977. *The Decomposition of Formic Acid and Methanol on Copper–Nickel Alloys*

By D. F. Quinn and Duncan Taylor

The kinetics of the heterogeneous decomposition of formic acid and methanol on copper–nickel alloys have been investigated at 10—25 mm. For the first 30—40% of the decomposition, the formic acid reaction is zero-order, and the rate, with increasing copper concentration, first decreases to a minimum at about 30 atom per cent copper, then rises to a maximum at 70—80%, and finally decreases to a value for copper which is less than that for the minimum. The rate for the major part of the methanol reaction conforms closely to the equation:

$$\text{Rate} = kk_1P_{\mathrm{MeOH}}/(1 + k_1P_{\mathrm{MeOH}} + k_2P_{\mathrm{CO}} + k_3P_{\mathrm{H_2}}),$$

where the P's represent pressures and the k's are constants, and follows the same trend with increasing copper concentration as does the formic acid reaction, but with the minimum and maximum more pronounced. The results are interpreted in terms of the activity–composition patterns based on the band theory of metals discussed by Bond and Mann, the rate-determining stage in both reactions being considered to involve the donation of electrons from negatively charged adsorbed species to the catalyst.

Recent kinetic work [1] on the metal-catalysed decomposition of formic acid, and infrared absorption studies of formic acid adsorbed on metals, indicate that the rate-determining stage of the zero-order decomposition is the breakdown of a negatively charged adsorbed formate ion intermediate. It has been argued [2] that optimum catalytic activity in a series

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[1] P. Mars, J. J. F. Scholten, and P. Zwietering, *Adv. Catalysis*, 1963, **14**, 35.

[2] W. M. H. Sachtler and J. Fahrenfort, " Actes 2me Congres Internationale de Catalyse (Paris, 1960)," Technip, Paris, 1961, vol. 1, p. 831.

of metals is observed in an intermediate region where neither the difficulty of formation of the ion nor its stability is too great. Earlier workers [3,4] favoured a positively charged intermediate and the operation of an electronic factor; in particular, for copper–nickel alloy catalysts, they suggested that the filling of the vacancies in the nickel *d*-band as the copper concentration is increased to 60 atom per cent decreases the probability of electron transfer to the alloy, resulting in a decrease in the activity of the catalyst in accordance with their observations. From both points of view, the rate-determining stage involves, in simple terms, donation of electrons to the catalyst. Since the calculated heats of reactions of copper and nickel with formic acid are roughly the same,[2] as also are the decomposition temperatures of the bulk formates,[1] it may therefore still be possible to detect the operation of an electronic factor for the copper–nickel system even though the effective intermediate is the formate ion. Bond [5] concluded that the increase in activation energy with increase in copper content, observed [6,7] for alloys containing greater than 80% of copper, together with an ill-defined maximum activity [6] at approximately 80% copper are the only indications of the expected electronic effect.

In an attempt to obtain further evidence for or against the electronic-factor concept, on the basis of the theoretical activity–composition patterns proposed by Bond and Mann,[8] the decomposition of formic acid on copper–nickel alloys has been re-examined. Furthermore, since the existence of an electronic effect will be most easily demonstrated when the difference in the activity of the parent metals is greatest, the dehydrogenation of methanol on the same alloys was investigated also.

EXPERIMENTAL

Catalysts.—The copper–nickel alloys were prepared in powder form by Best and Russell's method,[9] the reduction being carried out *in situ* in the reaction vessel for 24 hr. at 500° in a stream of purified electrolytic hydrogen. Surface areas were determined by the B.E.T. method with argon at −196° (14·4 Å^2 was taken for the cross-section area of the argon atom). Measurement of the unit-cell dimensions of the alloys with a Philips Diffractometer gave values agreeing to within ±0·002 Å with those of Owen and Pickup,[10] and confirmed that the catalysts were homogenous solid solutions.

Formic Acid and Methanol.—AnalaR formic acid was dried by partial freezing [11] until the melting point was 8·2°, further purified by trap-to-trap distillation, and stored at −78°. Methanol was dried with magnesium,[12] fractionally distilled with a 60-cm. column packed with glass helices, subjected to trap-to-trap distillation, and stored at −196°.

Reaction System and Procedure.—A conventional all-glass high-vacuum system was employed, with two liquid-nitrogen traps to protect the catalysts from mercury vapour from the diffusion pump. The cylindrical reaction vessel (volume 80 c.c.) was connected by 2-mm. capillary tubing to a Bourdon gauge fitted with an optical lever system, and then by a tap lubricated with Apiezon L grease to the manifold to which were attached the formic acid and methanol storage vessels, the hydrogen purification train, and a Macleod gauge protected by a liquid-nitrogen trap. An electric furnace was used to maintain the reaction vessel temperature constant to within ±0·1°, temperatures being measured with a calibrated thermocouple.

