Discussion

The results of this investigation indicate that the rise of a liquid in a fine vertical capillary may be accurately represented by the solution to the differential equation of motion in which the rate of change of the momentum of the contents of the capillary is assumed to be negligible. It also appears that here the end-drag effect is negligible. The data support the validity of the viscous drag term, the form of which results from the assumption of Poiseuille flow in the accelerated state. In addition, the rate of wetting and the rate of assumption of constant (zero) contact angle are apparently sufficiently rapid compared with the rate of ascent that they need not be considered. Thus considerable simplifications in both the experimental and theoretical treatment of the general problem result from the use of fine capillaries.

It may prove possible to utilize the results and techniques described in this paper for the estimation of the viscosity of small quantities of liquids. For a fairly short capillary where $\eta_a l \ll (\eta - \eta_a)h_\infty$, and where $\eta \gg \eta_a$, Eq. 2 reduces to the following equation for the viscosity

$$\eta = \frac{R^2\rho g t}{8h_\infty}\left[\ln\left(\frac{h_\infty}{h_\infty - h}\right) - \frac{h}{h_\infty}\right]^{-1} \qquad (3)$$

For the *initial* portion of the ascent, Eq. 3 may be approximated by expansion to yield the result

$$\eta = \frac{R^2\rho g h_\infty}{8}\left(\frac{t}{h^2}\right) = \frac{R\gamma}{4}\left(\frac{t}{h^2}\right) \qquad (4)$$

Thus, a plot of h^2 *vs.* t should be linear, with a slope $\gamma R/4\eta$. This is very similar to the result for a horizontal tube.[7]

It was found that the data plotted in this way did give straight lines in the initial portion of the ascent; however, the extent and accuracy of the data in the early rise was insufficient for a precise determination of the viscosity from the kinetic data. A rapid approximate micro viscosity determination suggests itself, however, using very fine tubes; the time required for a liquid to rise to a given height is proportional to viscosity divided by surface tension. Calibration with known liquids would make possible rapid relative measurements of viscosity.

CHICAGO 16, ILL. RECEIVED APRIL 20, 1951

[CONTRIBUTION NO. 415 FROM THE DEPARTMENT OF CHEMISTRY, KANSAS EXPERIMENT STATION, KANSAS STATE COLLEGE]

The Decomposition of Formic Acid at Low Temperatures[1]

BY H. N. BARHAM AND LOUIS WATTS CLARK

The purpose of the present work was to study the rate of the non-catalyzed decomposition of pure formic acid at low temperatures, and to determine the effects of water upon the rate of decomposition. The formic acid used possessed a purity of 99.9%. Calculated specific reaction velocity constants and temperature coefficients for the non-catalyzed reaction are descriptive of the stability of formic acid at various temperatures. Constants in the Arrhenius and Eyring equations also were calculated.

It is well known that only a few simple unimolecular reactions have been the subject of kinetic investigations. One that has received considerable attention is the decomposition of formic acid in the liquid phase, yielding water and carbon monoxide, in the presence of various catalysts.[2,3] While kinetic data of much value relative to the catalyzed decomposition of formic acid have been obtained, the decomposition of formic acid alone has not been studied. Reasons for this may have been (1) the difficulty of obtaining formic acid of high purity, and (2) the exceedingly slow rate of decomposition of formic acid at low temperatures. Although the rate of the non-catalyzed decomposition of liquid formic acid is quite slow, it was observed by the authors that the amounts of gas evolved with time from a 100-ml. sample of the dry acid between 40° and 100° were sufficiently large to be measured with accuracy. Using formic acid which was nearly 100% water-free, in a modified form of the apparatus designed by Walton,[4] the authors determined: (1) the influence of water on the rate of decomposition of the acid at two different temperatures, and (2) the rate of decomposition of the dry acid at nine different temperatures between 40° and 100°. These data then were used to calculate the temperature coefficients of the reaction, the stability of formic acid, and the thermodynamic constants in the Arrhenius[5] and Eyring[6] equations.

Experimental

Purification of Formic Acid.—Reagent formic acid of 96.0% purity was further dried by standing over Anhydrone for several days, then distilled at 30° under 20 mm. pressure. The product thus obtained tested 99.9% pure formic acid by titration with standard base using a weight buret, and showed the following physical properties: n^{20}_D 1.3710; d^4_{20} 1.2200; freezing point 8.1°.

