbed layer has been involved in the reaction. The results for polycrystalline silver at 200°C showed a curve similar to that of Fig. 1 except that only 83% of the adsorbed layer was involved in the reaction. Typical product analyses made during these experiments are shown for polycrystalline and epitaxed silver, at 200°C in Table 5, and 270°C in Table 6. There was no evidence for CO as a reaction product, but $^{14}CO_2$ had been formed from the decomposition of the labeled formic

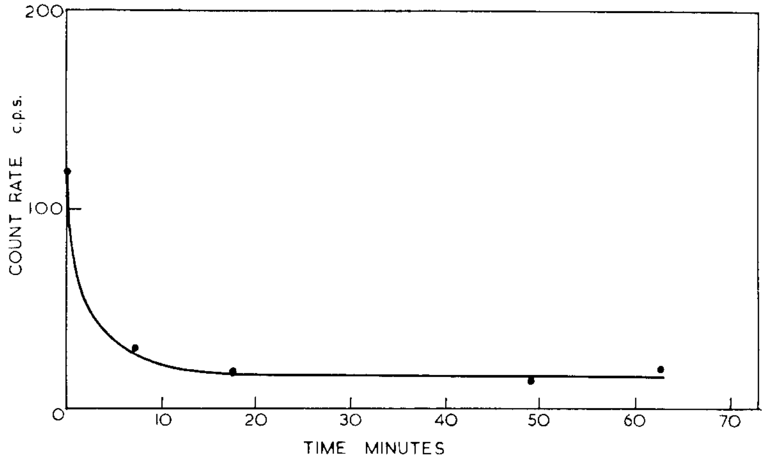


FIG. 1. Change in monolayer count with time during formic acid decomposition on (111) epitaxed silver on mica at 200°C.

acid. The count rate from the surface after a reaction is probably due to undecomposed $H^{14}COO^-$, because it will be shown that $^{14}CO_2$ will not remain adsorbed while the silver is pumped in a vacuum. However, it is not known if ^{14}CO could be adsorbed and hence contribute, but there is no evidence that it is a reaction product.

It is to be concluded that even after repeated reaction at 200° and 270°C, a num-

TABLE 5

ANALYSIS OF CHANGE IN ADSORBED LAYER AND PRODUCTS ARISING FROM THE DECOMPOSITION OF $H^{14}COOH$ ADSORBED LAYER IN PRESENCE OF 10 TORR $H^{12}COOH$ AT 200°C FOR 1 HR

				Products	
Step	Operation	Count rate (cps) detects	Pressure (torr) indicates	Δ Count rate (cps) measures	Δ Pressure (torr) measures
		Polycrystal Ag			
	Initial count rate of monolayer	Initial $C_L = 195$	10^{-5}		
I	−196°C after reaction	32	8×10^{-2}	$^{14}CO = 0$	$H_2 + CO = 8 \times 10^{-2}$
II	Evacuated −196°C	After reaction $C_L = 32$	10^{-5}	$^{14}CO_2 = 8$	$CO_2 = 9 \times 10^{-2}$
III	−100°C	40	9×10^{-2}		
		Epitaxed Ag			
	Initial count rate of monolayer	Initial $C_L = 124$	10^{-5}		
I	−196°C after reaction	12	1.5×10^{-1}	$^{14}CO = 0$	$H_2 + CO = 1.5 \times 10^{-1}$
II	Evacuated −196°C	After reaction $C_L = 12$	10^{-5}	$^{14}CO_2 = 12$	$CO_2 = 1.5 \times 10^{-1}$
II	−100°C	24	1.5×10^{-1}		

TABLE 6
Analysis of Change in Adsorbed Layer Arising from the Decomposition of $H^{14}COOH$ Adsorbed Layer in Presence of 10 Torr $H^{12}COOH$ at 270°C for 1 hr

	Polycrystal Ag	Epitaxed Ag
Initial count rate of substrate monolayer (cps)	208	118
Substrate count rate after reaction (cps)	7	7

ber of sites on the silver surfaces retain the $H^{14}COOH$ molecules originally adsorbed, and are inactive sites in the heterogeneous catalysis. The proportions of the adsorbed layer involved in the reaction for the two silver surfaces at 200°C and 270°C are shown in Table 7, averaged from a number of runs on different substrates.

TABLE 7
Proportions of Adsorbed Layer Involved in Exchange or Reaction with Gas-Phase HCOOH

		% Initial adsorbed layer removed during reaction	
Nature of reaction	Substrate temperature	Polycrystal Ag on Mica	Epitaxed Ag on Mica
Exchange	20°C	74	85
Decomposition	200°C	83	91
Decomposition	270°C	93	94

At room temperature a curve similar to Fig. 1 was observed, but no $^{14}CO_2$ was produced. In this case the adsorbed $H^{14}COOH$ exchanged rapidly with the $H^{12}COOH$ in the gas phase leaving $H^{12}COOH$ adsorbed on the silver. The results of the analysis are shown in Table 8. When the gas-phase formic acid was pumped off and more $H^{12}COOH$ was admitted to the system, little further change occurred. The proportion of the adsorbed layer exchangeable at room temperature is shown in Table 7.

