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The Catalytic Decomposition of Aqueous Formic Acid over Suspended Palladium Catalysts

D. M. RUTHVEN AND R. S. UPADHYE

Department of Chemical Engineering, University of New Brunswick, Fredericton, N. B., Canada

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Kinetic data are presented for the decomposition of aqueous formic acid over suspended palladium black catalysts. It is shown that the catalysts undergo continuous deactivation as a result of the absorption of a small but significant fraction of the hydrogen which is formed as a product of the reaction. The rate of deactivation is accounted for quantitatively and a simple reaction mechanism is proposed which gives a very satisfactory interpretation of the kinetic data. It is suggested that formic acid is rapidly and reversibly adsorbed by the catalyst to yield a surface formate and that it is the decomposition of this species which controls the overall reaction rate This mechanism appears to be consistent with evidence from vapor phase studies and values of the heat of adsorption calculated from the kinetic data agree well with the value estimated from thermochemical data.

INTRODUCTION

Although slurry phase catalyst systems, in which a reaction is catalyzed by a suspended solid catalyst, have many practical advantages and are therefore widely used in the chemical industry, few fundamental studies of this type of system have been reported. In this paper kinetic data are presented for the decomposition of an aqueous solution of formic acid with suspended palladium black as a catalyst. This reaction has been widely studied in the vapor phase and the mechanism has been fairly well established (*1*, *2*). It was, therefore, of some interest to see whether the evidence from the vapor phase studies could provide a consistent explanation of the kinetics of the slurry catalyzed reaction.

Formic acid can decompose in three ways (*1*):

$$H \cdot COOH = CO_2 + H_2, \tag{1}$$

$$H \cdot COOH = CO + H_2O, \tag{2}$$

$$2H \cdot COOH = CO_2 + H_2O + CH_2O. \tag{3}$$

Only reaction (1) which is characteristic of metal catalysts was observed in the present study. No traces of products other than CO_2 and H were ever detected.

EXPERIMENTAL

The rate of the reaction was followed in a closed system by measuring the rate of evolution of CO_2 and H from the reaction vessel which was maintained at a constant temperature in a thermostat. The reaction vessel was fitted with a magnetic stirrer and the reaction products were collected over water in a gas burette. The level of the gas burette was raised continuously during a run to maintain a constant pressure of 1 atm and the composition of the product gas was monitored at intervals using a Fisher Gas Partitioner. Before the start of each run the water in both the reaction vessel and the gas burette was saturated with carbon dioxide at a partial pressure of ½ atm to avoid errors arising from the appreciable solubility of carbon dioxide.

Complications arise because hydrogen, one of the primary products of the reaction, is absorbed to an appreciable extent by the palladium catalyst. The rate of hydrogen absorption is quite high for a fresh catalyst and gradually falls as the reaction proceeds. This phenomenon, which is discussed in detail later, is reflected in the concentration of hydrogen in the product gas which is low at the start of a run and rises to 50% as the reaction proceeds. The calculation of the formic acid concentration at any time was, therefore, based on the volume of CO_2 evolved. At the end of each run, samples of liquid were removed from the reaction vessel and the formic acid concentration determined by titration. The overall mass balance thus provided a check on the accuracy of the volumetric method of following the reaction.

Before the start of each run the catalyst was subjected to a standard pretreatment procedure which was developed to ensure a constant initial activity. The weighed sample of catalyst was placed in the reaction vessel and purged with hydrogen for 1 hr to remove traces of oxygen from the surface. The vessel was then evacuated for 12 hr at 250–300°C. The vacuum was released by purging with argon and the required quantity of distilled water was added while still maintaining the argon purge. The vessel was then transferred to the thermostat and purged with a 50:50 Ar–CO_2 mixture for ½ hr before the run was started by adding the required quantity of standard formic acid.

The reaction vessel contained 700 ml of liquid with 1–5 g-catalyst. The range of initial formic acid concentrations was 0.0475–0.875 *M* and runs were continued for several hours to 70–80% completion.

Three different palladium blacks were used as catalysts; the details are given in Table 1. Surface areas were measured with a Perkin–Elmer 212 D Sorptometer using nitrogen as the adsorbate at liquid nitrogen temperatures. The area occupied by a nitrogen molecule was taken to be 16.2 Å^2 (*3*). The area of the catalyst was found to be strongly dependent on the pretreatment and the values quoted should therefore be considered only as orders of magnitude which could be in error by as much as 50%.

