

Dehydrogenation of Formic Acid by Cu_3Au

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The rates of dehydrogenation of formic acid on ordered and disordered forms of the alloy Cu_3Au have been studied in the temperature range 460° to 650°K at formic acid pressures of 760 torr, where the reaction is zero order in acid vapor pressure. No significant correlation has been observed between the experimental activation energy and the degrees of long- and short-range order in the alloy, although activation energies between 7.5 and 23 kcal mole⁻¹ were detected. Activation energy changes were effected by heat-treatments; and a strong correlation between the activation energy of the reaction and pre-exponential frequency factor was observed, suggesting that active sites, possibly lattice vacancies, are important for the catalytic process.

INTRODUCTION

Studies of the behavior of alloy systems, particularly those containing transition metals (1-7) are especially relevant to discussions of the electronic factor in heterogeneous catalysis and related phenomena. Progressive modification of *d*-band vacancy concentration (2, 3) or the height of the Fermi surface (4) through an alloy series, whose lattice geometry remained constant and in which the dimensions of the unit cell varied only slightly, have demonstrated the reflection of the electronic factor of the bulk catalyst in the properties of the surface.

Work by Rienacker (8), on the high-pressure (zero order) dehydrogenation of formic acid on ordered and disordered (9) forms of the alloy Cu_3Au suggest that the experimental activation energy on the disordered alloy is 3.5 kcal mole⁻¹ higher than on the ordered form. The present work was undertaken in an attempt to elucidate the causes of the effect, for which Rienacker has offered no explanation.

Both ordered and disordered forms of the alloy are based on a face-centered lattice; common to both copper and gold in the completely ordered form, with copper atoms

at the center of each face and gold atoms at the corners. The completely disordered alloy has copper and gold atoms placed randomly on lattice points. Thermodynamic (10-13) and crystallographic (14, 15, 16) investigations reveal that order-disorder transition in Cu_3Au is not simple, and may be described in terms of long- and short-range order parameters (9, 15, 16, 17). Equilibrium long-range order [coherent over distances comparable with crystallite dimensions (14)] decreases as the temperature of the sample is raised from about 490° to 661°K , where it sharply falls to zero. Short-range order (over dimensions comparable with those of the unit cell), which evidently persists up to much higher temperatures (15, 16), may alternatively be described in terms of the effective size of ordered regions separated by three-dimensional ordering mistakes (14, 15). Catalytic studies are further complicated by the long (~ 50 hr) relaxation times of ordering processes (14) even in the region of the transition temperature, which allow studies to be made with alloys of metastable configuration.

The smeared (18) order-disorder transformation in Cu_3Au prohibits the application of classical phase equilibrium thermodynamics. It is, however, possible to estimate the energy differences between the two

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modifications from heat capacity (13) and electrochemical data (19), which together with reasonable estimates of configurational entropy differences between the modifications ($0.095 \text{ cal g atm}^{-1} \text{ }^\circ\text{K}^{-1}$) allow an upper limit to be set upon changes (20) in the height of the Fermi surface on disordering (0.03 eV or $0.7 \text{ kcal g atm}^{-1}$). No account of interaction energies (21) between copper and gold in lattices of different order has been taken, and the change in Fermi energy is probably very much smaller. Such small changes in Fermi energy and the very small difference in lattice parameters (14) between completely ordered and disordered forms ($a = 3.7430$ and 3.7485 \AA , respectively, at 633°K) seem unlikely to have direct effects, of the magnitude reported, on the activation energy of the catalytic process.

EXPERIMENTAL

Dehydrogenation of formic acid by Cu_3Au was effected in a modified Schwab reactor (22) in which the vapor of boiling formic acid (at 760 torr) was cycled over the heated catalyst. Rates of reaction were deduced from pressure changes in the system measured with a quartz spiral differential manometer ($\pm 5 \times 10^{-3}$ torr). All rates were determined in the presence of excess hydrogen, previously purified by diffusion through a palladium membrane. Hydrogen was admitted to the reactor along with outgassed formic acid so that the latter boiled at its normal boiling point.

