

Formic Acid Decomposition at Low Pressures on Flashed and Unflashed Platinum Wires

E. M. A. WILLHOFT* AND A. J. B. ROBERTSON

From the Department of Chemistry, King's College, Strand, London, England

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The catalytic activity of unflashed wires at formic acid reactant pressures of 10^{-4} torr and less was found to vary considerably from one specimen of wire to another. Flashing in vacuum or reduction in hydrogen at 970°K increased the activity of wires considerably, in some cases by as much as 500 times at 970°K . Hydrogen reduction was, however, characterized by a rapid loss of activity of the wire during continuous reaction at 970°K , whereas a flashed wire gave a steady activity at this and higher temperatures, corresponding to a reaction probability per collision of close to unity. The decay of activity could be attributed to saturation of the surface region by carbon deposited either from the decomposition of formic acid, or the cracking of residual gases. The retardation order at 527°K with respect to hydrogen was minus one on a freshly flashed wire, but zero on a wire which had been used for formic acid decomposition. This retardation order may therefore reflect the extent of carburization of the surface. The decay of activity with time of reaction at low reaction temperatures subsequent to flashing a wire is postulated to be governed by a dynamic equilibrium involving removal of carbonaceous matter from the surface by reaction with water vapor, and diffusion of carbon through the bulk metal. This equilibrium is described in terms of a Langmuir type of isotherm.

INTRODUCTION

Although much work (1, 2, 3) has been done on formic acid decomposition on various surfaces, few published data exist for metal surfaces and low reactant pressures. When wires of certain metals are used as catalysts they generally become extremely active if first heated in vacuum to a temperature just below the melting point (flashing). In fact, the probability (P) of reaction at a collision of a formic acid molecule with the metal is unity, or close to unity, for nickel, copper, platinum, palladium, niobium, and tungsten (4, 5). Duell and Robertson (4) described these extremely active wires as superactive. However, the reason for superactivity is uncertain and further work is needed. Here we describe experiments with formic acid and platinum which show that the super-

active state of this metal can be produced by reduction in hydrogen at only 970°K , as well as by flashing in vacuum. Furthermore, the superactivity phenomenon was very sensitive to contamination, and indeed could be explained in such terms without proposing any specific catalytic effect due to vacancies, in contrast to the previous proposals of Duell and Robertson (4) for nickel and copper. Formic acid decomposition on metals at low pressures occurs mainly by a first-order dehydrogenation and is a useful system for studying the effect of various pretreatments on the absolute activity of the catalyst. In this paper, the decay of activity with time previously noted (4, 5) is given particular attention.

EXPERIMENTAL

The apparatus consisted of a conventional Pyrex glass high-vacuum flow system with Pollard mercury vapor and oil rotary pumps and was similar to that used

* Presently at the Gas Council, London Research Station, Michael Road, London, S.W.6.

with ammonia (6). Formic acid was leaked into the reaction vessel, which was at room temperature, at a known rate and passed over the electrically heated catalytic platinum wire. Unreacted gas was condensed out onto a liquid-air trap at the exit of the reaction vessel, and noncondensable gases were pumped out by a mercury vapor pump backing the liquid-air trap. The reaction rate was measured with a Pirani gauge by following the build-up of pressure in a known volume. The probability P of reaction of a molecule of formic acid at a collision with the catalyst was found as previously described (6).

Hydrogen was obtained from cylinders and further purified by diffusion through a heated palladium thimble. Oxygen, White Spot nitrogen, and propylene were also obtained directly from cylinders. The propylene was further purified by several vacuum distillations using liquid air as refrigerant. The formic acid was of AR quality and was vacuum-distilled several times using Cardice (solid CO_2)/methanol. The wires obtained from Johnson-Matthey were spectroscopically pure specimens of 150- and 75- μm diameter of usual lengths, 37 and 30 cm, respectively. The usual pretreatment of the wires consisted of rinsing in AR carbon tetrachloride and then in distilled water followed by rapid transference of the specimen to the reaction vessel which was then pumped to a pressure approaching 10^{-6} torr as indicated by a McLeod gauge. End cooling effects of the catalytic filaments were insignificant at temperatures in excess of about 700°K .