TABLE 1
Specific Areas of Catalysts

Catalyst	Specific area m^2/g
1 B.D.H. batch 36777	6.85
2 B.D.H. batch 36874	3.4
3 Matheson batch 9832-PX2-7	2.7

Results and Discussion

Preliminary experiments showed that the catalyst loses activity continuously during the course of a run. Before useful kinetic data could be obtained it was therefore essential to determine the cause of the deactivation and to devise a satisfactory regeneration and pretreatment procedure which would give a consistent and reproducible initial catalyst activity. The procedure which was eventually developed is described above but it is of interest to consider briefly the steps by which this solution was reached.

Bubbling carbon dioxide or hydrogen through the reaction vessel prior to a run did not affect the catalyst activity, suggesting that these gases are not directly responsible for the deactivation. It was observed that the catalyst activity fell, not only during the course of a run, but also between runs. This raised the possibility that the deactivation was caused by traces of air in the system. In order to eliminate oxygen from the surface, the dry catalyst was purged with hydrogen for several hours before the start of a run and great care was taken to exclude air from the system. An increase in activity was observed. The temperature and time of the hydrogen pretreatment were therefore increased in an attempt to reach the upper limit of catalyst activity. Contrary to expectation, catalyst which had been pretreated with hydrogen at elevated temperatures (200°C) for several days showed scarcely any catalytic activity. It thus appeared that the initial increase in activity caused by hydrogen pretreatment was due to removal of traces of oxygen (formation of moisture was observed) but that prolonged hydrogen pretreatment at elevated temperatures resulted in the formation of palladium hydride which is evidently not an active catalyst for this reaction.

Since hydrogen is formed on the catalyst surface during the course of a run it became evident that the continuous fall in activity which was observed during the course of a run could be due to the slow formation of palladium hydride. This was confirmed by analysis of the product gases which showed that a significant amount of hydrogen is in fact absorbed by the catalyst. Runs were continued for a period of 12 hr after which the reaction rate became very slow even though the formic acid concentration was still appreciable. The quantity of hydrogen absorbed by the catalyst was calculated from the mass balance. The final atomic ratio H:Pd was thus found to be ~0.7 for most runs, in agreement with the hydride composition as given by the equilibrium isotherm (*4*).

The observation that bubbling gaseous hydrogen through the slurry prior to a run had no significant effect on the catalyst activity can be explained if it is assumed that the rate at which a palladium slurry absorbs hydrogen from the gas phase is very low. This was confirmed by direct experimental measurement of the rate of hydrogen absorption in the absence of formic acid. However, when hydrogen is formed on the catalyst surface, presumably as an adsorbed atom, some of the hydrogen is never desorbed but is "permanently" absorbed as palladium hydride. The rate at which the catalyst absorbs hydrogen is therefore dependent on the presence of formic acid and in the absence of formic acid deactivation of the catalyst by absorption of hydrogen from the gas phase is very slow. The hydrogen which is absorbed by the palladium may be removed by evacuation at elevated temperatures thus restoring the activity of the catalyst to its original level. This process is greatly facilitated by the presence of a trace of oxygen in the system and in the complete absence of oxygen the regeneration procedure was found to be less effective.

The continuous deactivation of the catalyst which was observed during a run complicates the analysis of the kinetic data since it is not possible to obtain the rate constant and reaction order directly from the concentration–time curve without due allowance for the variation in catalyst activity. The procedure which was followed was to set up a mathematical model for the system and then to calculate the model parameters from the experimental concentration-time curves using the least-squares criterion.

Suppose that the decomposition of formic acid is a reaction of order n,

$$\frac{-dc}{dt} = k'c^n, \tag{4}$$

while the deactivation of the catalyst can be represented by a zero-order process,

$$\frac{-dk'}{dt} = \alpha, \tag{5}$$

where k' is the rate "constant" at any time t. Combining Eqs. (4) and (5) and integrating with the initial condition $c = c_0$ at $t = 0$ gives

$$c^{1-n} - c_0^{1-n} = (n-1)\left(k'_0 t - \frac{\alpha}{2} t^2\right), \tag{6}$$

where k'_0 is the initial value of the rate constant k'.

