slope of unity, and even at an HCl activity of 365 (10.9 N) there is no evidence of a leveling off of % T. Optical density determinations on the same solutions at 400 mμ—the region of an absorption maximum for Ni^{++}—showed a much smaller decrease in % T as a function of concentration, while at 350 mμ the transmission of the solution 10.9 M in HCl had decreased only 18.5% with respect to the $NiCl_2$ in H_2O blank. Since log (extinction coefficient) for $NiCl_2$ in H_2O drops from 0.70 at 390 mμ to ~0 at 425 mμ,[9] the change in the contribution by the Ni^{++} ion to the adsorption peak at 425 mμ must be negligible. It is thus concluded that the unity slope of the log % T *vs.* log [HCl] plot at 425 mμ implies that the growth of this peak is dependent on the first power of the chloride ion activity. Since $NiCl_2$ in dilute solutions in the absence of other anions yields only $Ni(H_2O)_6^{++}$, the first order dependence of % T on [HCl] must be a consequence of the formation of $NiCl^+$ from Ni^{++}.

From these data it is concluded that in solutions up to ~11 N in HCl, only two nickel species—Ni^{++} and $NiCl^+$—are present in appreciable extent in the aqueous phase, and that no significant concentrations of negatively charged complexes such as $NiCl_3^-$ are formed in the Dowex-1 resin phase under the conditions of the present work.

At the present time, it is not understood why Ni(II), which behaves as a Lewis acid toward nitrogen (54 ammine complexes are listed by Sidgwick[14]) and which readily forms anionic cyanide complexes,[15,16] forms no anionic complexes with chloride and bromide ions, in contrast to the behavior of Co(II), Cu(II) and Zn(II). Manganese, the only other divalent element of the first transition period which also shows a small extent of adsorption from concentrated HCl by Dowex-1, is nevertheless sufficiently well held[5] by 16 and 24% DVB resin, that a ready separation from Ni(II) in 12 M HCl can be effected.

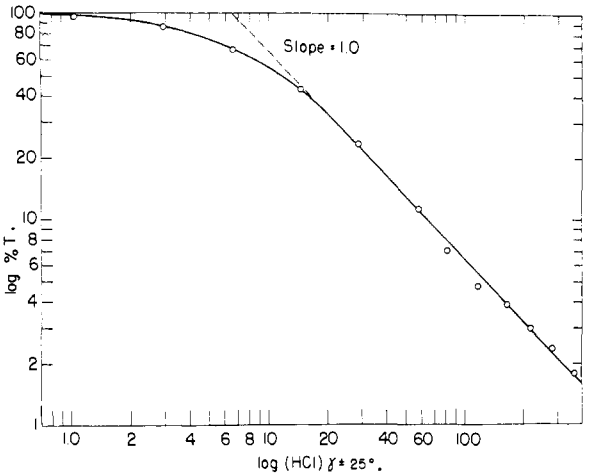


Fig. 1.—Transmission *vs.* HCl activity for Ni(II) at 425 mμ.

The authors wish to thank Mr. A. A. Fournier, Jr., for making a part of the optical density determination reported in this work, as well as Professor C. D. Coryell for a number of valuable discussions.

(14) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1439.

(15) W. F. Pickering, *Anal. Chim. Acta*, **8**, 344 (1953).

(16) Indeed, the cyanide complex is so strong, that Ni(II) activity placed on a 24% DVB Dowex-1 column which had been pretreated with 1 M NaCN could not be eluted from the column within 15 column volumes even with 0.2 M HCl as the elutriant.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY]

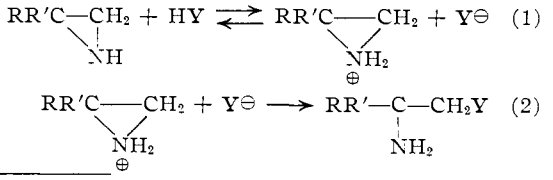
Reactions of Ethylenimines. VII. Hammett ρ Constants for Ring Opening with Benzoic Acids

BY DONALD H. POWERS, JR.,[1a] VIRGINIA B. SCHATZ[1b] AND LEALLYN B. CLAPP

RECEIVED AUGUST 29, 1955

Hammett constants were determined for the ring opening of 2-ethylethylenimine (ρ = +1.66) and 2,2-dimethylethylenimine (ρ = +1.50) with five substituted benzoic acids in dioxane at 45°. Two alternative rationalizations are proposed to account for these high positive ρ-values.