RESULTS

It is well established (1, 2, 3) that formic acid reacts on metal surfaces to give predominantly the dehydrogenation products. Baines (5) showed the products on platinum wires to correspond to 90% dehydrogenation and 10% dehydration. Although this stoichiometry was assumed in the present work unless explicitly stated to the contrary, it was noted that if 100% dehydrogenation instead of 90% occurred, the reaction rate estimated from the Pirani

gauge galvanometer deflection rate was greater than the true rate by only 2%.

Production of Superactive Wires by Reduction

The pressure of formic acid in the absence of reaction was 2×10^{-4} torr in these experiments, and the wire diameter was 150 μm . A 15-min exposure of a nonflashed wire at 1040°K to H_2 at 10-torr pressure increased the activity at this temperature by a factor of more than 100 to give $P = 0.15$. However, when this was followed with a 20-min exposure at 1040°K to residual gases (high vacuum) a loss of activity resulted to give $P = 6 \times 10^{-2}$, which further decreased to 3×10^{-2} after an additional 40-min exposure of the heated filament to high vacuum. This filament was again reduced in hydrogen under conditions identical with those used before, and then kept in high vacuum at 1040°K for 23 min. The rate of disappearance of activity was then followed with formic acid continuously passing over the catalyst at 1040°K . Values of P at various times were 2 min, 2×10^{-1} ; 12 min, 1×10^{-1} ; 26 min, 6×10^{-2} . Flashing the filament for about 30 sec several times in high vacuum increased the activity to give P close to unity. This remained constant for at least 10 min of continuous reaction at 1040°K .

An attempt was made to estimate an apparent activation energy for formic acid decomposition on another new wire which had not been flashed. This specimen was kept at 870°K in high vacuum for 15 min, at the end of which P was 3×10^{-4} at 870°K . The filament temperature was then decreased to 770°K and P found to have increased to 1.4×10^{-3} . At 670°K the activity was observed to decay with time of reaction; e.g., values of P after various times were $\frac{1}{2}$ min, 6.2×10^{-4} ; $1\frac{1}{2}$ min, 4.9×10^{-4} ; $2\frac{1}{2}$ min, 3.6×10^{-4} ; $4\frac{1}{2}$ min, 2.2×10^{-4} . The temperature was then reduced to 440°K when activities steady for at least 3 min of reaction were noted at subsequent temperatures up to 973°K , provided the measurements were made with increasing temperatures. These steady

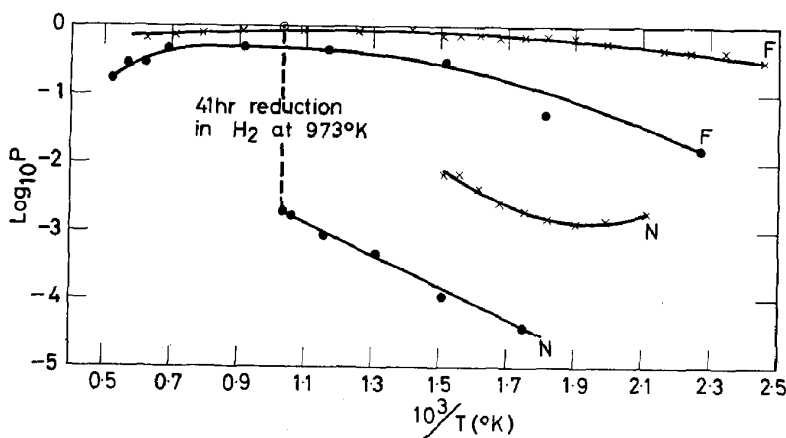


FIG. 1. Decomposition of formic acid on nonflashed (N) and flashed (F) platinum wires: ●, pressure in absence of reaction, 2×10^{-4} torr, and wires 150- μ m diam; ×, pressure in absence of reaction, 6×10^{-5} torr, and wires 75 μ m diam; ○, activity of 150- μ m wire after reduction in hydrogen for 41 hr at 970°K. The dashed line shows the effect of the reduction.

activities (Fig. 1) gave $P = 10^{-0.30} \times \exp(-10\,700/RT)$.