The experimental data were tested against this expression using the method of least squares. The lack of linearity presented some computational problems but a satisfactory computer program was developed to select the best values of the model parameters n, k'_0, and α (*5*). The model did not, however, fit the data well as shown by large residual errors and parameters which varied with the initial formic acid concentration. The model was therefore modified by assuming the deactivation process to be first order so that in place of Eq. (5) we have

$$\frac{-dk'}{dt} = \alpha k'. \tag{7}$$

Integrating Eqs. (4) and (7) with the same initial conditions gives

$$c_0^{1-n} - c^{1-n} = (1-n)\frac{k'_0}{\alpha}(1 - e^{-\alpha t}) \tag{8}$$

The fit of the experimental data to this expression was tested in the same way. The model fitted the data well giving small residual errors and consistent values for the parameters which showed no significant variation with initial formic acid concentration. A value of $n \simeq \frac{1}{2}$ was obtained for all runs. The program was therefore modified by fixing the value of $n = \frac{1}{2}$ so that, in place of Eq. 8, we have

$$c_0^{\frac{1}{2}} - c^{\frac{1}{2}} = \frac{k'_0}{2\alpha}(1 - e^{-\alpha t}). \qquad (9)$$

The values of k'_0 and α calculated from this empirical rate equation are summarized in Table 2 and the experimental and theoretical concentration time curves for two typical runs are shown in Fig. 1. The reaction rate was shown to be directly proportional to catalyst concentration and the values quoted for k'_0 are therefore expressed on the basis of unit catalyst concentration [(g-mole·liter)$^{1/2}$/min·g-catalyst]. It is apparent that, on this basis, the rate constants are substantially the same for all three catalysts and average values, together with activation energies are summarized in Table 3. There is no significant variation in activation energy among the catalysts. The values quoted for catalysts 1 and 2 are considered to be somewhat more reliable as they are based on larger numbers of runs.

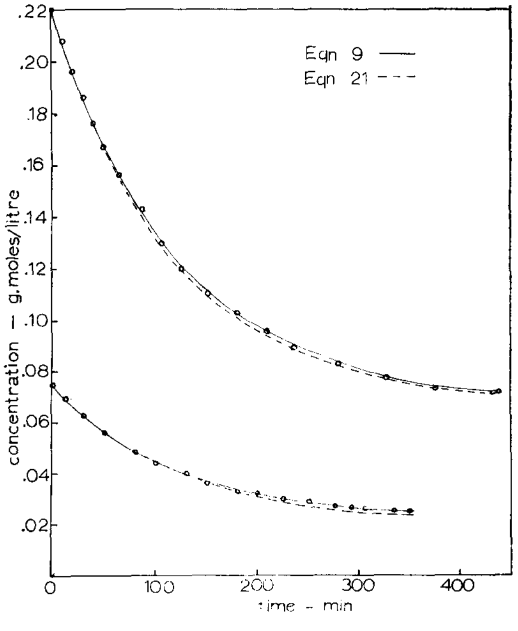


FIG. 1. Typical concentration-time curves.

Kinetic parameters obtained for runs in which the hydrogen ion concentration in the solution was altered by the addition of sulphuric acid are also included in Table 3. No significant change in reaction rate was observed. Since formic acid is a weak acid, addition of sulphuric acid causes a large increase in the hydrogen ion concentration and therefore a large decrease in the formate ion concentration with relatively little effect on the concentration of undissociated formic acid. It thus appears that the species which is active in the decomposition reaction is the undissociated molecule rather than either the hydrogen or formate ion. This conclusion is confirmed by the observation that the reaction ceases in alkaline solution under which conditions no undissociated formic acid is present.

REACTION MECHANISM

Equation (9) provides a satisfactory concise empirical correlation of the kinetic data obtained in this study but it is of interest to attempt to explain the form of this rate equation in terms of a reaction mechanism consistent with the evidence derived from vapor phase studies. On most metals formic acid is adsorbed dissociatively and the presence of formate radicals on the surface has been established by infrared spectroscopy as well as from other evidence (*1*, *2*). Carbon dioxide and hydrogen are both less strongly adsorbed than formic acid and the rate of desorption of these gases is apparently rapid (*6*). Depending on the particular metal and the conditions, the rate controlling step is either the rate of adsorption of formic acid or the decomposition of the surface formate (*7*).