The Hammett ρ constants for the ring opening of the ethylenimine ring by substituted benzoic acids were determined for 2-ethylethylenimine and 2,2-dimethylethylenimine in an endeavor to throw more light on the reactions of this small ring. Previous work on the ring opening of substituted ethylenimines indicated that the following steps are involved when the attack of a nucleophilic agent occurs at the unsubstituted carbon



(1) (a) Jesse Metcalf Fellow, 1953–1954; (b) Edwin P. Anthony Fellow, 1952–1954.

Meguerian and Clapp[2] suggested that when HY was thiophenol the slow step was probably a proton transfer following hydrogen bridge formation. The results of the present work with substituted benzoic acids can also be interpreted as indicating that the rate-determining step is a proton transfer or dependent on a proton transfer.

The ρ-values found for the reactions of 2-ethylethylenimine and 2,2-dimethylethylenimine with five substituted benzoic acids in dioxane at 45° are +1.66 ± 0.17 and +1.50 ± 0.17, respectively (Fig. 1). The difference between the ρ-values for the two imines is within experimental error. The difference is probably real, however; the ratios of the rates of reaction of the two imines with the benzoic acids do not vary in a random manner but there

(2) G. H. Meguerian and L. B. Clapp, THIS JOURNAL, **73**, 2121 (1951).

is a regular increase in the ratio of the rates $k_{dimethyl}/k_{ethyl}$ from *p*-nitrobenzoic to *p*-anisic acid. Hence the difference in ρ is probably inherent in the reactions and not due to experimental error. Differences in base strength alone should be reflected in the rate of each reaction and the curves (Fig. 1) should be parallel and hence have the same slope (ρ).

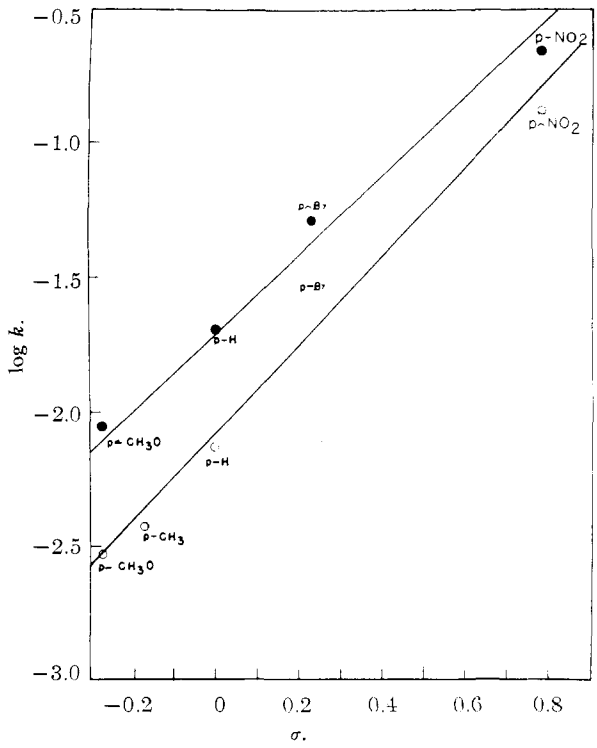


Fig. 1.—Hammett plots for the reactions of *p*-substituted benzoic acids with 2-ethylethylenimine (lower line, open circles) and 2,2-dimethylethylenimine (upper line, closed circles).

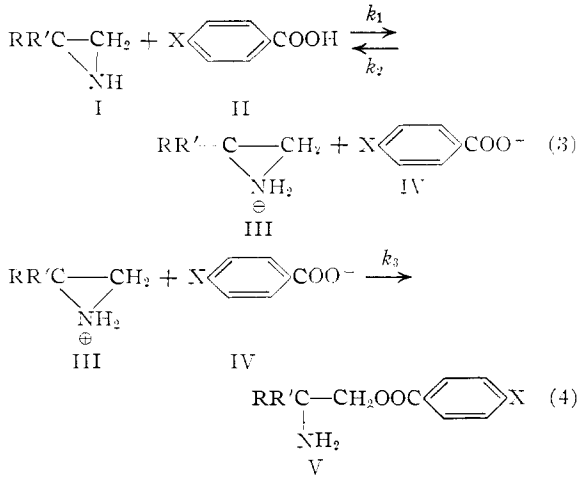
Finding different ρ-values for such closely related compounds is not necessarily surprising. Slight structural changes may cause large changes in ρ.[3] For example, a ρ-value of -0.771 is given for the reaction of phenoxide ion with propylene oxide and -0.946 for the same reaction with ethylene oxide.[4]

