dicating that the skewness is more nearly related to the surface areas of the molecules than their volumes. Such a treatment has been proposed by Langmuir.[19] Values of

$$-\frac{A_2}{A_0}\Big/\left(\frac{V_1 - V_2}{V_1 + V_2}\right)^2$$

appear to be highly temperature dependent, increasing rapidly near the temperatures corresponding to phase separation. This is a measure of the flattening of the free energy function and may be attributed to clustering. In the case of the quasi-chemical model of solutions,[20] the first-order correction to the free energy due to non-random mixing introduces a term in $(x_1x_2)^2$.

In the earlier studies,[10,21] the volume of mixing functions were found to be virtually symmetrical. Careful analysis[4] of the perfluoro-*n*-hexane–*n*-hexane system has shown them to be slightly skewed toward the fluorocarbon axis, the maximum occurring at $x = 0.524$ at 25°. This can be at least qualitatively explained by the relationship first

$$\Delta V = \frac{\alpha T F^E}{\delta^2}$$

proposed by Scatchard[22] and later by others,[23,24] where α and δ are the thermal coefficient of expansion and solubility parameter of the isolated components. The excess free energy functions are skewed toward the hydrocarbon axis, but the larger thermal coefficients of expansion and lower solubility parameters of the fluorocarbons combine to produce a coefficient which is concentration dependent in such a way that the excess volume function is nearly symmetrical. This was not the case for the perfluoromethane–methane system recently studied by Croll and Scott,[25] where the thermal coefficient of expansion of perfluoromethane was found to be smaller than that of methane and the solubility parameter larger.

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[19] I. Langmuir, "Colloid Symposium Monograph," Vol. III, The Chemical Catalogue Co., Inc., New York, N. Y., 1925.

[20] See ref. 2, p. 146, also E. A. Guggenheim, "Mixtures," The Clarendon Press, Oxford, 1952, p. 64; Prigogine, "The Molecular Theory of Solutions," North-Holland Publ. Co., Amsterdam, 1957, p. 63.

[21] J. H. Simons and J. W. Mausteller, *J. Chem. Phys.*, **20**, 1516 (1952).

[22] G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

[23] See ref. 2, p. 138.

[24] R. L. Scott, *Disc. Faraday Soc.*, **15**, 47 (1953).

[25] I. M. Croll and R. L. Scott, *J. Phys. Chem.*, **62**, 954 (1958).

ORONO, MAINE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN]

The Decomposition of Formic Acid Vapor on Nickel Surfaces[1]

BY ROSWELL J. RUKA, L. O. BROCKWAY AND JAMES E. BOGGS[2]

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A study of the decomposition rate of formic acid in a flow system is combined with an examination of the nickel surfaces used as catalysts. Electron microscopy, electron diffraction and vacuum microweighing techniques are applied. Reproducible rates and activation energies are attained with specimens of different crystallographic and physical structure when careful attention is given to the pre-treatment of the surfaces and specially purified formic acid is used. An initially high decomposition rate declines to a steady state. The rate of this decline is a function of the pre-treatment of the nickel. Nickel formate films were detected only under special conditions and do not play a part in the decomposition under conditions for which the reaction has usually been studied.

The kinetics of the decomposition of formic acid vapor over hot nickel surfaces have been studied by several investigators. However, little is known concerning the role of the nickel surface in the reaction.

The present study was undertaken to correlate kinetics measurements with an examination of the surface of the nickel catalyst, using the techniques of electron microscopy, diffraction and vacuum microweighing.

Formic acid decomposes by two important processes at pressures near 1 atmosphere and temperatures between 25 and 500°

$$HCOOH \longrightarrow CO_2 + H_2 \qquad (1)$$

$$HCOOH \longrightarrow CO + H_2O \qquad (2)$$

Both reactions are catalyzed by glass.[3] Nickel is reported[4,5] to catalyze the first reaction predominantly. Studies of the kinetics of the nickel-catalyzed reaction have given widely differing results.

Rienäcker,[5] using a static system, reports that the nickel-catalyzed decomposition follows zero-order kinetics. Wide variations are reported for both the decomposition rate and the activation energy of the reaction, activation energies between 12 and 30 kcal./mole having been reported by various investigators for different nickel preparations. Some investigators report a dependence of activation energy on the physical state of the nickel. For example, Rienäcker[6] reports an acti-

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[1] A portion of this work is taken from the Ph.D. dissertation of Roswell J. Ruka, The University of Michigan, Ann Arbor, Michigan, 1954.