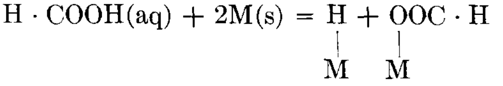
Under the conditions of the present study, owing to the high concentration of water in the liquid phase, it would appear reasonable to assume that the palladium surface is always largely covered with adsorbed water molecules. If it is also assumed that the adsorption of formic acid

TABLE 2

KINETIC PARAMETERS FOR THE DECOMPOSITION OF FORMIC ACID ACCORDING TO EQ. (9)

Catalyst	Temp (°C)	c_0 (g-mole/liter)	$k'_0 \times 10^5$ $\left[\frac{(\text{g-mole}\cdot\text{liter})^{1/2}}{\text{min}\cdot\text{g-catalyst}}\right]$	$\alpha \times 10^3$ min^{-1}
No. 1	64.0	0.0475	39.8	17.6
		0.0705	32.5	9.3
		0.0932	30.5	9.0
		0.1032	29.1	6.7
		0.137	33.0	6.0
		0.221	32.5	7.2
pH = 2.0		0.112	30.0	6.8
pH = 1.29		0.112	27.0	5.4
pH = 0.89		0.112	24.5	5.0
	32.6	0.221	7.45	4.0
		0.442	5.95	2.7
No. 2	64.0	0.119	28.8	4.3
		0.075	20.5	4.1
		0.075	22.2	4.5
		0.224	34.6	9.3
	31.2	0.223	5.12	2.3
		0.875	5.4	4.8
No. 3	64.0	0.238	29.4	7.2
		0.238	29.4	7.2
	30.5	0.238	5.0	3.0

is rapid and reversible compared with the rate at which formic acid decomposes, a dynamic equilibrium will be established so that, at any instant, a small fraction of the surface sites is occupied by formic acid. The dynamic nature of the equilibrium will ensure that the molecules adsorbed on the surface are continually exchanged with molecules from the liquid phase and that at any instant each surface site has the same small probability of being occupied by formic acid. In accordance with the evidence from the vapor phase studies it is further assumed that formic acid is dissociatively adsorbed as a formate radical and hydrogen atom, thus requiring two neighboring surface sites.



$$\mathrm{H\cdot COOH(aq) + 2M(s) = \underset{\displaystyle M}{\underset{|}{H}} + \underset{\displaystyle M}{\underset{|}{O}}OC\cdot H}$$

rapid equilibrium. (10)

The adsorbed formate radical has a small finite probability of decomposing by a unimolecular process to form gaseous car-

TABLE 3

AVERAGE RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE DECOMPOSITION OF FORMIC ACID ACCORDING TO EQ. (9)[a]

	Average values at 64°C				
Catalyst	k'_0	k'_0/A	α	E'_1 (kcal)	E'_2 (kcal)
1	3.08×10^{-4}	4.5×10^{-5}	0.008	9.6	5.4
2	2.64×10^{-4}	7.8×10^{-5}	0.006	9.5	2.8
3	2.94×10^{-4}	11.0×10^{-5}	0.007	10.6	5.1

[a] k'_0 is defined by Eq. (9) [(g-mole · liter)$^{1/2}$/min · g-catalyst]; A is specific area in m^2/g (Table 1); Activation energies are defined by $k'_0 = k'_\infty \exp(-E'_1/RT)$ and $\alpha = \alpha_\infty \exp(-E'_2/RT)$.

TABLE 4

Kinetic Parameters for the Decomposition of Formic Acid According to Eq. (21)