High positive ρ-values indicate that the reaction is favored by a low electron density on the carboxyl group in the benzoic acid. This is compatible with the ionization step (eq. 1) which would be favored by a low electron density on the carboxyl group but incompatible with high electron density on $Y^{\ominus}$ in a nucleophilic attack by carboxylate ion (eq. 2). It is not unreasonable that in a solvent of low dielectric constant such as dioxane (2.2) a proton transfer from a strong acid to a weak base might be slow. Congo red dissolved in dioxane gave a blue color with dry hydrogen chloride which changed very slowly (over a 9-hour period) to orange (basic) in the presence of an excess of 2,2-dimethylenimine.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 197.

(4) Ref. 3, p. 190; D. R. Boyd and E. R. Marle, *J. Chem. Soc.*, **105**, 2117 (1914).

A second rationalization[5] will also account for the high positive ρ-value, namely, postulation of a rate-determining ring-opening step dependent on the equilibrium constant of the proton transfer step. In eq. 3 the equilibrium constant $K_{eq} = k_1/k_2$ may also be set equal to $[ImH^+][A^-]/[Im]$

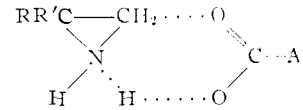


$[HA]$ and the rate of the over-all reaction $dx/dt = k_3[ImH^+][A^-]$ where $[ImH^+]$, $[Im]$, $[HA]$ and $[A^-]$ are concentrations of immonium ion (III), imine (I), substituted benzoic acid (II) and anion (IV), respectively. By further substitution $dx/dt = k_3K_{eq}[Im][HA]$ and the ρ value for the over-all reaction is then a composite of those for K_{eq} and k_3.

By extrapolation of the calculated ρ-values for ionization of benzoic acid in dioxane–water,[6] a ρ-value of not less than $+1.50$ was obtained for ionization in pure dioxane, assuming, of course, that ionization is not a discontinuous function at zero water concentration. It can be shown that ρ_1 for k_1 is smaller than ρ_{eq} for K_{eq} and from previous argument ρ_1 (for the forward reaction) will be positive. The reverse reaction should be aided by a high electron density on the carboxylate ion so ρ_2 should be negative. Hence ρ_1 should be less than ρ_{eq}. If ρ_2 is small but negative and ρ_3 is small (or negative), the over-all ρ-value might still be as high as $+1.66$ (or $+1.50$), the numbers actually found. A determination of the effect of changing the electron density on the benzoate ion was recently reported[6b] as -0.2 and -0.12 in two dissimilar reactions. If ρ_3 is, indeed, of this order of magnitude, the over-all ρ-values in the present work are acceptable for this second rationalization.

The heats of activation for the reaction of 2-ethylethylenimine with benzoic and *p*-nitrobenzoic acids at 45° were found to be 17.0 and 16.8 kcal./mole, respectively. These values are higher than Meguerian[2] found for the reaction with thiophenol in carbon tetrachloride (11.0 kcal./mole). The

(5) A referee suggested that the cyclic transition state represented below is a good possibility in a medium of low dielectric constant such as dioxane where charge separation is unfavorable. This picture is, indeed, compatible with the observed ρ-values.



(6) (a) J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 485 (1941); (b) L. R. Parks, G. S. Hammond and M. F. Hawthorne, THIS JOURNAL, **77**, 2903 (1955).

TABLE I

SUBSTITUTED BENZAMIDO ALCOHOLS, $RR'C(CH_2OH)-NHCO-C_6H_4-X$

Substituent X	Yield, % in solvent $CHCl_3$	Yield, % in solvent Dioxane	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
			R = CH_3, R′ = CH_3						
H	98	68	88.5–89.8[a]						
CH_3		75[b,c]							
Br		91	93.0–94.7	48.54	48.81	5.19	5.15	5.15	4.98
CH_3O	61	88[d]							
NO_2	99	98[b,e]	120.0–120.8[f]						
			R = C_2H_5, R′ = H						
H	98	87	97.5–98.5[g]						
CH_3	89	74	114.1–115.0	69.54	69.50	8.27	8.26	6.76	7.01
Br		82	128.3–129.0	48.54	48.62	5.19	5.13	5.15	5.40
CH_3O	80	91	115.8–117.8	64.55	64.27	7.68	7.63	6.27	6.41
NO_2	77	84	112.4–113.5	55.45	55.51	5.92	6.01	11.76	11.89