[2] Department of Chemistry, The University of Texas, Austin 12, Texas.

[3] W. L. Nelson and C. J. Engelder, *J. Phys. Chem.*, **30**, 470 (1926).

[4] G. Rienäcker and H. Bade, *Z. anorg. allgem. Chem.*, **248**, 45 (1941).

[5] G. Rienäcker and N. Hansen, *ibid.*, **285**, 283 (1956).

[6] G. Rienäcker, *Z. Elektrochem.*, **46**, 369 (1940).

vation energy of 25 kcal./mole for rolled nickel and 12 kcal./mole for annealed nickel, while Schwab and Schwab-Agallidis[7] found 21.1 and 18 kcal./mole, respectively, for cold-worked and for "twice annealed" nickel. The initial decomposition rate has often been found to change radically with time and with different pre-treatments of the nickel.

Two mechanisms for the catalytic decomposition of formic acid have been proposed. One assumes that the rate-determining step is the transfer of electrons between adsorbed formic acid molecules and the metal catalyst. The second suggests that under special conditions a metal formate film may form and subsequently decompose.[8] However, decomposition of formic acid vapor over nickel has been reported[5] as low as 120°, a temperature at which nickel formate may be dried without apparent decomposition.[9]

Experimental

Materials.—All nickel specimens were taken from two batches of nickel. Sample A was a special research grade from the International Nickel Co. in the form of foil 4.1 cm. wide and 0.005 cm. thick. Major impurities indicated spectroscopically were 0.1 to 0.001% Si, Al, Cu and Ca. Sample B was prepared by melting Mond carbonyl nickel pellets in a zircon tube electric furnace under a hydrogen atmosphere. Nickel prepared in this way consisted of a few large crystals, some of which were ground to (100), (110) and (111) crystallographic orientations and electropolished, while the remainder of the ingot was rolled to strips 1.8 cm. wide and 0.018 cm. thick. A spectroscopic study of sample B showed larger relative amounts of Si, Al and Cu, and a trace of Fe. All samples were electropolished before use.

The formic acid used was Eastman 98%, the major impurity being water. The acid was dried with boric anhydride. Different methods of further purification had a pronounced effect on the decomposition rate, as discussed below.

Electron Microscopy.—All electron micrographs were taken with an RCA EMB electron microscope. Parlodion replicas were made of the nickel surfaces using the method described by Hall.[10] Standard polystyrene latex particles were used as a magnification standard. The replicas were shadowed at a 30° angle with palladium.

Electron Diffraction.—Patterns were taken with 50KV electrons. For high temperature patterns, an adaptation of a high temperature specimen holder described by Gulbransen[11] was used.

Vacuum Microbalance.—A gravity-type microbalance with a quartz suspension fiber was mounted in a Pyrex housing. A vacuum of 10^{-7} mm. could be obtained up to operating temperatures of 425° after a prolonged degassing treatment. The apparatus has been described in detail elsewhere.[1] Nickel specimens were counter-balanced with a combined platinum and quartz weight adjusted to the same volume as the nickel specimen.

Kinetics Apparatus.—The kinetics apparatus was a modification of that described by Schwab and co-workers[7,12] and is described in detail elsewhere. At the beginning of the run, the reaction tube could be filled with air, hydrogen or argon as desired. Formic acid vapor was not allowed to enter the reaction zone until the nickel sample had been heated to temperature. Data for activation energy curves were obtained on successive heating and cooling cycles, which gave a check for the attainment of steady-state conditions.

Results and Discussion

Decomposition Rate Studies.—The decomposition rate of formic acid was followed between 225 and 480°, using nickel strips of about 100 cm.^{2} geometric area. In this temperature range, some decomposition, catalyzed by the Pyrex walls of the apparatus, was observed in the absence of the nickel sample. Blank runs were made and the appropriate values subtracted from the rates measured in the presence of the catalyst, the correction amounting to 3 to 15% of the observed activity depending on the temperature.