Catalyst	Temp	$k_0\left(\frac{\text{g-mole}}{\text{min}\cdot\text{g}}\right)$	$\alpha \times 10^3$ (min^{-1})	$b \times 10^3 \left(\frac{\text{liter}}{\text{g-mole}}\right)^{1/2}$
1	64.0	0.103	16.6	3.7
		0.102	8.8	3.1
		0.100	9.3	3.1
		0.101	6.6	2.9
		0.102	5.4	3.2
		0.099	7.3	3.3
		0.097	6.3	3.9
		0.099	7.2	3.1
		0.10	5.3	2.5
		0.109	4.9	2.3
	32.6	0.036	0.93	1.3
		0.035	0.99	1.2
2	64.0	0.0466	4.1	4.3
		0.039	5.3	6.9
		0.0465	8.8	6.1
		0.0468	4.4	4.7
	31.2	0.0205	4.5	2.6
		0.0205	2.6	2.5
3	64.0	0.128	4.9	1.8
		0.129	6.6	2.2
	30.5	0.059	3.2	0.8

bon dioxide and an adsorbed hydrogen atom:

$$\underset{\substack{|\\ \mathrm{M}}}{\mathrm{OOC\cdot H}} = \underset{\substack{|\\ \mathrm{M}}}{\mathrm{H}} + \mathrm{CO_2(g)}$$

slow rate controlling step (11)

If the formate radical decomposes in this way, it will leave two adsorbed hydrogen atoms on adjacent sites which will then desorb rapidly:

$$\underset{\substack{|\\ \mathrm{M}}}{\mathrm{H}} + \underset{\substack{|\\ \mathrm{M}}}{\mathrm{H}} = \mathrm{H_2(g)} + 2\mathrm{M}$$

rapid desorption. (12)

This is basically similar to the reaction mechanism proposed by Fahrenfort *et al.* (*2*) to account for the decomposition of formic acid vapor over nickel catalysts. It is however assumed that, under the conditions of the present study the catalyst surface is only sparsely covered with adsorbed formic acid so that the decomposition reaction proceeds by an intramolecular mechanism. Under these conditions the same fraction of surface sites will be occupied by hydrogen atoms and formate radicals. This 1:1 stoichiometric ratio would not necessarily hold at high surface coverages owing to the possibility of hydrogen desorption by an intermolecular mechanism.

If the adsorption equilibrium according to Eq. (10) can be represented by a Langmuir model, we have

$$k_a c(1 - 2\theta)^2 = k_d \cdot \theta^2, \tag{13}$$

where k_a is the adsorption rate constant, k_d is the desorption rate constant, and c is the formic acid concentration. Hence

$$\theta = \frac{b\sqrt{c}}{1 + 2b\sqrt{c}},$$

where $b^2 = k_a/k_d$ is the adsorption equilibrium constant for reaction (10). The overall reaction rate will be controlled by the unimolecular decomposition of the formate radical according to Eq. 11 so that the reaction rate may be written

$$\frac{-dc}{dt} = k\theta = \frac{kb\sqrt{c}}{1 + 2b\sqrt{c}}. \qquad (15)$$

The experimental evidence indicates that some of the hydrogen formed on the catalyst surface is absorbed as palladium hydride and that it is this process which is responsible for the continuous deactivation of the catalyst. The dynamic adsorption equilibrium ensures that, at any instant, each surface site has the same probability of being occupied by a hydrogen atom. If it is assumed that a hydrogen atom at the surface has a small but finite probability of being absorbed as palladium hydride, and that the loss in catalytic activity is proportional to the quantity of hydrogen absorbed by the catalyst, the rate of catalyst deactivation will simply be proportional to the number of active sites:

$$\frac{-d\phi}{dt} = \alpha(1 - \phi), \qquad (16)$$

where

ϕ is the fraction of initially available sites which have been deactivated at time t, and α is a rate constant which represents the probability of deactivation of any particular site. Integration of Eq. (16) with $\phi = 0$ at $t = 0$ gives

$$1 - \phi = e^{-\alpha t} \qquad (17)$$

The rate of formic acid decomposition which is proportional to the number of unpoisoned sites will therefore be given by

$$\frac{-dc}{dt} = k_0 e^{-\alpha t} \cdot \frac{b\sqrt{c}}{1 + 2b\sqrt{c}}. \qquad (18)$$

If the fraction of the surface sites occupied by formic acid is small, as was assumed in the derivation of the model,

$$2b\sqrt{c} \ll 1,$$

and Eq. (17) reduces to

$$\frac{-dc}{dt} = k_0 b e^{-\alpha t} \cdot \sqrt{c}, \qquad (19)$$

which on integration with $c = c_0$ at $t = 0$ gives

$$c_0^{1/2} - c^{1/2} = \frac{k_0 b}{2\alpha}(1 - e^{-\alpha t}), \qquad (20)$$

which is identical to the empirical rate Eq. (9) with $k'_0 = k_0 b$.