The filament at 970°K was then reduced in H_2 at 10-torr pressure for 41 hr. This increased P to unity at this temperature. The outgassing correction at the end of this reduction corresponded to less than 1% of the pressure build-up in the known backing volume due to formic acid decomposition in the reaction vessel. The high activity at this temperature was, however, short-lived, as can be seen from values of P taken at various times of continuous reaction: 3 min, 1; 26½ min, 0.29; 4 hr, 0.038. A subsequent ½-hr high-vacuum exposure at 970°K resulted in a further reduction of P to 1.8×10^{-2} . A further 15 hr at 970°K in an unpumped vacuum of about 10^{-5} torr decreased the activity of the filament giving $P = 5.7 \times 10^{-3}$ at 970°K. Thus, no spontaneous increase of activity occurred in vacuum in contrast with the decayed activity of a flashed nickel wire. The wire was next heated to 1910°K in high vacuum for 5 min and the activity measured at various temperatures, flashing the filament for ½ min immediately prior to each run. The results are shown in Fig. 1. A decay of activity during the first 10 min of reaction was only observed at temperatures below 550°K. Rapid decay occurred at temperatures of 440°K and less, some

values of P at 440°K being ½ min, 1.5×10^{-2} ; 4-6 min, 1.3×10^{-3} ; 17-20 min, 8.4×10^{-4} .

The steady activity of a flashed wire above 550°K was to be contrasted with the decay of activity at 1040°K of a wire cleaned by reduction in hydrogen. The extent of activation by reduction in hydrogen was dependent both on the reduction time and the filament temperature. This is clearly demonstrated by the results in Table 1, for a single new nonflashed speci-

TABLE 1
VALUES OF P AFTER REDUCTION IN HYDROGEN

Reduction time in H_2 at 10 torr	Reaction temp. (°K)	Initial value of P
0 hr	870°	1.1×10^{-3}
14 hr at 870°K	870°	1.1×10^{-2}
34½ hr at 870°K	970°	1.6×10^{-1}
5 min at 1020°K	870°	1.0

men of wire. After the 5-min H_2 reduction at 1020°K followed by measurement of P at 970°K the wire temperature was reduced to 440°K. This gave $P = 3.5 \times 10^{-3}$, which is comparable to the flashed activity after 3 min of continuous reaction (for the combination of pumping speeds used). A platinum wire was readily inactivated by heating it to 1840°K for 5 min in propylene at 10^{-2} torr ($P = 5 \times 10^{-4}$ at 1570°K).

Subsequent flashing of the filament in vacuum did not restore the activity for formic acid decomposition, neither did 35 min of heating in vacuum at 1610°K. In fact, this latter procedure reduced P still further to 3×10^{-5} at 1610°K.

Factors Affecting the Absolute Activity and Its Change with Time

This work was carried out with faster pumping speeds so that the steady state pressure of formic acid in the reaction vessel (in the absence of reaction) was 6×10^{-5} torr. This increased the accuracy for measurement of P approaching values of unity (4). Wires of 75- μ m diameter were used. The activity of this wire before flashing was much greater than that of the previous 150- μ m diameter specimen. For example, a wire which had not previously been outgassed or subjected to a temperature in excess of the reaction temperature of 950°K, gave the following values of P for formic acid for various reaction times: 0-5 min, 3.0×10^{-2} ; 10-12 min, 4.0×10^{-2} ; 17-18 min, 5.4×10^{-2} ; 25-28 min, 11.2×10^{-2} ; 38-40 min, 11.8×10^{-2} . Values of P above 950°K for a flashed wire were found to decrease with increasing temperature, e.g., 710°K, 0.65; 951°K, 0.76; 1107°K, 0.66; 1413°K, 0.61. At 650°K the activity of another new filament was decreased by keeping it in residual gases for 10 min; P fell from 2.2×10^{-2} to 8.5×10^{-3} . On raising the filament temperature to 998°K the activity was again found to increase with time of reaction from an initial P of 7×10^{-2} to a steady value of 0.52. One-hour reduction in H_2 at 998°K increased P to 0.59. Flashing the wire further increased P to 0.68.