The extent of exchange with increased pressure of $H^{12}COOH$ in the gas phase was also investigated. With the substrate and its $H^{14}COOH$ adsorbed layer at room temperature, a constant vapor pressure of 5×10^{-3} torr of $H^{12}COOH$ was maintained in the system for a few minutes, after which time it was condensed into the cold finger at −196°C and the count rate from the adsorbed layer measured. A small amount of exchange had occurred. This was repeated with the aliquot at the same pressure but no further exchange was observed. The pressure of the gas admitted to the system was increased to a new value and further exchange was detected when the gas phase was condensed at −196°C. If the original pressure of 5×10^{-3} torr $H^{12}COOH$ was now used, no further exchange occurred. The pressure of formic acid admitted to the system was then increased progressively, and the extent of exchange followed, when the gas phase was condensed at −196°C, until a pressure of 10 torr was reached. The results for poly-

TABLE 8
Exchange of $H^{14}COOH$ Adsorbed Layer with 10 torr $H^{12}COOH$ at Room Temperature[a]

		Polycrystal Ag		Epitaxed Ag	
Step	Operation	Count rate (cps)	Pressure (torr)	Count rate (cps)	Pressure (torr)
	Initial count rate of monolayer	Initial $C_L = 195$	10^{-5}	Initial $C_L = 124$	10^{-5}
I	Trapped −196°C after exchange	45	10^{-5}	19	10^{-5}
II	Evacuated −196°C	After exchange $C_L = 45$	10^{-5}	After exchange $C_L = 19$	10^{-5}
III	−100°C	45	10^{-5}	19	10^{-5}

[a] Count rate does not change after first few minutes of exchange.

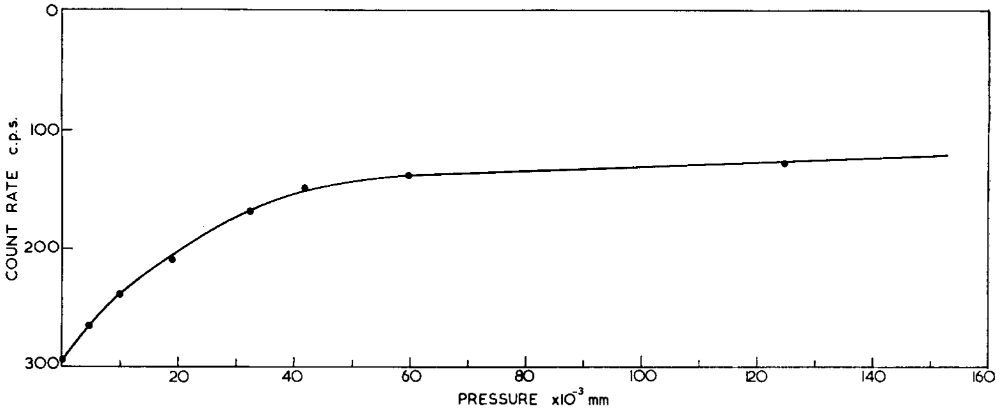


FIG. 2. Exchange of $H^{12}COOH$ gas with a monolayer of $H^{14}COO^-$ adsorbed on a polycrystalline silver film on mica; variation of exchange with pressure. The count rate includes the contribution from the layer adsorbed on the counter window.

crystalline silver on mica (Fig. 2) demonstrate that little exchange occurs at low formic acid pressures, and that the amount exchangeable increases with increase in formic acid pressure.

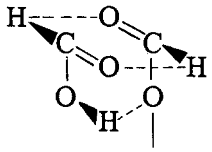
3. Adsorption of $^{14}CO_2$. Pure $^{14}CO_2$ was prepared by the decomposition of $H^{14}COOH$. No detectable amount of adsorption was observed on polycrystalline silver films at room temperature and a pressure of 10^{-1} torr.

DISCUSSION

Infrared studies on the adsorption of formic acid on nickel, gold (*9*), and silver and copper (*10*), have established the presence of $HCOO^-$ on the surface, although on nickel there is evidence for a covalently bound species at −60°C (*11*). In addition, spectroscopic evidence has been presented for the existence of an undissociated formic acid molecule on surfaces of nickel (*9, 10, 12, 13*). The presence of formate ions on these surfaces does not necessarily mean that they constitute the activated complex, and isotope work, using deuterated formic acid, has been carried out to elucidate the reaction mechanism and the nature of the activated complex (*9, 10, 14, 15*). Hirota *et al.* (*12*) showed that on nickel catalysts there may be an exchange reaction of an adsorbed formic acid molecule with an adsorbed formate ion, via an intermediate complex. Mars *et al.* (*16*) point out that the question of bimolecularity of this reaction has not been settled.

