NOTES

On the Pressure Dependence of the Decomposition
of Formic Acid on Silver Catalysts

Although the decomposition of formic acid has often been employed in the study of catalysis by metals, the reaction mechanism is still in doubt. Some information about the sequence of reaction steps should be obtainable from the dependence of the rate of reaction on the pressure of formic acid in the gas phase.

The rates at 453 K and 511 K were measured in an all-glass static system (1) at pressures of formic acid in the range 10^{-3}–63 Torr. The catalysts were 100-nm thick films deposited at 298 K in a vacuum of $<10^{-6}$ Torr onto circular glass disks, (22 × 0.1 mm with 2 mm holes) in a metal bell-jar (Vacuum Generators Ltd.) sealed with Viton O-rings and pumped by sorption, Ti-getters and ion-pumps. Silver (Johnson and Matthey Ltd., 99.999% pure) evaporated from Ta-filaments was condensed onto the glass disks on a tray covered with freshly condensed silver. The system was opened, the disks turned over and another film deposited. The catalysts (surface area ≤ 350 cm^2) were mounted on a glass rod and sealed in a reactor tube (~ 99 cm^3) which was heated externally.

At the start of a reaction the reactor was opened to a tube with side arm (~ 58 cm^3) in which the reactant pressure had been established with a constant temperature bath around a separate reservoir of formic acid. After 300–900 s, the reservoir was isolated and the pressure of condensables reduced to $<10^{-3}$ Torr in ~ 10 s by cooling the side arm to 77 K. The residual pressure (H_2 + CO) was measured with a capacitance micromanometer (Consolidated Electrodynamics Corp. Type 23-105, range

5×10^{-4}–5×10^{-3} Torr). After evacuation, the pressure of CO_2 was measured with the side arm at 195 K. Products trapped in the reservoir were measured separately and the reaction on the walls of the system determined in the absence of catalysts. Dehydrogenation was virtually the only reaction occurring on the catalysts.

The change of rate of reaction at 453 K and 511 K with pressure of formic acid is shown in Figs. 1a and b, respectively. The encircled points, which are each averages of 3–9 rate determinations have relative standard deviations of ±2.5%. The points were fitted by analytical expressions based on the assumptions that:

(a) reaction rate is proportional to some power of the surface concentration of formic acid:

$$r = k_0 \theta^y. \tag{1}$$

(b) adsorption of formic acid may be described by a Langmuir isotherm (2):

$$\theta = bp/(1 + bp). \tag{2}$$

Combining (1) and (2) gives

$$r = k_0[bp/(1 + bp)]^y, \tag{3}$$

which was rearranged for computation as

$$1/r^{1/y} = a + (c/p), \tag{4}$$

With $k_0 = 1/a^y$, and $b = a/c$.