Apparatus.—The apparatus used in studying the rate of decomposition of formic acid was patterned after that of Walton, with the following modifications: (1) a mercury sealed stirrer was substituted for the shaker; (2) a cold water condenser was attached to the reaction flask; (3) a tube of Ascarite was inserted between the condenser and the water-jacketed buret; (4) all sections of the apparatus were connected by standard taper joints; and (5) an electrically heated, thermostatically controlled oil-bath was used in lieu of a water-bath.

Gas Analysis.—Analysis in an Orsat apparatus confirmed the observation of Branch[7] that the only gas produced by the decomposition of formic acid was carbon monoxide.

Effect of Water.—At a temperature of 98.6° the initial rate of evolution of carbon monoxide by a 122-g. sample of formic acid was found to be over 100 ml. per hour. However, the rate gradually decreased with time, reaching after

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(1) From the Ph.D. Thesis of Louis Watts Clark, Kansas State College, May, 1950.

(2) Walton and Stark, *J. Phys. Chem.*, **34**, 359 (1930).

(3) (a) Schierz, THIS JOURNAL, **45**, 447 (1923); (b) Schierz, *ibid.*, **45**, 455 (1923); (c) Schierz and Ward, *ibid.*, **50**, 3240 (1928).

(4) Walton, *Z. physik. Chem.*, **47**, 185 (1904).

(5) Arrhenius, *ibid.*, **4**, 226 (1889).

(6) Wynne-Jones and Eyring, *J. Phys. Chem.*, **3**, 492 (1935).

(7) Branch, THIS JOURNAL, **37**, 2316 (1915).

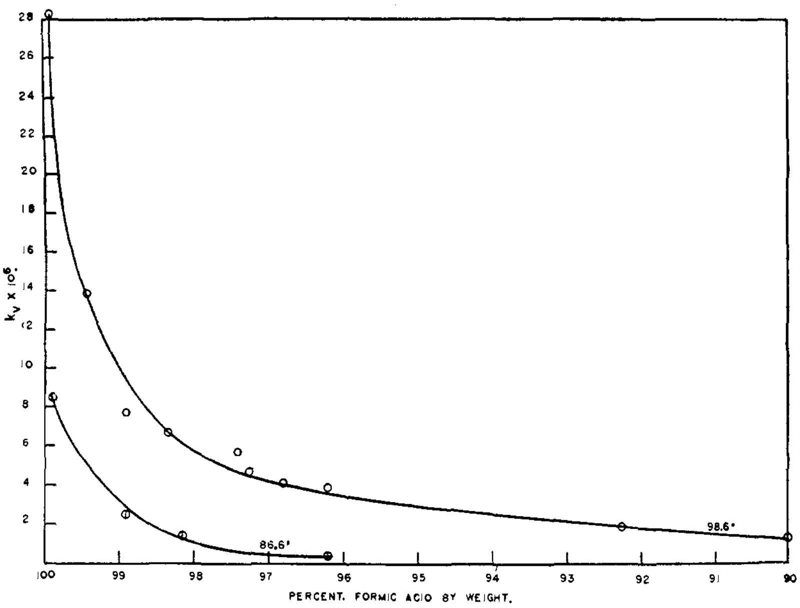


Fig. 1.—Effect of water on the rate of decomposition of formic acid.

eight days a value of 6 ml. per hour. Evidently the water produced concomitantly with the carbon monoxide acted as a negative catalyst on the decomposition of the remaining molecules of formic acid.

A supplementary experiment was performed with a second 122-g. sample of the formic acid at 98.6°. In this experiment 180-mg. samples were withdrawn from the reaction flask from time to time and the concentration of acid determined by titration. This experiment was repeated at 86.6°. The data obtained in these experiments are shown graphically in Fig. 1. It will be seen that the inhibitory effect of water on the rate of decomposition of formic acid is most pronounced between 98 and 100% formic acid.

Effect of Temperature.—A 122-g. sample of formic acid was placed in the reaction flask, the desired temperature established, and, after equilibrium conditions were attained, volume, temperature and pressure readings were taken at suitable intervals until the rate of decomposition could be determined with certainty. The procedure was repeated at nine different temperatures between 40° and 98.6°. From these data the specific reaction velocity constant for the reaction at each selected temperature was calculated. Results are recorded in Table I. It should be noted that at the higher temperatures the initial rates were taken as the true rates, due to the subsequent disturbance caused by the rapidly accumulating water. At the lower temperatures the amount of water formed during the time required to carry out an experiment was too small to have a measurable effect on the rate.