The use of ^{14}C isotopes in the present study has shown that a rapid exchange of ^{14}C-formic acid with ^{12}C-formic acid takes place on surfaces of silver at room temperature (Table 8). Desorption experiments have shown that in the absence of the gas phase the adsorbed layer is strongly adsorbed since only a quarter of the adsorbed ions were removed during heating at 200°C for 1 hr (Tables 3, 4). The unexpected rapid exchange of 70% to 80% of the adsorbed ions with gas-phase formic acid may be explained by the following model.

Suppose that the strongly bound formate ions are sites for adsorption of weakly bound formic acid molecules in the presence of the gas phase. Interaction between the two species could occur to form an intermediate complex of the form:



At low temperatures in the presence of the gas phase this complex may be the intermediate through which exchange occurs, i.e.,

$$H^{12}COOH + H^{14}COO^- \rightleftharpoons H^{12}COOH{\cdot}H^{14}COO^- \rightleftharpoons H^{12}COO^- + H^{14}COOH \quad (1)$$

It is proposed that at higher temperatures this complex could be activated sufficiently to decompose according to

$$H^{12}COOH{\cdot}H^{14}COO^- + H_{ad} \rightarrow {}^{12}CO_2 + {}^{14}CO_2 + 2H_2 \quad (2)$$

This would leave the site available for adsorption of another formate ion followed by interaction of a formic acid molecule. An alternative mechanism was proposed by Hirota *et al.* (*12*) from their deuterated acid work:

$$H^{12}COOH{\cdot}H^{14}COO^- + H_{ad} \rightarrow {}^{12}CO_2 + H_2 + H^{14}COO^- + H_{ad} \quad (3)$$

The production of ${}^{14}CO_2$ as a decomposition product (Table 5) apparently favors mechanism (2). However, it is possible that exchange of $H^{12}COOH$ occurs before decomposition takes place, and the $H^{14}COOH$ liberated in the gas phase is then available to return to the surface and decompose to form ${}^{14}CO_2$. Mechanism (3) is therefore not excluded by this result. Both mechanisms comply with reported deuterated acid work in that H_2, HD, and D_2 can be formed as primary products. However, although the true nature of the complex and how it decomposes remains obscure, it seems likely that it is an intermediate species and takes part in the decomposition.

This model, therefore, suggests that in the absence of gas-phase formic acid, which produces adsorbed formic acid molecules on the surface, decomposition of the adsorbed formate ions is difficult, and they are desorbed at 200°C without decomposing (Table 4). The model accounts for the adsorption results (*8*) where it was found that in the higher pressure range of the experiment the weak reversible adsorption was directly proportional to the amount of strongly adsorbed species. The exchange reaction (1) should be considerably reduced at low gas-phase pressures or not occur at all. The results of the experiments shown in Fig. 2 prove this to be the case.

The significance of the results obtained from the decomposition of $H^{12}COOH$ gas in the presence of $H^{14}COOH$ monolayers will now be examined (Table 7). Since it takes about 8 hr at 200°C to desorb the strongly bound monolayer from the surface, the desorption rate must be slow compared with the removal of $H^{14}COOH$ from the surface by reaction or exchange. In addition, since the coverages on silver under reaction conditions (*17*) are about the same as the coverages formed in the present series of experiments at room temperature and lower pressures (*8*), it can be assumed that the removal of the initially adsorbed $H^{14}COO^-$ layer was due to reaction at these sites. It is proposed that the number of $H^{14}COO^-$ ions removed from the surface during reaction be identified with the number of active sites on the surface at which the activated complex decomposes according to reaction (2) or (3) above.

Table 7 shows that at the temperatures studied the fraction of the adsorbed layer involved in the reaction is always 10% greater on single crystals than on polycrystals. It is to be concluded, therefore, that adsorption and reaction must occur on (111) surfaces. It has already been shown (*8*) that approximate values for coverages on the (111) and on atomically rough patches are 8×10^{13} mols./cm^2 and 18×10^{13} mols./cm^2, respectively. On 1 cm^2 of a surface of polycrystalline silver on mica containing 30% (111) there would therefore be adsorbed 2.4×10^{13} mols. on the (111) patch and 12.6×10^{13} mols. on the remainder of the surface, giving an overall coverage of 15×10^{13} mols./cm^2. Examination of Table 7 shows that at 200°C, for a similar type of surface, 83% of the adsorbed layer, (12.5×10^{13} mols.) has been involved in the catalytic reaction. An inactive patch (2.5×10^{13} mols.) has not been touched despite prolonged and repeated catalysis on the surface. There are therefore at least three different types of patch on this 1-cm^2 surface which are shown schematically below for polycrystalline and epitaxed films.