To carry out a run with either formic acid at 80—200° or methanol at 140—330°, the appropriate storage vessel was allowed to warm to room temperature, opened briefly to the pumps, and

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[3] G.-M. Schwab, *Discuss. Faraday Soc.*, 1950, **8**, 166; *Trans. Faraday Soc.*, 1946, **42**, 698; G.-M. Schwab and E. Schwab-Agallidis, *Ber.*, 1943, **76**, 1228.

[4] D. A. Dowden and P. W. Reynolds, *Discuss. Faraday Soc.*, 1950, **8**, 184.

[5] G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962, p. 424.

[6] G. Rienäcker and H. Bade, *Z. anorg. Chem.*, 1941, **248**, 45.

[7] P. Fuderer-Luetic and I. Brihta, *Croat. Chem. Acta*, 1959, **31**, 75.

[8] G. C. Bond and R. S. Mann, *J.*, 1959, 3566.

[9] R. J. Best and W. W. Russell, *J. Amer. Chem. Soc.*, 1954, **76**, 838.

[10] E. A. Owen and B. Pickup, *Z. Krist.*, 1934, **88**, 116.

[11] A. S. Coolidge, *J. Amer. Chem. Soc.*, 1930, **52**, 1874; A. J. Ewins, *J.*, 1914, **105**, 354.

[12] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, London, 3rd edn., 1956, p. 169.

then opened to the reaction vessel to admit the reactant to the desired pressure (10—25 mm.). The increase in pressure due to the decomposition was then recorded as a function of time. For runs with formic acid below 110°, small corrections to the pressure increases were made to allow for the dimerisation of the acid; above 110° the corrections were insignificant. The zero-order rates for formic acid (observed for up to 30—40% decomposition), and the initial rates for methanol, were calculated in the units mol. site^{-1} sec.$^{-1}$, assuming $1{\cdot}6 \times 10^{15}$ metal sites per cm.^{2} of B.E.T. area. At the end of runs with formic acid, no carbon monoxide could be detected in the gas phase by infrared absorption measurements, and only traces were detected by use of a palladosulphite detector tube. The methanol products were assumed to consist only of hydrogen and carbon monoxide. Reproducibility of rates from run to run was within ±5% provided that the reaction system was evacuated to less than 10^{-5} mm. for 1 hr. between runs. Blank runs in the absence of catalyst gave negligible rates of decomposition at temperatures up to 270° with formic acid and up to 400° with methanol.

RESULTS AND DISCUSSION

For the formic acid reaction, the variation of activity with alloy composition is shown in Figure 1. The pattern is similar to that found previously [6] and appears to be a case intermediate between the A and B idealised activity–composition patterns proposed by Bond and Mann [8] on the basis of the band theory of metals. In A, the controlling factor in the activity is the concentration of holes in the *d*-band, $[h_d]$, which diminishes to zero as the concentration of copper increases from zero to 60 atom per cent; in B, on the other hand, the activity increases progressively as $[h_d]$ decreases, until at 60% of copper there is a sudden decrease in activity, a pattern to be expected if there is a continuous decrease in the strength of adsorption as the holes in the *d*-band are filled. A combination of the A and B effects would qualitatively reproduce the activity pattern of Figure 1, provided that the critical copper concentration is nearer to 80 than 60%. That a significant $[h_d]$ may persist above 60% has been suggested,[13] and, furthermore, the catalysts here used were shown to be paramagnetic when the copper content was 49·6—82·2%. Activation energies (kcal. mole.$^{-1}$, ±0·7 kcal.) and pre-exponential factors (molecules site^{-1} sec.$^{-1}$) were as follows:

At. % Cu	0	20·1	29·3	49·6	63·8	69·2	82·2	92·6	100
Activation energy	24·2	23·9	20·8	23·8	26·6	26·1	23·4	24·7	20·3
$\log_{10} A$	10·6	10·4	8·5	10·4	12·0	12·0	9·9	9·7	7·0

A reasonable compensation effect is evident. No marked rise in activation energy occurs at the copper-rich end of the range, in contrast to the observations of Reinäcker and Bade.[6]