TABLE I

EFFECT OF TEMPERATURE ON THE RATE OF DECOMPOSITION OF FORMIC ACID

Temp., °C.	Ml. CO (at S.T.P.) produced per hr. by 122 g. formic acid	$k \times 10^6$ (min.$^{-1}$)
40.0	0.15	0.042
47.4	.32	.090
51.1	.58	.163
53.6	.90	.253
60.4	1.86	.520
65.3	4.90	1.375
76.5	16.60	4.658
86.6	30.4	8.527
98.6	100.7	28.255

Discussion

Temperature Coefficients.—From the data shown in Table I, a plot of log k_v *versus* $1/T$ was constructed (Fig. 2). Temperature coefficients were then calculated from values obtained from Fig. 2. The temperature coefficient was found to be 3.60 for the 40–50° interval, 3.35 for the 50–60° interval, 3.13 for the 60–70° interval, 2.88 for the 70–80° interval, 2.69 for the 80–90° interval, and 2.57 for the 90–100° interval.

Stability of Formic Acid.—Using k_v values obtained from Fig. 2, the number of grams of water which would be formed in one year at various temperatures by 122 g. of formic acid was calculated, assuming that no decrease in the rate occurred with time. These calculations showed that 3.0 g. of water would be produced at 50°, 0.06 g. at 20°, and 0.002 g. at 0°.

Energy of Activation.—From the slope of the line in Fig. 2 the energy of activation, E, in the Arrhenius equation, for the thermal decomposition of formic acid, was found to be 25,660 calories. In the case of formic acid containing 1.0% water, E was found to be 26,920 calories, based upon the data of Fig. 1.

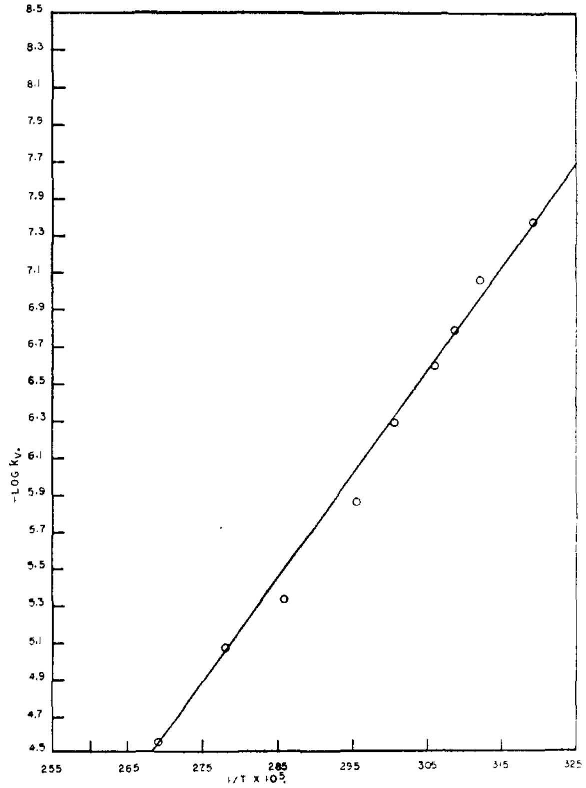


Fig. 2.—Effect of temperature on the decomposition of formic acid.

Enthalpy, Entropy and Free Energy of Activation.—The enthalpy of activation, the entropy of activation and the free energy of activation at 25°, in the Eyring equation, also were calculated for both cases. For pure formic acid these values were 24,630 calories, −21.4 e.u., and 31,010 calories, respectively; for 99.0% formic acid they were 25,970 calories, −20.0 e.u., and 31,930 calories, respectively. These results are consistent with absolute reaction rate theory.

MANHATTAN, KANSAS RECEIVED MAY 5, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some 1-Naphthylsilicon Compounds

BY HENRY GILMAN AND CECIL G. BRANNEN

Several new 1-naphthylsilicon compounds were synthesized to extend the study of steric hindrance in arylsilanes. Tri-1-naphthylsilane and some of its derivatives exhibited unusual stability toward hydrolytic reagents and were further substituted by organolithium reagents with difficulty. A bimolecular nucleophilic substitution reaction mechanism is employed to account for this stability and to illustrate the steric requirements of these compounds. The value of the halogen–metal interconversion method of preparing organolithium reagents for synthetic purposes is demonstrated.

Several investigators[1] have reported that steric factors are concerned in the reactions of various silanes. It is our belief that the reactions of 1-naphthylsilicon compounds can be explained on a similar basis. We have based this idea on the observations that the tri-1-naphthylsilyl derivatives are relatively inert toward hydrolytic reagents and organolithium compounds, and that tri-1-naphthylsilanol is not converted to the disiloxane by treatment with acid.