Integration of Eq. (17) with the same initial condition gives

$$\frac{c_0^{1/2} - c^{1/2}}{b} + c_0 - c = \frac{k_0}{2\alpha}(1 - e^{-\alpha t}). \qquad (21)$$

The experimental data were fitted to this equation using a least-squares computer program designed to select the best values of the parameters k_0, α, and b. The model fitted the data well and the values of the parameters are summarized in Table 2. Theoretical curves for two typical runs are included in Fig. 1.

It will be seen that the values of b are all quite small ($\sim 10^{-3}$) in accordance with the assumption that the surface is only sparsely covered with formic acid. Taking an average value of $c = 0.1$ g-mole/liter and $b = 3.0 \times 10^{-3}$ gives $\theta = b\sqrt{c} \sim 10^{-3}$. The condition $b\sqrt{c} \ll 1.0$ for the empirical rate equation to be a valid approximation is therefore fulfilled and it will be seen that, for all runs, $k_0 b \simeq k'_0$.

The values of b and α show considerable scatter which is not surprising considering the indirect way in which these values were calculated. However, the order of magnitude is quite consistent and there appears to be no significant trend with initial formic acid concentration. The rate constants k_0 appear to be quite consistent for each catalyst although there is some variation between the different catalysts. Average values of the specific rate constants, expressed on the basis of unit surface area (k'_0/A and k_0/A) were calculated using the specific areas given in Table 1. These values, which are included in Tables 3 and 5, show about the same range of variation between the catalysts as the rate constants expressed on a weight basis. In view of the uncertainty in the surface areas these figures must be regarded only as orders of magnitude and it is not possible to state with certainty whether or not the specific activity varies significantly among the catalysts. Any such differences in specific activity must, however, be relatively small.

TABLE 5

AVERAGE VALUES OF RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE DECOMPOSITION OF FORMIC ACID ACCORDING TO EQ. (21)

	Average values at 64°C						
Catalyst	k_0 $\frac{\text{g-mole}}{\text{min} \cdot \text{g}}$	k_0/A $\frac{\text{g-mole}}{\text{min} \cdot \text{m}^2}$	α (min^{-1})	b $\left(\frac{\text{liter}}{\text{g-mole}}\right)^{1/2}$	ΔH^a (kcal)	$E_1{}^b$ (kcal)	$E_2{}^c$ (kcal)
1	0.107	0.0148	0.00768	0.0031	11.6	6.4	12.8
2	0.0448	0.0132	0.00565	0.0055	9.5	4.3	4.7
3	0.128	0.048	0.0057	0.0020	9.4	4.5	3.5

[a] ΔH is defined by $\frac{\partial \ln b^2}{\partial T} = \frac{\Delta H}{RT^2}$.

[b] E_1 is defined by $k_0 = k_\infty e^{-E_1/RT}$.

[c] E_2 is defined by $\alpha = \alpha_\infty e^{-E_2/RT}$.

The values of b, however, do show a significant variation between the catalysts since it is apparent from Table 4 that the range of variation for a given catalyst is considerably smaller than the variation between catalysts. According to the proposed mechanism b^2 is the adsorption equilibrium constant for reaction (10). The Van't Hog isochore $\partial \ln b^2/\partial T = \Delta H/RT^2$ may therefore be used to calculate the heat of adsorption of formic acid from the temperature variation of b. Values of ΔH calculated in this way are included in Table 5. The values of ΔH ($\sim +10.0$ kcal) show no significant variation among the catalysts implying that although the adsorption equilibrium constant varies significantly the heat of adsorption is substantially the same for all the catalysts.

The phenomenon of endothermic adsorption is relatively uncommon although it has been pointed out that when adsorption is dissociative it may well be endothermic (*7*). The present values also refer to adsorption from an aqueous solution rather than from the vapour phase and there is a difference of approximately 11.0 kcal between the enthalpy of formic acid in solution and in the vapor phase (*8*). The observed values of ΔH ($\simeq + 10.0$ kcals) thus suggest that the enthalpy of adsorbed formic acid is approximately the same as that of formic acid vapor, implying that adsorption from the vapor phase to the catalyst surface would be thermoneutral or even mildly exothermic.