Typical kinetic data for the methanol dehydrogenation reaction are shown in Figure 2, in which the linear plot corresponds to the integrated form [14] of the equation:

$$\text{Rate} = kk_1P_{\text{MeOH}}/(1 + k_1P_{\text{MeOH}} + k_2P_{\text{CO}} + k_3P_{\text{H}_2}),$$

where the *P*'s represent pressures and the *k*'s are constants. The equation fitted the kinetics in the great majority of the runs up to 90% decomposition. The slope and intercept of the linear plot are given, respectively, by $(k_3 + 0{\cdot}5k_2 - 0{\cdot}5k_1)/(1 + 2k_3P_0 + k_2P_0)$ and $kk_1/(1 + 2k_3P_0 + k_2P_0)$ from which, in principle, the values of the rate constant k and of k_3/k_1 and k_2/k_1 can be calculated, knowing the slope and intercept for three values of P_0, the initial methanol pressure. Unfortunately, the solution of the appropriate equations for k was so sensitive to small errors in the slope and intercept values that reliable and consistent values of k were not obtained. Therefore, in the activity–composition pattern in Figure 1, initial rates are used. The pattern is very similar to that for the formic acid reaction, but with the minimum and maximum more accentuated. The interpretation of

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[13] B. R. Coles, *Proc. Phys. Soc.*, 1952, **65***B*, 221.

[14] A. Lawson and S. J. Thomson, *J.*, 1964, 1861 (ref. 52).

the pattern is acordingly believed to be the same as in the formic acid case, and the rate-determining stage to be the decomposition of adsorbed $CH_3O(\delta-)$. Over the whole range of catalyst composition, the activation energies calculated from the temperature coefficient of the initial rates were within the range 21—24 kcal. mole^{-1}, except for the 49·6% copper alloy where the value was 27. The values could not be determined to better than ±2 kcal. mole^{-1}. The pre-exponential factors varied with composition in a manner similar to that for the formic acid reaction, but the values were approximately two orders of magnitude less.

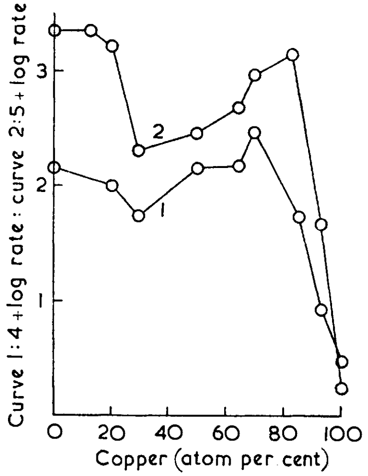

FIGURE 1. Variation of the rate of decomposition of formic acid (1) at 150°, and methanol (2) at 200°, with the proportion of copper in the catalysts. Rates are in molecules site^{-1} sec.$^{-1}$.

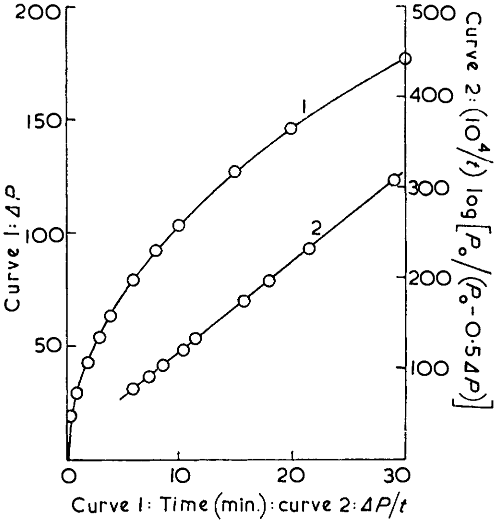

FIGURE 2. Curve 1. Plot of ΔP, the pressure increase, against time for the decomposition of methanol at 200° on a catalyst containing 63·8 atom per cent of copper.
Curve 2. Plot of $(10^4/t)\log_{10}[P_0/(P_0 - 0{\cdot}5\Delta P)]$ against $\Delta P/t$ for the data in curve 1. P_0 is the initial methanol pressure in the same units as ΔP.

Sachtler, Dorgelo, and Jongepier[15] recently studied the phase composition and work function of vacuum-deposited copper–nickel alloy films, and concluded that the catalytic activity of the alloys, provided that they are in true thermodynamic equilibrium, should remain constant over the range 2—80 atom per cent of copper. This is clearly not the case with the powdered alloys here used. On the other hand, it is to be noted that, particularly for the methanol reaction, the activation energies vary comparatively little with alloy composition.

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CHEMISTRY DEPARTMENT UNIVERSITY OF EDINBURGH. [*Received March* 30*th*, 1965.]

[15] W. M. H. Sachtler, G. J. H. Dorgelo, and R. Jongepier, *J. Catalysis*, 1965, **4**, 100.