The product gases were analyzed using a Hempel-type apparatus. In each determination CO_2, H_2 and CO were found, while CH_4 was absent. Catalysis by the Pyrex walls of the reactor accounted for all of the CO produced within experimental error.

Flow rates of decomposition gases were measured while slowly raising and lowering the furnace temperature through several cycles. The values during periods of increasing temperature were indistinguishable from those obtained while the temperature was falling except under the conditions discussed below. The activation energy for the reaction was 20 ± 1 kcal./mole with all specimens of nickel used. Since the reaction is of zero order,[5] the activation energy is not dependent on the HCOOH pressure.

By careful control of experimental conditions, it was found possible to obtain reproducible formic acid decomposition rates, all of which fell within 20% of the upper line in Fig. 1. Lack of control of certain factors led to a variable and slower rate of reaction. It is possible that the various effects

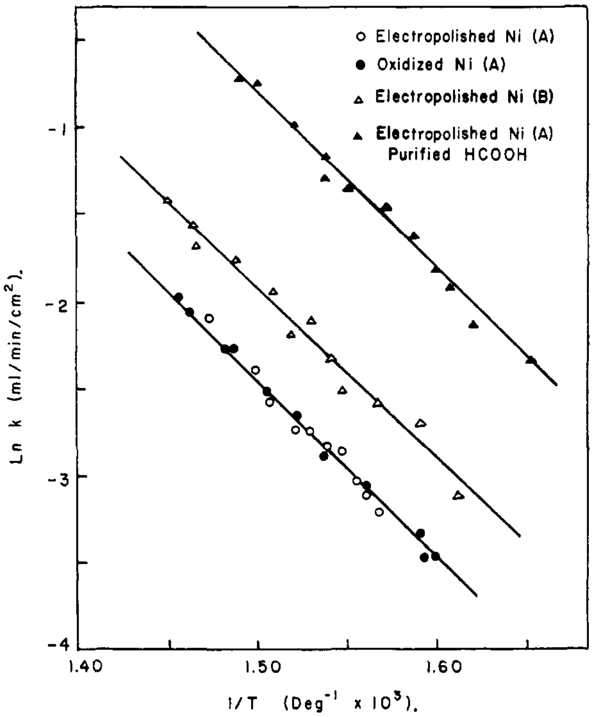

Fig. 1.—Arrhenius plot of formic acid vapor decomposition rate under various conditions. The rate is based on the geometric surface area.

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(10) C. E. Hall, "Introduction to Electron Microscopy," McGraw-Hill Book Co., New York, N. Y., 1953.

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described below account for many of the variations in the data published in the literature on this reaction. Of these factors the two most important are the gas in which the nickel is heated to temperature and the purity of the formic acid.

Markedly different initial results were obtained depending on whether the nickel sample was heated to temperature in an atmosphere of air, hydrogen or argon before the formic acid vapor was admitted. Preheating in air to a temperature of 250° resulted in variable initial decomposition rates. These values were very much larger than the value observed after an hour or two when the system had reached a steady state. In a separate experiment an initially oxidized nickel specimen was heated to temperature in argon before it was exposed to formic acid vapor. A high but declining initial activity was also noted for this specimen. In contrast to these exepriments, electropolished nickel specimens heated in argon passed over hot copper showed only a small increased initial activity, while electropolished specimens heated in hydrogen showed a nearly normal decomposition rate after only a few minutes.

Although nickel oxidizes when heated in air in the reaction chamber, the oxide is reduced by the gas mixture formed on decomposition of formic acid. Confirmation of this was obtained by electron diffraction patterns. Electron micrographs show a preferential roughening of certain crystals faces after oxidation. The increased catalytic activity noted with the initially oxidized specimens may be due to the larger area exposed by the roughened surface. This high initial activity gradually decreases, probably due to gradual sintering of the porous nickel surface left after reduction of the oxide by reaction gases. Although such sintering was not observed directly, effects ascribed to the sintering of porous evaporated nickel films have been observed by Beeck[13] in the temperature range of the present experiments.