A new filament was kept at 556°K in high vacuum for 1 hr. P values were measured from 473° to 664°K. Flashed activities were then measured. Results for the flashed and nonflashed wires are included in Fig. 1. The greater activity of the thin wire compared with the thicker one was confirmed. The flashed activity at 408°K was found to decay rapidly with time, e.g., $< \frac{1}{2}$ min, $P = 0.36$; 10 min, $P = 1.9 \times 10^{-2}$; 20 min, $P = 6 \times 10^{-3}$; 80 min, $P =$

6×10^{-3} . No recovery of activity at 408°K occurred during an 18-min exposure of the filament to high vacuum at this temperature. Almost complete recovery at 408°K occurred, however, during a 15-min exposure to high vacuum at 920°K ($P = 0.31$ at 408°K). Again, the activity at 408°K disappeared rapidly with time of reaction.

A closer examination was made of the effect on the decay of activity of (1) residual gases, (2) reactant, and (3) hydrogen. Three separate runs were carried out, all at 527°K, using a new and flashed wire. (a) The flashed filament was exposed to high vacuum (i.e., residual gases) and the activity measured at periodic intervals, each measurement taking about 2 min. (b) The decay of the flashed activity was followed with formic acid flowing continuously over the filament. (c) The decay of the flashed activity was followed with formic acid plus added hydrogen passing continuously over the filament. The partial pressure of H_2 at the commencement of run (c) was kept constant and comparable to that produced naturally during the decomposition of formic acid. The results of experiments (a), (b), and (c) are shown in Fig. 2, where it is seen that hydrogen exerts a retardation effect but does not accelerate the decay of activity. A similar observation was made at 470°K. At 470°K without added H_2 there was a mere 20% reduction of activity after 5 min of reaction, whereas for the earlier slower pumping speed conditions and the slightly lower temperature of 440°K, there was an almost tenfold reduction in the initial activity after only 5 min of reaction.

The poisoning effect of residual gases at low temperatures was amply confirmed in the following experiment: A flashed wire was immersed in N_2 (20 torr), at 470°K for 1- and $6\frac{1}{4}$ -hr periods. The activity at the end of each exposure (after removal of the N_2) was found to be the same as the subsequently determined flashed activity ($P = 0.23$). It seemed probable that the N_2 inhibited diffusion of residual gases to the wire. It was noted that decay of activity occurred as soon as reaction com-

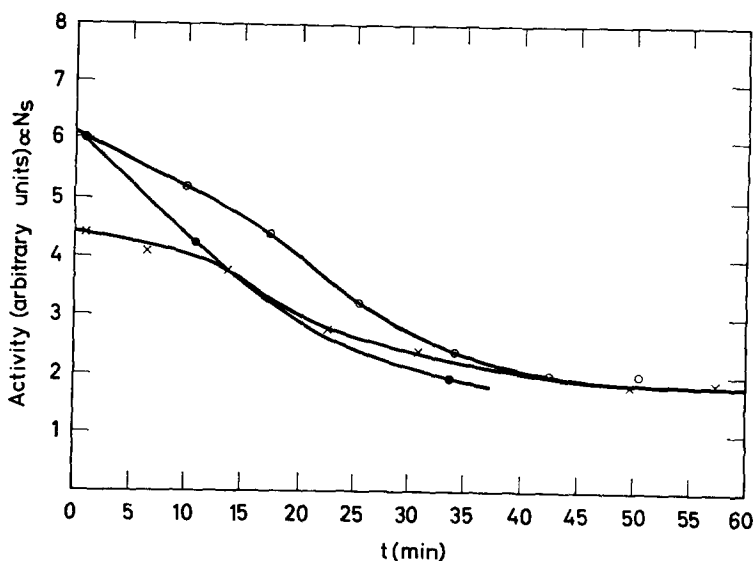


Fig. 2. Decay of activity at 527°K of a flashed wire: ●, in presence of residual gases; ○, in presence of formic acid at a pressure of 6×10^{-5} torr; ×, in presence of formic acid and added H_2 .

menced, e.g., $< \frac{1}{2}$ min, $P = 0.23$; 26 min, $P = 0.16$; 36 min, $P = 0.14$; 56 min, $P = 0.13$.

In general, it was found necessary to flash a filament several times before a maximum P for a particular temperature was obtained. Baines also observed this for platinum (5). The activity slowly lost as a result of several hours of reaction at 1105°K could be recovered by the H_2 reduction treatment. For example, continuous reaction for about 7 hr reduced P from 7×10^{-1} to 9.7×10^{-2} ; 15-min reduction at this temperature in H_2 recovered the activity to give $P = 0.53$. This decayed however, to $P = 0.29$ after only 3–4 min of reaction.