The values of ΔH obtained from the kinetic data may be compared with values calculated from tabulated thermodynamic data. Unfortunately accurate thermodynamic data are not available for the palladium–formic acid system. An approximate estimate of the heat of adsorption of formic acid may, however, be made from standard enthalpy data if it is assumed that the heat of formation of the chemisorbed surface formate is approximately the same as that of the bulk formate.

This assumption is to some extent justified by the work of Fahrenfort *et al.* (*2*) who obtained good agreement between the experimentally measured heats of adsorption of formic acid vapor on nickel and the values estimated thermochemically.

On this basis the heat of adsorption is estimated as follows:

	$H \cdot COOH(aq)$	$+ \; 2Pd(s) =$	$H{-}Pd(s)$	$+ \; H \cdot COO \cdot Pd(s)$
$\Delta H_{298}{}^f$kcal	-98.0 (*8*)	0	-10 to -13.5 (*9*)	-78 (*2*)

There is some uncertainty as to the heat of adsorption of hydrogen on palladium which varies with surface coverage. The above data however suggest that ΔH lies between $+6.5$ kcal and $+10.0$ kcal in good agreement with the value of approximately +10.0 kcal obtained from the kinetic data.

Since the overall rate constant $k'_0 = k_0 b$ it follows that the overall activation energy $E'_1 = E_1 + \Delta H/2$. Both terms evidently contribute approximately equally (~5.0 kcal) to the overall activation energy of ~10.0 kcal. The values of α, the rate constant for catalyst deactivation, do not vary significantly among the catalysts and at 64°C the mean value of approximately 0.006 min^{-1} corresponds to a catalyst half life of 2 hr.

CONCLUSION

The decomposition of aqueous formic acid over suspended palladium black catalysts proceeds at a rate which is proportional to the square root of the formic acid concentration. The activity of the catalyst declines continuously during the course of a run and the experimental evidence suggests that this deactivation is due to the absorption of hydrogen. On this point the evidence is, however, circumstantial since it is based largely on the observed effect of hydrogen pretreatment. Other possibilities, such as the formation of a surface carbonyl, cannot be entirely ruled out since any poisoning mechanism leading to a first-order decline in activity (i.e., rate of deactivation proportional to catalyst activity) would explain the kinetic data equally well. The kinetics of this reaction may be satisfactorily explained if it is assumed that the catalyst surface is sparsely covered with dissociatively adsorbed formic acid in equilibrium with the liquid phase and that the overall reaction rate is controlled by the intramolecular decomposition of the surface formate radical. Although this mechanism must be regarded as tentative as it is based only on kinetic evidence, the assumptions involved appear to be physically reasonable and consistent with evidence from vapor phase studies. Differences in the specific activity of different palladium blacks are relatively small but there are significant differences in the adsorption equilibrium constants. The heat of adsorption calculated from the kinetic data is approximately +10.0 kcal and is essentially the same for all the catalysts studied. This value agrees well with the heat of adsorption estimated from thermochemical data thus providing additional evidence in support of the proposed reaction mechanism.

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REFERENCES

1. MARS, P., SCHOLTEN, J. F., AND ZWEITERING, P., *Adv. Catal. Relat. Subj.* **14**, 36 (1963).
2. FAHRENFORT, J., VAN REYEN, L. L., AND SACHTLER, W. M. H., *in* "The Mechanism of Heterogeneous Catalysis" (J. H. De Boer, ed.), Elsevier, Amsterdam, 1960.
3. ANDERSON, R. B., "Experimental Methods in Catalytic Research," Academic Press, New York/London, 1968.
4. LEWIS, F. H., "The Palladium-Hydrogen System," Academic Press, New York/London, 1967.
5. UPADHYE, R. S., MSc thesis, University of New Brunswick, New Brunswick, Canada, 1969.
6. TAMARU, K., *Trans. Faraday Soc.* **55**, 1191 (1959).
7. THOMAS, J. M., AND THOMAS, W. J., "Heterogeneous Catalysis," Academic Press, New York/London, 1967.
8. ROSSINI, F. D. *et al.*, *Nat. Bur. Stand. U. S. Circ.* 500 (1952).
9. BOND, G. C., "Catalysis by Metals," Academic Press, New York/London, 1962.