The second important factor is the apparent inhibiting effect of impurities present in the formic acid. This was first noted during prolonged reaction of formic acid. After about 12 hr. at 380° (or longer at a lower temperature), the decomposition rate of the acid increased slowly to a higher value which then appeared to remain steady indefinitely. On the assumption that the rate change was due to the removal of an inhibiting impurity from the formic acid after long reaction over the nickel, several methods for further purification of the dried formic acid were tried. The best of these consisted of passing the formic acid through a column containing Amberlite IRA-410 anion-exchange resin. Acid purified in this manner gave immediately the same high decomposition rate that was otherwise obtained only after long reaction.

For the dried but otherwise untreated acid, nickel sample A gave a lower steady-state activity over the first several hours than nickel sample B. These results are shown in Fig. 1. With either nickel sample, the catalytic activity gradually approached the value observed for the purified acid, which gave the same result with either nickel sample. Thus it appears that impurities in the reactant can cause different rates with different samples of catalyst, differences which could be erroneously attributed to the catalyst itself.

Crystal Structure and Heat Treatment.—Possible effects of crystal orientation and of annealing were also studied. Although no kinetics experiments on nickel single crystals could be made because of the rather limited surfaces available to us, some variation was possible because of the different crystallographic nature of the two polycrystalline nickel samples used. Sample A nickel showed some evidence of preferred orientation which was the same before and after heating in formic acid vapor for several hours between 200 and 450°. Sample B, after 98% reduction by cold rolling, showed a highly oriented fiber structure, with the (110) fiber axis at a tilt to the rolling plane. Again, little reorientation or grain growth could be detected after heating in the range 200–450°.

The sheet nickel formed by rolling sample B was very hard and elastic. Portions of this sheet were annealed at 1000° in a hydrogen atmosphere for 10 hr. Considerable grain growth occurred and much less preferred orientation was observed. The annealed sheet was soft and flexible with crystals about 0.5 mm. in size. In spite of the large differences in structure and purity, all of the nickel specimens after electropolishing gave the same activation energy and specific activity for decomposition of the resin-treated formic acid vapor. This is in disagreement with the observations of Rienäcker,[6] who reported an activation energy twice as high for rolled nickel as for annealed. Differences in experimental method may be responsible for this disagreement since Rienäcker's studies were made in a static system where a varying activity during the course of an experiment might appear as a higher or lower activation energy. In addition there is no evidence that he electropolished the nickel surface after annealing.

Although the nickel single crystals available were not sufficiently large for use in kinetics studies, they were given vacuum heat treatments along with polycrystalline samples A and B to determine if impurities would cause surface film formation which could be detected by electron diffraction. Specimens were heated *in vacuo* at 2×10^{-7} mm. at 400° for 60 hr. The purer sample (A) showed only a nickel pattern under electron diffraction. The less pure sample (B) gave a strong γ-Al_2O_3 pattern, even though the aluminum content of the bulk metal was only 0.01 to 0.1%. A nickel single crystal from sample B subjected to the same treatment showed clear γ-Al_2O_3 patterns on both the (100) and (111) faces in addition to several very weak unidentified lines. Thus it is evident that very small quantities of impurities in a metal catalyst may concentrate in the surface layers during annealing or outgassing treatments and could possibly play an important part in activity changes noted when the outer surface is not removed by electropolishing or equivalent treatment.

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Most of the kinetic studies were made with the purer nickel sample A, but even strips from sample B showed no surface formation of Al_2O_3 after extended treatment with formic acid in the kinetics apparatus. It may be that the flow of formic acid was sufficient to carry away oxygen resulting from degassing of the container walls before it came in contact with the nickel specimen. In any event, only nickel patterns were obtained by electron diffraction and the catalytic activity of the two samples with resin-treated acid was identical.

Nickel Formate Film Formation.—In view of the suggestion[8] that the decomposition of formic acid vapor on nickel may involve the intermediate formation of a nickel formate film in some instances, a study of the conditions under which such a film can develop was undertaken. Since the X-ray diffraction pattern of anhydrous nickel formate is not known, a sample was prepared from sample B nickel. In order to obtain material of suitable crystal size, nickel millings were treated with anhydrous formic acid in a Soxhlet extractor. The continuous recycling of fresh formic acid over the metal led to the gradual accumulation of crystalline product in the lower chamber of the extractor. The dried product was analyzed for carbon and hydrogen giving results in close agreement with the theoretical values for anhydrous nickel formate. The interplanar spacings from an X-ray diffraction pattern are given in Table I.