Retardation Order by Hydrogen

The hydrogen retardation order was determined by measurement of the activity in the presence of various known relative partial pressures of added hydrogen. The filament was flashed in high vacuum prior to each run. H_2 was leaked into the apparatus independently of the formic acid through a sintered glass filter tube connecting the H_2 storage flask to the reaction vessel. The H_2 leak rate was deter-

mined immediately after each run so that the build-up of pressure due to formic acid decomposition in the presence of the added H_2 could be calculated by difference. If the kinetic retardation order with respect to H_2 is given by n , and D_1 and D_2 refer to formic acid decomposition rates in molecules sec^{-1} in the absence and presence, respectively, of added H_2 it can be seen that

$$\frac{D_1}{D_2} = \frac{(N_e - N_{s,1})}{(N_e - N_{s,2})} \left[\frac{(D_H + D_2)}{D_1} \right]^n \quad (1)$$

where D_H refers to the rate in molecules sec^{-1} at which added H_2 is leaked into the reaction vessel simultaneously with the formic acid. $N_{s,1}$ and $N_{s,2}$ are the number of molecules of formic acid decomposed per second on the catalyst in the absence and presence of the added H_2 . Equation (1) is derived directly from Eqs. (1) and (4) given previously (6). The various D quantities are directly proportional to the Pirani readings, (and hence partial pressures in the reaction vessel) and these can therefore be used directly in Eq. (1). In calculating n it was assumed for simplicity that the reaction occurred exclusively by dehydro-

genation. The retarding effect of H_2 for various filament temperatures is shown in Fig. 3. Calculated n values refer to conditions prevailing during the first 3 min of reaction. The retardation orders for each temperature were $470^\circ K$, 0.25; $527^\circ K$, 0.76; $1105^\circ K$, 0.63.

DISCUSSION

Flashing a platinum wire is found, in agreement with earlier results of Baines (5), to activate it so that the decomposition rate of formic acid becomes almost equal to the collision rate over a wide temperature range. This result is also obtained when a wire is reduced with H_2 at temperatures slightly less than $1000^\circ K$. In the case of $150\text{-}\mu m$ diameter platinum, reduction of the unflashed wire increased the reaction probability by a factor of 500. However, after the reduction treatment the high activity soon decayed to a lower value when reaction occurred. These observations strongly suggest that high activity corresponds to a reaction surface devoid of certain easily reduced and volatile contaminants. This is not to suggest that the filament yielded a clean surface immediately subsequent to a high-temperature flash, but rather, that a more uniform and less contaminated surface was produced

which probably contained foreign matter capable of decomposing formic acid with a high reaction efficiency. The negative temperature coefficient of P for both the flashed and unflashed wires (Fig. 1) suggests that bulk diffusion of foreign matter is an important factor in determining the absolute activity of the wire (6). Diffusion both to and from the surface may occur, as Le Goff and Letort (7) observed, with carbon in tungsten. It is likely that chemical processes aiding removal of surface matter occur due to background gases such as water vapor and oxygen. It was significant that in later work (8) on the nickel-formic acid system, the maximum flashed activity at a particular temperature was obtained after a greater number of flashings compared to platinum, the latter having a higher flashing temperature.

It is likely that in a wire flashed several times diffusion of bulk contaminant becomes increasingly easy on account of the increased vacancy and dislocation content (9). The rapid decay of activity characteristic of reduced filaments suggests that chemical reduction of the wire at about $1000^\circ K$ appears to be a process involving only the surface region, and that purging of the bulk is negligible and is limited by the relative slowness of diffusion of foreign