[a] J. H. Billman and E. E. Parker, THIS JOURNAL, 66, 538 (1944), report m.p. 89–90°. [b] Compound was isolated as $RR'C(CH_2OOC-C_6H_4-X)-NH_3^+{}^-OOC-C_6H_4-X$. [c] *p*-Toluic acid salt, m.p. 158.0–159.3°, neut. equiv. calcd. for $C_{19}H_{22}NO_4$, 328; found, 331. [d] *p*-Methoxybenzamide obtained as an oil and converted to the *p*-methoxybenzoate ester in low yield, 26%, m.p. 143.2–143.5°. *Anal.* Calcd. for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.42; H, 6.38; N, 4.16. [e] *p*-Nitrobenzoate salt, m.p. 167.5–168.5°. Neut. equiv. calcd. for $C_{18}H_{19}N_3O_6$, 405; found, 395. [f] Reference 11 gives m.p. 118–119°. [g] J. H. Billman and E. E. Parker, ref. *a*, report m.p. 98–99°; M. G. Ettlinger, THIS JOURNAL, **72**, 4792 (1950), reported m.p. 99.5–100.5°.

entropies of activation for the same two reactions were −25 and −19 cal./mole/degree, respectively.

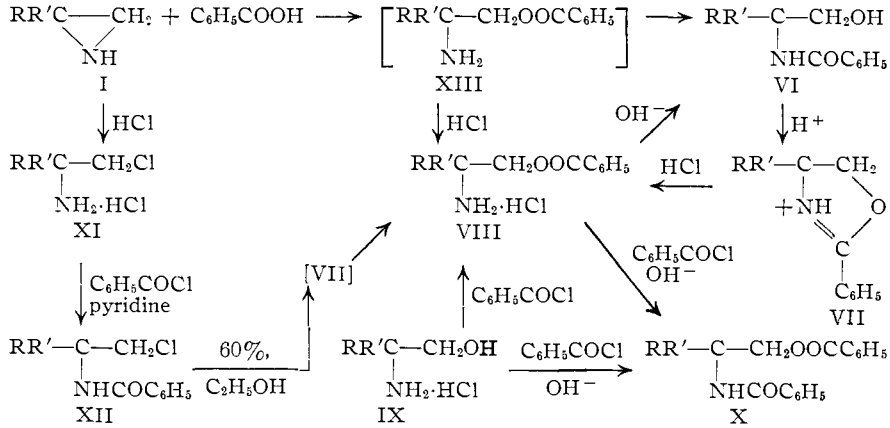
Estimation of the progress of the reaction of the imine with the substituted benzoic acid to give a β-aminoalkyl benzoate was made by a conductometric titration in dioxane, a method previously found suitable for mixtures of strong and weak acids or bases.[7] Three endpoints were found where a mixture of 2-ethylethylenimine, the substituted benzoic acid and the salt of β-aminobutyl benzoate was treated with the excess standard sodium hydroxide and then titrated with standard hydrochloric acid in 50% dioxane. The first and sharpest end-point corresponded to a change in conductance when the excess sodium hydroxide was neutralized, the second when the unreacted imine was neutralized, and the third to the conversion of substituted benzoate ion to undissociated acid. At the beginning of this work the first two end-points were determined in a number of runs to establish the order of the reaction. After it was found that the reaction was first order in substituted benzoic acid and first order in imine, only the first end-point was determined. All the data in Table II and the plots in Fig. 1 are taken from these later determinations, based on second-order kinetics.

(7) A. Weissberger, "Techniques of Organic Chemistry," Ed. 2, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1949, Part II, p. 1674 ff.

The structures of the compounds produced in the two series of reactions (A and B, Chart I) were established by methods that have been applied to other amino alcohol derivatives. When the ethylenimines (IA and B) were treated with benzoic acid in chloroform, the free amino benzoates (XIIIA and B) were never isolated; if the reaction mixtures were worked up in neutral or basic media, the benzamides VI were obtained and in acid medium, the salts VIII. The structures of VIIIA and B were established by synthesis from the known amino alcohol hydrochlorides (IXA and B) using Cope's[8] method. Compounds VIIIA and B were also synthesized from the chlorobenzamides (XII) whose structures were known (XIIA,[9a] XIIB[9b]).