The exponent y in Eq. (4) was varied in steps of 0.01 over the range 0.33–2.00, and values for (a) and (c) obtained from weighted least-square fitting. For the selection of the best fit, the value of y (y_m) corresponding to the minimum of the mean
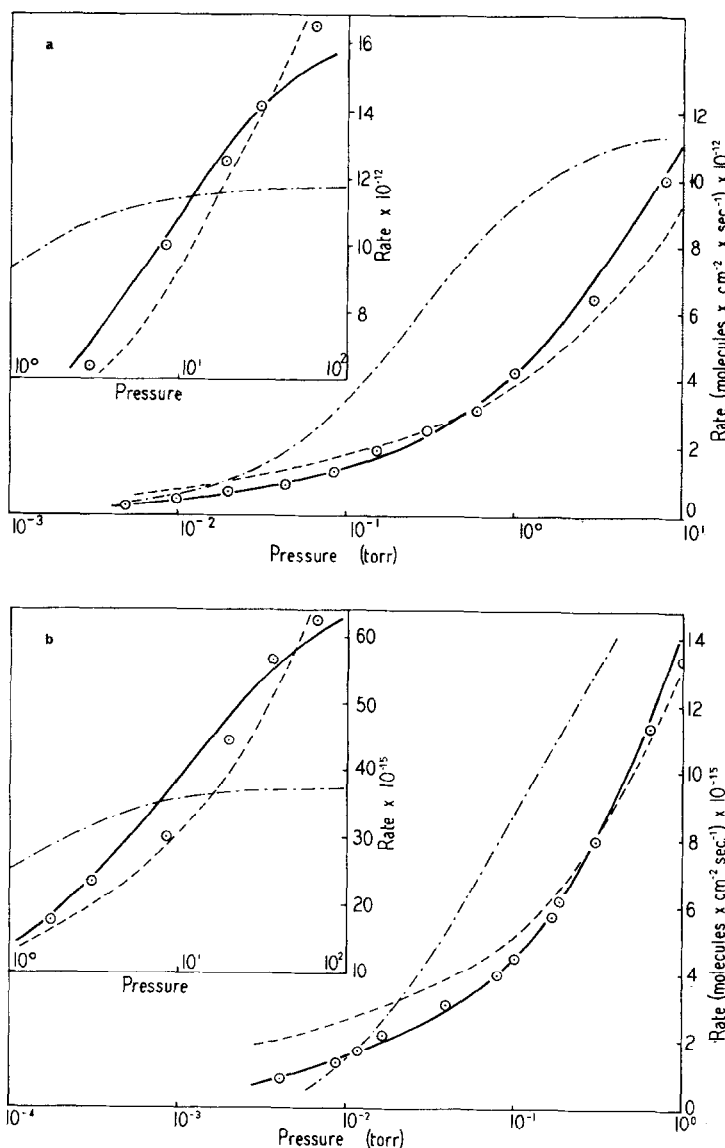
FIG. 1. Rate of decomposition of HCOOH (molecules $\times$ cm^{-2} $\times$ s^{-1}) vs pressure of HCOOH (Torr) in the gas phase at (a) 453 K, (b) 511 K. The encircled points ($\odot$) mark the average experimental rates. The curves have been calculated according to Eq. (4) (see text) with the following values for the exponent y: —— $y = 0.5$; - - - $y = 0.36$; --- --- $y = 1.0$.

sum of squares (MSS), was determined, where $\text{MSS} = ((r_0 - r_c)/r_0)^2/(N - 1)$; $N =$ number of points, $r_0 =$ observed rate, and $r_c =$ calculated rate. (See Fig. 2.) The 95% confidence limits of y_m are 0.56–0.43 and 0.51–0.44 for 453 K and 511 K, respectively. The variation of fit with y over the pressure range is illustrated with curves for $y = 1.0$, 0.5, and 0.36 (Figs. 1a,b).

Values of k_0 and b for these values of y are given in Table 1.

The apparent activation energy $E_a = 29.4 \pm 0.4$ kcal mole^{-1} and the log of the preexponential factor log $A = 27.5 \pm 0.5$ in the zero-order range, derived from the temperature dependence of k_0 (at $y = 0.5$), are close to previous values for such films (1). Equation (4) (with $y = 0.5$) was also
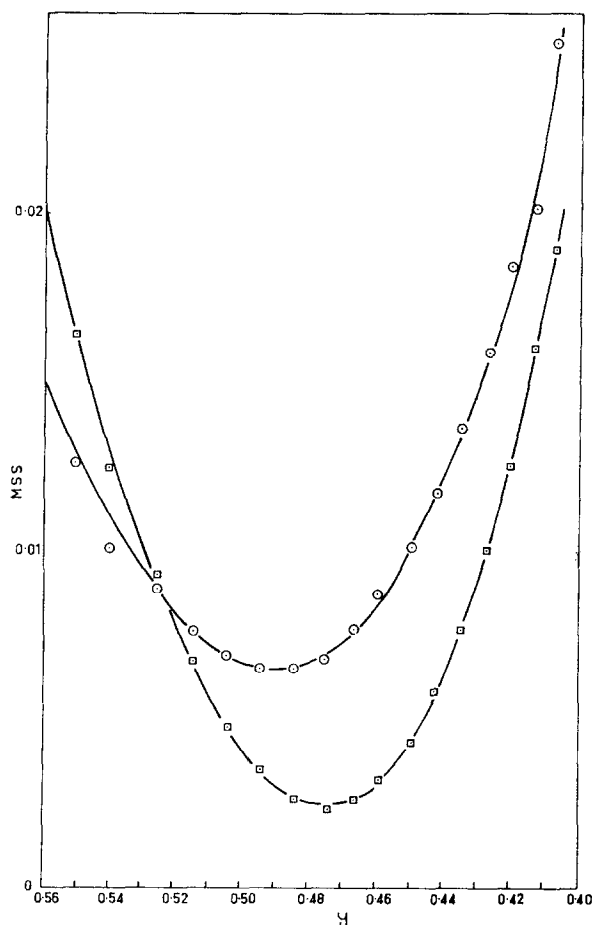
Fig. 2. Plot of mean sum of squares, MSS $= [(r_0 - r_c)/r_0]^2/(N - 1)$ vs exponent y in Eq. (4) (see text). $\bigcirc$, 453 K; $\square$, 511 K.

fitted to previous data (1) for formic acid pressures in the range 2–80 Torr on catalysts of different surface structures. In this case, values for E_a and log A also agreed with those reported for 63 Torr (1).