TABLE I

X-RAY PATTERN OF ANHYDROUS NICKEL FORMATE

I/I_0 Relative intensity	D_{hkl} Interplanar spacing	I/I_0 Relative intensity	D_{hkl} Interplanar spacing
s	8.47	vw	2.99
ms	8.04	m	2.86
w	7.04	m	2.79
m	6.60	m	2.62
m	4.89	m	2.55
m	4.50	w	2.423
m	4.34	w	2.362
w	4.06	vw	2.313
w	3.99	w	2.255
vw	3.80	m	2.177
vw	3.55	m	2.02
w	3.37	vw	1.945
vw	3.20	vw	1.612

Using electron microscopy and diffraction techniques, no evidence of nickel formate film formation was obtained in the temperature range in which the nickel surface shows active catalysis. However, experiments at lower temperatures between 30 and 55° showed that an anhydrous nickel formate film is produced when nickel is exposed to an atmosphere nearly saturated with formic acid. Under these conditions, multilayer adsorption of the formic acid becomes possible. Corrosion of the metal surface may then be similar to the reaction with liquid formic acid.

As an additional method for detecting the formation of a thin film, a nickel sample was suspended from one arm of the microbalance described above and its weight was followed during the course of the formic acid decomposition. At 400, 300, 200 and 50°, with 3.5 cm. pressure of formic acid vapor, no change of weight which could correspond to more than a monolayer of formic acid was observed.

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Kinetics of the Permanganate Oxidation of Formic Acid and Formate Ion in Aqueous Solution

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The kinetics of the permanganate oxidation of formic acid in aqueous perchloric acid were examined in the temperature range 15 to 35°. The reaction, $2MnO_4^- + 3HCOOH + 2H^+ \rightarrow 2MnO_2 + 3CO_2 + 4H_2O$, appears to proceed through two independent paths in which the rate-determining steps are bimolecular reactions of permanganate with formic acid and formate ion, respectively. The kinetics are thus of the form, $-d[MnO_4^-]/dt = [MnO_4^-][HCOOH](k_1 + k_2K_i/[H^+])$, where $k_1 = 1.1 \times 10^9 \exp[-16400/RT] M^{-1}$ sec.$^{-1}$ and $k_2 = 7.8 \times 10^9 \exp[-13000/RT] M^{-1}$ sec.$^{-1}$. The formate ion reaction (k_2) exhibits a large deuterium isotope effect ($k_{HCOO^-}/k_{DCOO^-} = 7$) which suggests cleavage of the C–H bond in the rate-determining step. The absence of a corresponding isotope effect in the formic acid reaction (k_1) suggests that it proceeds by a different mechanism. A difference in mechanism for the two paths is also indicated by the observation of a considerable solvent deuterium isotope effect for k_2($k_2^{H_2O}/k_2^{D_2O} = 0.38$) but not for k_1. The reaction is susceptible to pronounced catalysis by Fe^{+++} (but not by Na^+, Ag^+, Cu^{++} or Co^{++}). The kinetics suggest that the catalytic path involves reaction of HCOOH or $HCOO^-$ with a $FeMnO_4^{++}$ complex. It seems likely that the initial reduction products of MnO_4^-, in the uncatalyzed and catalyzed reactions, are Mn(V) and Mn(VI), respectively.

Introduction

Some features of the kinetics of the permanganate oxidation of formic acid and formate salts in aqueous solution have been examined previously by Mann, Hill and Tompkins[2] and by Wiberg and Stewart.[3] In both investigations the kinetics were identified with a rate-determining reaction between permanganate and formate ion in which manganese-(V) is formed as an intermediate. Even in solutions of *p*H as low as 1.7, in which formic acid is predominantly un-ionized, there appeared to be no

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(1) Holder of a National Research Council Bursary, 1956–1957. Assistance from the National Research Council in the form of a grant-in-aid of this work is also gratefully acknowledged.

(2) D. R. Mann and F. C. Tompkins, *Trans. Faraday Soc.*, **37**, 201 (1941); L. M. Hill and F. C. Tompkins, *Trans. Roy. Soc. S. Africa*, **29**, 309 (1942); **30**, 59 (1943).

(3) K. B. Wiberg and R. Stewart, THIS JOURNAL, **78**, 1214 (1956).