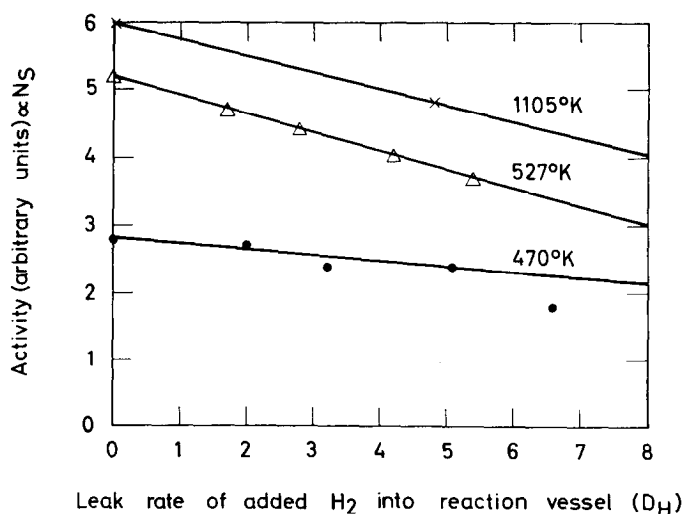


FIG. 3. Retardation of formic acid decomposition by hydrogen at various filament temperatures: X, $1105^\circ K$; Δ , $527^\circ K$; \bullet , $470^\circ K$.

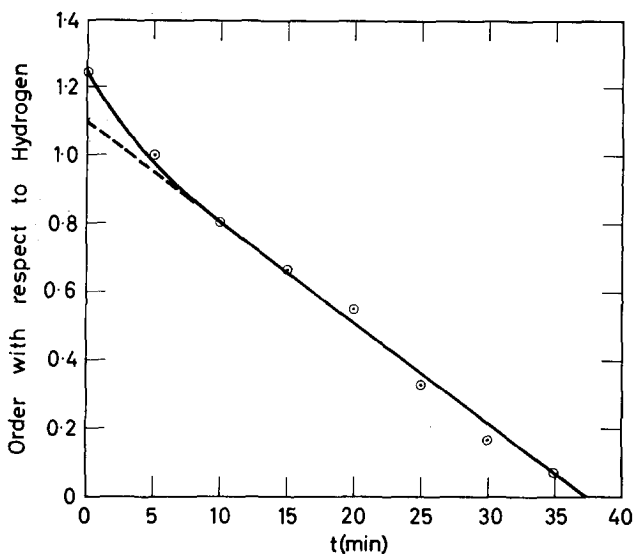


Fig. 4. Retardation order by hydrogen during the decay of the flashed activity at 527°K.

matter through the metal crystal lattice. On this view, decay of activity is due to saturation of the surface region by products from residual gases and reactant. However, on a flashed wire the deposited contaminant (possibly carbon or containing carbon) is removed from the surface region by inward bulk diffusion. This hypothesis for the sustained superactivity is an alternative to that of Duell and Robertson (4) which invoked vacancies. Both hypotheses are somewhat conjectural. Baines (5) not only observed a carbonaceous deposit on platinum wires after lengthy formic acid reaction, but has also shown that such a filament, after flashing, still had a relatively high activity. Rieker (10) concluded that carbon is deposited by a side reaction. It seems, therefore, that carbon is also capable of decomposing formic acid, but to a lesser extent than a carbon-free and flashed metal surface. The slight negative temperature coefficient in P at high temperatures is postulated to occur as a result of increased extent of carbon deposition at higher temperatures.

If the decay of activity observed at 527°K (Fig. 2) is caused by carburization by the cracking of residual gases, as opposed simply to chemisorption of these gases, then the carburized surface is characterized by a zero kinetic order with re-

spect to hydrogen, the freshly flashed surface having a value of minus unity. The kinetic order was calculated with Eq. (1) from curves of Fig. 2. The decrease in retardation order with reaction time during the activity decay at 527°K is shown in Fig. 4. It appears that the extent of carburization of the surface, either by gas-phase contamination or diffusion from the bulk of the metal wire is indicated by the numerical value of the apparent retardation order by hydrogen. It is, on this view, therefore hardly surprising to observe fractional negative orders even at temperatures as low as 527°K. P is equal to 0.15 when the kinetic order with respect to hydrogen is zero, and the surface may be fully carburized.