It has been considered in this treatment that the inactive sites are present as part of the rough surface and not of the (111) patch. The justifications for this are as follows: (i) The (111) patch is likely to be more homogeneous in the nature of the sites than the rough patch. (ii) It is pos-

NUMBERS OF ACTIVE SITES AT 200°C

1 cm^2 Polycrystal Ag			1 cm^2 Epitaxed Ag		
(111) patch	2.4×10^{13}			7.2×10^{13}	(111) patch
Rough patch	10.1×10^{13}	Active complex	Rough patch	1.2×10^{13}	Active complex
	2.5×10^{13}	Inactive		0.6×10^{13}	Inactive

sible to work out the number of active sites per cm^2 for the (111) and complex patches, from both the polycrystalline silver, and epitaxed silver catalysts, and consistency in the results obtained from both catalysts is only maintained when the above assumptions are made. The number of active sites/cm^2 for the (111) surfaces, n_1, is therefore 8×10^{13} sites/cm^2 and the number, n_2, for the complex surface 13×10^{13} sites/cm^2. It is realized that these values depend on the reliability of the estimates of the proportion of (111) present and should therefore be treated as only approximate values. They do, however, serve to illustrate the following points.

From his results on catalysts prepared under the same conditions as the present ones, Jaeger (*5*) has deduced values of 16 and 31.5 kcal/mole for the activation energies of reaction on the (111) and complex surfaces, respectively, and $10^{21.5}$ and $10^{28.5}$ for the respective pre-exponential factors. From this information, rates of reaction at 200°C on the (111) and the complex surfaces can be calculated. These are 2×10^{14} and 1×10^{14} mols./cm^2 sec, respectively. For a heterogeneous surface, the Arrhenius equation can be split up into a number of terms corresponding to the number of "homogeneous" patches in the surface. Thus, for a homogeneous patch i,

$$K_i = n_i \frac{kT}{h} \exp\left(\frac{\Delta S_i}{R}\right) \exp\frac{-E_i}{RT}$$

where K_i is the rate constant, E_i the activation energy, ΔS_i is the change in entropy when the adsorbed state is elevated to the activated complex, and n_i is the number of active sites on the patch i. Subscript 1 refers to the (111) patch and subscript 2 to the complex patch. Considering reaction at 200°C, values of n_1 and n_2 at this temperature have been calculated as above; $kT/h = 10^{13}$ sec^{-1} and the values of E_1 and E_2, K_1 and K_2 are known. Calculation then gives $\Delta S_1 = -26$, and $\Delta S_2 = +4$ cal/mole degree. These results are based on mechanism (3), i.e., only the formic acid molecule is decomposing. If mechanism (2) is considered, i.e., both the formic acid molecule and formate ion are decomposing, then the experimental rates must be halved before applying them to the Arrhenius equation. This, however, makes little difference to the calculated entropy changes with $\Delta S_1 = -25$ and $\Delta S_2 = +3$ cal/mole degree.

Clearly the compensation which occurs in this reaction is achieved by entropy changes on certain types of surface and not by changes in the number of active sites. The entropy change on the rough surface is small, but it is interesting to consider what might cause the large negative entropy change associated with the flat (111) surface, i.e., a loss in the degrees of freedom of the adsorbed species in being elevated from the adsorbed state to the activated complex. On the basis of the model presented here, interaction of an adsorbed formate ion with an adsorbed formic acid molecule to form an activated complex might well be the cause of the negative change in entropy. There are several ways in which this could occur. It seems likely that of the two species on the surface, the strongly adsorbed formate ion would be the least mobile and would perhaps have lost its translational degrees of freedom but retained its rotation. The weakly adsorbed formic acid molecule is likely to retain two degrees of translational freedom as well as rotation. When the adsorbed molecule interacts with the ion to form the activated complex, then two degrees of translational freedom are lost. Rotation of the complex is an order of magnitude slower than the vibration of its bonds, and hence it is likely that the total entropy change will be concentrated in the subsequent decomposition of the complex. The loss of two degrees of freedom of the formic acid molecule gives rise to an entropy change of 26 cal/mole degree and is thus of the correct order of magnitude to explain the experimental results. On the rough surface, translation of the formic acid molecule is considerably more difficult because it has high energy barriers to cross, and so, although formation of the activated complex requires little entropy change, the process of formation is more difficult. The question of the bimolecularity of this reaction seems to have been more clearly established.

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