Formic acid was prepared from analytical grade acid ($>99\%$) by drying with anhydrous calcium sulfate and subsequent sublimation, after storage over anhydrous copper sulfate, into the storage section of the vacuum apparatus. The acid was outgassed by repeated sublimations, before being admitted to the reaction chamber.

The copper-gold alloy wire (0.071-cm diameter) used as catalyst in the present work was analyzed chemically and found to have the composition 51.24 wt % gold, 48.76 wt % copper, which corresponds to an alloy composition of $\text{Cu}_{2.95}\text{Au}$. The composition and homogeneity of the wire were checked by accurate determination of the

lattice parameters of fully annealed sections removed from each end of the catalyst specimen.

The catalyst specimen was freed from strain and possible surface oxidation by annealing at 780°K for 5 days in an atmosphere of pure hydrogen. The catalyst was further annealed in hydrogen at temperatures, and for periods, appropriate to the degree of ordering desired in the alloy; and finally outgassed at 10^{-6} torr, before being quenched to some temperature within the range in which kinetic studies were made. All heat treatments were performed in the reactor.

The rates of reaction were determined over periods between 2 and 15 min, depending upon reaction temperature and the catalyst modification. Cumulative periods over which measurements were made for each modification was always short (~ 2 hr) compared to the relaxation time of the ordering process (~ 50 hr) at the highest temperature within the range.

Catalyst structures were determined at the end of each series by X-ray crystallographic examination (23) using Debye-Scherrer techniques. Structure determination was performed at the end, rather than the beginning, of each series, as exposure of catalyst materials to air would have necessitated cleaning and possible structure modification.

Long-range order parameters were obtained from the relative intensities of the 210 (superlattice) and 200 (fundamental) reflections, and interpolation of data derived by Wilchinsky (15).

Lattice parameters, which Betteridge (16) has shown to be linearly related to the short-range order parameter, were calculated from the d spacings corresponding to observed X-ray reflections, and refined by extrapolation to $\sin^2 \theta = 1$ (23).

RESULTS

Experimental specific rate constants for the dehydrogenation reaction were found to fit the Arrhenius equation (Fig. 1) from which the experimental activation energy (ΔE) and the pre-exponential frequency factor B were derived using the method of

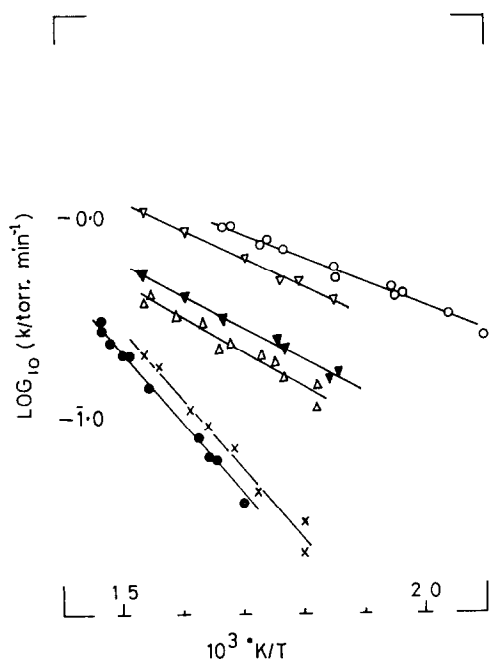


FIG. 1. Dependence of rate of dehydrogenation of formic acid by Cu_3Au on catalyst form and reaction temperatures: \times , Series 1; \circ , Series 2; \triangle , Series 3; \bullet , Series 4; ∇ , Series 5; \blacktriangledown , Series 6.

least squares. The characteristic frequencies of the reaction B_m (molecules $\text{cm}^{-2} \text{sec}^{-1}$) were obtained from B (torr min^{-1}) from a knowledge of the volume (250 ml) of the reaction system, the geometrical area of the catalyst (5.6 cm^2), and the pressure of formic acid (760 torr) over it.

Table 1 shows values of ΔE and B_m for a single catalyst specimen subject to successive and different heat-treatments (Series 1 through 5) and a separate sample (6) identical in chemical composition, but badly strained and dislocated by cold-working. This sample was subsequently annealed and held at 790°K before quenching (7). Also contained in Table 1 are the temperature ranges over which kinetic measurements were made, the lattice parameters, and estimated long-range order parameters of the catalysts.