Hydrolysis, either acid- or base-catalyzed, of most chlorosilanes is easily effected and usually precautions must be taken to prevent its occurrence. However, hydrolysis does not occur with several triarylchlorosilanes containing an ortho-substituent, such as *o*-tolyl[2], *o*-anisyl[2] and 1-naphthyl, until relatively drastic conditions are imposed. Under some conditions tri-1-naphthylchlorosilane is unaffected by weak base while triphenylchlorosilane is completely hydrolyzed when similarly treated. Likewise, tri-*o*-tolyl- and tri-1-naphthyl-silane do not visibly evolve hydrogen when treated with potassium hydroxide in piperidine,[3] while triphenylsilane in the control experiment gives a vigorous evolution of the gas.

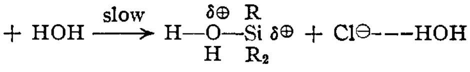
The action of an excess of 1-naphthyllithium on silicon tetrachloride and on ethyl silicate affords only the tri-substituted derivative even though high temperatures and long reaction periods are used. Others have observed similar results with sterically-hindered radicals, such as *o*-tolyl,[1f] *o*-anisyl,[2] isopropyl,[1b] and cyclohexyl,[1e] while *t*-butyllithium[1d] gave only the di-substituted silane.

Formic acid[4] has been used to convert silanols to the corresponding disiloxanes but this reagent is without effect on tri-1-naphthylsilanol. Apparently this disiloxane cannot be made by treating hexachlorodisiloxane with an excess of 1-naphthyllithium.

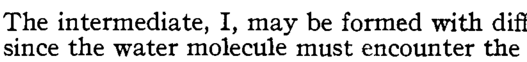
It has been emphasized[5] that steric hindrance should not be associated with a particular reactant or over-all chemical reaction but is a property of a particular reaction mechanism. In order to postulate that steric requirements are the principal factors in the reactions of 1-naphthylsilicon compounds, an S_N2 mechanism must be assumed to operate ordinarily in the hydrolysis of silanes. There appears to be ample data from recent reports to justify this assumption and these reactions furnish additional evidence for this postulation. Furthermore, it follows that the ionization (S_N1) mechanism is much slower than is the case with carbon compounds.

Price[1c] has shown by kinetic studies that the rate of alkaline cleavage of the Si–H bond in trialkylsilanes decreases with increasing bulk of the alkyl groups. This order is the same as that observed in carbon compounds undergoing nucleophilic attack and this cleavage is postulated as proceeding by an S_N2 mechanism. Actual steric requirements are not mentioned, but an explanation is given in terms of the field effects of the entering and constitutive groups. In the present case the groups are larger, leading to the expectation that in this type of mechanism the rate should be retarded.

Swain[6] has shown that the data of reaction rate studies of the hydrolysis of triarylsilyl fluorides is inconsistent with the idea of a siliconium ion intermediate (an S_N1 type) and suggests that many reactions of organosilicon compounds may proceed through pentacovalent silicon intermediates. The slow rate of hydrolysis of tri-1-naphthylsilyl chloride is predicted on the basis of these experiments if large steric requirements are postulated for the naphthyl groups. As presented by Swain the reaction may proceed as



$$\overset{\delta\oplus}{R_3Si}\text{—}\overset{\delta\ominus}{Cl} + HOH \xrightleftharpoons{\text{fast}} H\text{—}\underset{H}{\overset{\delta\oplus}{O}}\text{—}\underset{R_2}{\overset{R}{Si}}\text{—}\overset{\delta\ominus}{Cl}\ (I) \qquad (1)$$



$$(I) + HOH \xrightarrow{\text{slow}} H\text{—}\underset{H}{\overset{\delta\oplus}{O}}\text{—}\underset{R_2}{\overset{R}{Si}}\,\delta\oplus + Cl^{\ominus}\text{---}HOH \qquad (2)$$

$$R = \text{1-naphthyl}$$

The intermediate, I, may be formed with difficulty since the water molecule must encounter the bulky naphthyl groups in step (1).

However, the reactions studied by the previously mentioned workers[6,1d] were relatively rapid and it is possible that the S_N1 reaction was not evident only

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[1] (a) F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946); (b) H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947); (c) F. P. Price, *ibid.*, **69**, 2600 (1947); (d) L. J. Tyler, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2876 (1948); (e) W. H. Nebergall and O. H. Johnson, *ibid.*, **71**, 4022 (1949); (f) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

[2] Unpublished studies from this Laboratory by Dr. G. N. R. Smart.

[3] A test devised by F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 848 (1921), and modified by Gilman and Clark.[1b]

[4] Unpublished studies from this Laboratory by H. W. Melvin.

[5] I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 174 (1946).

[6] C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).