Decomposition of formic acid on a non-flashed platinum wire may be considered as follows. Let θ_c be the total fractional coverage of the surface by contaminants 1, 2, . . . , n , each giving fractional coverages $\theta_1, \theta_2, \dots, \theta_n$. On the basis of a Langmuir-type equilibrium (6) involving diffusion of contaminants from the interior of the wire to the surface

$$\begin{aligned}
 D_1 C_1 (1 - \theta_c) + D_2 C_2 (1 - \theta_c) + \dots \\
 + D_n C_n (1 - \theta_c) = k_1 \theta_1 \exp(-E_1/RT) \\
 + k_2 \theta_2 \exp(-E_2/RT) + \dots \\
 + k_n \theta_n \exp(-E_n/RT) \quad (2)
 \end{aligned}$$

where $D_i C_i$ gives the rate of approach of contaminant i to the surfaces and $k_i \theta_i \exp(-E_i/RT)$ gives the rate of removal of contaminant i to the gas phase. In a steady state the terms in Eq. (2) are separately equal to one another for a specific contaminant, i.e., $D_i C_i (1 - \theta_c) = k_i \theta_i \exp E_i/RT$. Now decomposition of formic acid at a flashed surface occurs with $P \sim 1$ over a wide temperature range (450–1800°K.) This is consistent with a transition state possessing two-dimensional translational and rotational freedom at the catalyst surface. For the nonflashed wire, terms allowing for contaminants must be introduced. These are contained in Eq. (2). The decomposition from 450–1800°K on a nonflashed surface is therefore given by

$$P = 1 - \theta_c + \theta_1 B_1 \exp(-E_1/RT) + \theta_2 B_2 \exp(-E_2/RT) + \dots + \theta_n B_n \exp(-E_n/RT) \quad (3)$$

where $B_i \exp(-E_i/RT)$ is the probability of decomposition of a formic acid molecule when it collides with the surface covered with contaminant i . This equation can be considerably simplified if the contaminant in the nonflashed wire is predominantly of a single type. Identification of foreign material requires mass-spectrometric study.

The decomposition of formic acid on a flashed surface may be formulated in terms of a Langmuir isotherm. Deposition of contaminant (possibly carbon) by residual gases and reaction appears to be the main cause for loss of activity during reaction. The rate of surface contamination r_R by the cracking of residual hydrocarbons is given by

$$r_R = p_R(1 - \theta_g)k_R \quad (4)$$

where p_R is the pressure of residual hydrocarbons, k_R a temperature-dependent velocity constant, and θ_g the fractional coverage due to the contaminant. The contamination rate r_F by formic acid is similarly given by

$$r_F = p_F(1 - \theta_g)k_F \quad (5)$$

The contaminant layer, if it is carbon, is unlikely to be removed by the low pres-

sure of hydrogen present in the gas phase since such a process is inconsistent with the thermodynamics of the synthesis of methane from carbon and hydrogen. It is, however, thermodynamically feasible to remove such a layer by water vapor present either in residual gases or even provided by the formic acid itself. Let the rate of this removal process be given by $p_W \theta_g k_W$ where p_W and k_W are the water partial pressure and the velocity constant, respectively. At elevated temperatures approaching 830°K [see, for example, NH_3 decomposition on carburized platinum (6)] carbon diffusion from the bulk to the surface may occur and so contribute to the surface deposition rate. Equating the deposition rate of carbon at the surface with its removal rate by water we obtain

$$p_F(1 - \theta_g)k_F + p_R(1 - \theta_g)k_R + DC(1 - \theta_g) = \theta_g k_W p_W \quad (6)$$

from which

$$\theta_g = \frac{p_F k_F + p_R k_R + DC}{k_W p_W + p_F k_F + p_R k_R + DC} \quad (7)$$

where DC gives the rate of diffusion of carbon through the bulk to the surface for a bulk concentration C of carbon. At low temperatures ($\sim 500^\circ\text{K}$) contamination of the flashed surface seems to occur mainly by residual gases so that

$$\theta_g = \frac{p_R k_R}{k_W p_W + p_R k_R} \quad (8)$$

Contamination by carbon from formic acid becomes important at higher temperatures and θ_g is given by

$$\theta_g = \frac{p_F k_F + p_R k_R}{k_W p_W + p_F k_F + p_R k_R} \quad (9)$$

At still higher temperatures, diffusion of carbon through the bulk to the surface occurs and $p_F k_F \gg p_R k_R$ so that

$$\theta_g = \frac{p_F k_F + DC}{k_W p_W + p_F k_F + DC} \quad (10)$$

These equations may be correlated with the previous experimental observations.

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