DISCUSSION

The data in Table 1 indicate no simple correlations between the kinetic parameters

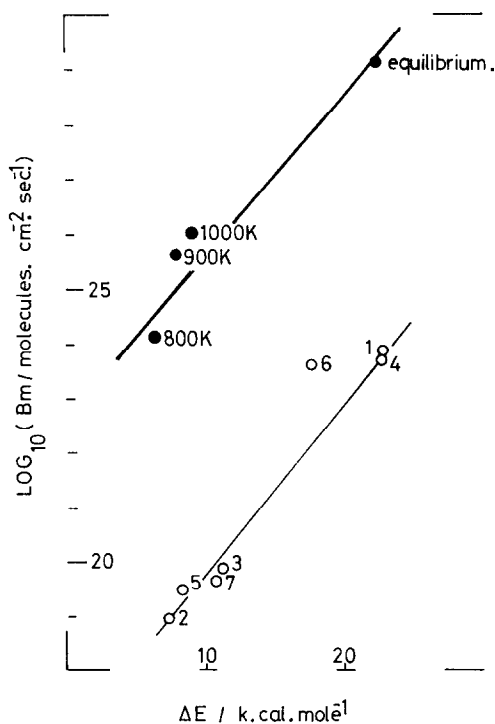


FIG. 2. Compensation effects in dehydrogenation of formic acid by Cu_3Au : \circ , experimental; \bullet , calculated.

of the formic acid dehydrogenation on the alloy Cu_3Au and its long- or short-range order. The system does, however, exhibit a positive compensation (1) between the experimental activation energies and pre-exponential frequency factors. (See Fig. 2.)

It has been demonstrated (24, 25) that correlations of the type observed may arise in systems in which the overall rate of reaction is the sum of parallel processes of comparable magnitude, but with different temperature coefficients; and if the relative contribution of each process depends in some way upon experimental conditions or the history of the system.

It has been proposed that compensation effects for formic acid dehydrogenation on various alloys and pure metals (26-29) are due to orientation of crystallites in polycrystalline catalyst surfaces. The importance of such effects has been demonstrated for copper by single-crystal work (30). Other studies on silver (30-33), however, have

TABLE 1
 CATALYTIC DEHYDROGENATION OF FORMIC ACID^a VAPOR BY Cu₃Au

Series	Sample treatment	Lattice ^b parameter at 288°K Å	Long-range order parameter	ΔE (kcal mole ⁻¹)	B _m (molecules cm ⁻² sec ⁻¹)	Temperature range (°K)
1	635°K 24 hr	3.738	0.8	22.9	7.1 × 10 ²³	520–650°
2	Sample from 1, 770°K 0.5 hr	3.737	0.5	7.5	8.1 × 10 ¹⁸	475–600°
3	Sample from 2, 780°K 4.2 hr	3.738	0.1	11.3	6.9 × 10 ¹⁹	550–650°
4	Sample from 3, 670°K 240 hr	3.741	0	22.9	4.4 × 10 ²³	585–680°
5	Sample from 4, 780°K 125 hr	3.749	0	9.2	3.0 × 10 ¹⁹	540–650°
6	Cold-worked sample held at 780°K 10 hr	3.746	0	17.9	4.1 × 10 ²³	460–550°
7	Sample from 6, held at 653°K 100 hr, 780° 10 hr	3.747	0	10.4	4.3 × 10 ¹⁹	543–650°

^a 760 Torr pressure.

^b ±0.001 Å.

revealed variations of experimental activation energies, and compensation on surfaces of well-defined orientation.

Surface heterogeneity arising from contamination or the presence of lattice defects has also been suggested as a likely cause of compensation effects (24, 25, 34). The presence of frozen-in defects in flashed nickel and copper (35) filaments has been held responsible for superactivation of these metals; a proposal which has been countered (26) by the suggestion that flashing at high temperatures results in a cleaner and consequently more active surface. Activation of nickel catalysts by defects has been disputed in a communication (36) in which it was reported that the absolute activity of filaments subjected to extreme torsional deformation remained unchanged. Since, however, the absolute activity of systems subject to compensation effects remains substantially unchanged over certain small temperature ranges, it would be unwise to draw firm conclusions in the absence of experimental detail.