Values of the heat of adsorption of formic acid (ΔH_{ads}) during reaction calculated from b (at the 95% confidence limits of y_m) were 2.2–9.8 kcal mole^{-1} at 453 K, and

3.4–7.0 kcal mole^{-1} at 511 K. These values indicate physical adsorption rather than chemisorption which agrees with observations on silver powder catalysts (2).
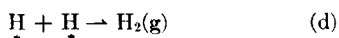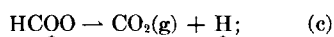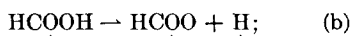
As the values of E_a, log A and ΔH_{ads} agree with those reported (1, 2), we believe that the model underlying Eq. (3) is valid. The application of equilibrium expressions to derive virtual pressures of adsorbed species

TABLE 1

VALUES OF k_0 AND b IN EQUATION (3) (SEE TEXT) FOR SELECTED VALUES OF THE EXPONENT y

		1.0	0.5	0.36
	y			
453 K	k_0 (molecules $\times$ cm^{-2})	1.2×10^{13}	1.7×10^{13}	5.1×10^{13}
	b (Torr^{-1})	3.2	-6.7×10^{-2}	8.8×10^{-4}
511 K	k_0 (molecules $\times$ cm^{-2})	4.2×10^{14}	7.0×10^{14}	7.8×10^{14}
	b (Torr^{-1})	3.4	4.3×10^{-2}	7.1×10^{-3}

in the gas phase, and a Langmuir isotherm for gas mixtures to describe adsorption of these species during reaction (3), leads to a pressure dependence of the reaction rate other than that observed. This discrepancy probably arises from the irreversibility of the dissociation of adsorbed HCOOH. We prefer, therefore, to discuss the results in terms of published reaction mechanisms.

The good fit over the whole range of pressures we interpret as indicating the same rate-determining step throughout. At low pressures the order of the reaction tends to 0.5. This makes a bimolecular surface reaction unlikely (4, 5), but the following scheme (6):

$$HCOOH(g) + * \leftrightharpoons HCOOH; \qquad (a)$$

$$HCOOH \rightarrow HCOO + H; \qquad (b)$$

$$HCOO \rightarrow CO_2(g) + H; \qquad (c)$$

$$H + H \rightarrow H_2(g) \qquad (d)$$

can account for the pressure dependence of the reaction. In the above scheme, step (c) has been postulated to be rate-determining (1, 7), i.e.,

$$r = k_r \theta_{HCOO}.$$

If this is the case, and (i) the equilibria (a) and (b) are not appreciably disturbed, (ii) if $\theta_{HCOO} \approx \theta_H \ll \theta_{HCOOH}$ so that $\theta_{HCOOH} = (1/K_d)\theta_{HCOO}^2$, then

$$r = k_r K_d^{1/2} \theta_{HCOOH}^{1/2},$$

and substitution from (2) gives

$$r = k_r K_d^{1/2}[bp/(1 + bp)]^{1/2},$$

which is Eq. (3) with $k_0 = k_r K_d^{1/2}$ and $y = 0.5$, i.e., close to y_m.

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Infrared Study of Cation-Exchanged Mordenites and Y Faujasites Adsorbed with Ammonia and Pyridine

Many reactions over synthetic zeolites as an excellent solid acid catalyst have been studied. In some cases, it has been found that the catalyst activity and the distribution of the reaction products depended on the geometric relation between the zeolite pore system and the molecular shape (1, 2). Disproportionation of alkylbenzenes over

synthetic zeolites has often been studied (3–8), and in the case of disproportionation of ethyltoluenes over H mordenite catalyst, it has been shown that the distribution of produced trialkylbenzenes was affected by the pore size of the catalyst (7, 8).

The authors have also reported previously on the vapor phase disproportionation