The reversible character of the effects in this work (Table 1, Series 1 through 4) is difficult to reconcile with explanations involving catalyst contamination.

The qualitative dependence of the experimental activation energy upon the temperature and duration of the annealing processes given in Table 1 suggests an active-site mechanism for the reaction on lattice defects. The equilibrium concentration of

defects, even in the surface of a metal where the energies of formation (E_f) are of the order of half those of the equivalent defects within the bulk (37), are small, but sufficient to account for the observed frequency of the dehydrogenation: 10³–10⁹ molecules site⁻¹ sec⁻¹ (from Table 1), and 10⁷ molecules defect⁻¹ sec⁻¹ at 750°K for single lattice vacancies defects with an estimated energy of formation in the surface of 11.5 kcal mole⁻¹. [Estimated from data for copper and gold (38).] The maximum frequency predicted (37) by the statistical theory of reaction rates (kT/h) is approximately 10¹³ sec⁻¹.

Energy barriers to migration of defects (E_m) are generally small; and as Stone (39) points out, mobility of surface defects in the surface may be an important factor in contributing to catalytic phenomena. Migrating defects likely to be of importance (38) in Cu₃Au are the single lattice vacancy ($E_f = 11.5$ kcal mole⁻¹, $E_m = 11.5$ kcal mole⁻¹), the double lattice vacancy ($E_f = 17.3$ kcal mole⁻¹, $E_m = 4.6$ kcal mole⁻¹), but not the interstitial ($E_f = 60$ kcal mole⁻¹, $E_m = 1$ kcal mole⁻¹). The rate at which defects transfer from one site to another may be written (40)

$$r = (E_m/\mathfrak{N}h) \exp(-E_m/RT) \text{ sec}^{-1}$$

where \mathfrak{N} is Avogadro's number and h , Planck's constant.

Although it is apparent that defects of the above type could give rise to compensation

effects, calculations show that variations of the relative concentrations of these defects in frozen equilibrium with the higher temperatures used in catalyst heat-treatments cannot explain the extremes of compensation observed in this work.

Variations of experimental activation energies and pre-exponential factors over a sufficiently large range may be obtained if it may be assumed that, whereas the defect concentration in the surface of catalysts annealed at the higher temperatures remains substantially unchanged during kinetic measurements, in the catalysts annealed at the lowest temperatures, the concentration of surface defects is close to the equilibrium values at all temperatures within the range over which rate studies were made. Since the energy of formation of defects in the surface is approximately half that of the same defect in the bulk, the energy barrier to diffusion of defects into the bulk from the surface where they are formed (41) will be greater by approximately the energy of formation of the defect in the surface, than the barrier to diffusion towards the surface. This situation would permit defect concentration in the surface to achieve steady state concentrations close to equilibrium values, provided that the bulk concentrations are small. Alloys annealed at the higher temperatures will contain an excess of defects. In a crystal with dimensions of only a micron, the number of single defects in the surface at 650°K is about 10⁵ and those in the bulk 3 × 10⁹, and is probably sufficient to maintain high surface concentrations during the dehydrogenation reaction.

The combined rate of migration of defects within the surface

$$r_{\Sigma} = \frac{N}{\delta h} \sum_i E_{mi} \exp\left(\frac{-E_{mi}}{RT}\right) \exp\left(\frac{-E_{ti}}{RT}\right)$$

molecules cm⁻² sec⁻¹

where N is the concentration of surface atom sites ($\sim 10^{15}$ cm⁻²), shows adequate compensation between

$$\frac{-Rd(\ln r_{\Sigma})}{d(1/T)}$$

and

$$\ln r_{\Sigma} + \frac{(1/T) (d \ln r_{\Sigma})}{d(1/T)}$$

which may be identified, respectively, with the ΔE and $\ln B_m$ of the dehydrogenation reaction (see Fig. 2). The estimated rate of migration of defects in the surface is 10⁶ greater than the rates of dehydrogenation on catalysts and suggests that the conformation of the adsorbate molecules at the time of a defect transition determines whether or not the adsorbate decomposes.

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