CHART I

SERIES A, R = R′ = CH_3; SERIES B, R = H, R′ = C_2H_5



(8) A. C. Cope and E. M. Hancock, THIS JOURNAL, **66**, 1448 (1944).

(9) (a) G. H. Coleman, G. M. Mullins and E. Pickering, *ibid.*, **50**, 2739 (1928). (b) G. H. Coleman and H. P. Howells, *ibid.*, **45**, 3084 (1923).

Both VIII and IX were readily converted to the benzamido benzoates (X). The benzamido alcohol VIA and the amino benzoate VIIIA were readily interconvertible as has been shown in other cases.[10] Distillation of VIA caused dehydration to VIIA, identified as the picrate, but VIB was distilled unchanged.

By analogy, the other eight benzamido alcohols listed in Table I are assumed to have the structures given; 2-*p*-nitrobenzamido-2-methyl-1-propanol was reported[11] with very similar properties during the course of this work.

Experimental[12]

Substituted Benzamido Alcohols. 2-*p*-Nitrobenzamido-2-methyl-1-propanol.—The benzamido alcohols described in Table I were obtained by a general procedure modeled after the one given here for 2-*p*-nitrobenzamido-2-methyl-1-propanol. A solution of 10.5 g. (0.063 mole) of *p*-nitrobenzoic acid in 200 ml. of chloroform was prepared and 2.20 g. (0.031 mole) of 2,2-dimethylethylenimine in 25 ml. of chloroform was added. The solution was refluxed for 3 hours and then allowed to stand at room temperature for 3 days. The cooled solution was washed with ice-cold 5% sodium hydroxide until acidification of the aqueous layer gave no precipitate of *p*-nitrobenzoic acid. Four grams (0.024 mole) of *p*-nitrobenzoic acid was recovered. The chloroform layer was dried over magnesium sulfate and the chloroform removed by distillation, leaving 7.30 g. (99%) of 2-*p*-nitrobenzamido-2-methyl-1-propanol, m.p. 114–118°. Recrystallization from chloroform–hexane raised the m.p. to 120.0–120.8°.[11]

Three cases of exceptional behavior in these reactions are noted in Table I.

2-Phenyl-4,4-dimethyl-2-oxazoline Picrate (VIIA Picrate).—In an attempt to purify 2-benzamido-2-methyl-1-propanol (VIA) by distillation before its identity was known, a few drops of a colorless oil, b.p. 98–100° (10 mm.), $n^{20}D$ 1.5276, was obtained which was soluble in dilute hydrochloric acid and gave a picrate from water solution. From 1.53 g. of VIA, 0.39 g. (12%) of 2-phenyl-4,4-dimethyl-2-oxazoline picrate resulted. The picrate was recrystallized from 95% ethanol; m.p. 132.2–132.8°.

Anal. Calcd. for $C_{17}H_{16}N_4O_8$: C, 50.50; H, 3.99; N, 13.86. Found: C, 50.66; H, 4.10; N, 13.68.

The oxazoline has been reported[13] but no properties are recorded.

2-Amino-2-methylpropyl Benzoate Hydrochloride (VIIIA). Procedure A.—Dry hydrogen chloride was bubbled into a cold absolute ethanol solution of 0.20 g. of 2-benzamido-2-methyl-1-propanol for a few minutes. The solution was heated a few minutes on the steam-bath and then evaporation of the ethanol gave 0.24 g. (100%) of the ester hydrochloride, m.p. 215–220°. Recrystallization from absolute ethanol or equal mixtures of ethanol and ethyl acetate gave beautiful long needles, m.p. 223.0–224.6° (closed tube).[14]

Procedure B.—The same hydrochloride VIIIA was obtained in quantitative yield from 2-benzamido-1-chloro-2-methylpropane[8,15] (XIIA) by heating a 60% ethanol solution of the compound at 90° for one hour; m.p. 210–215°. Recrystallization from absolute ethanol gave a m.p. 224–226°.

Procedure C.—The ester hydrochloride was identified by synthesis from 2-amino-2-methyl-1-propanol hydrochloride (IXA), m.p. 204–206°,[16] using Cope and Hancock's[7] method. Mixed m.p.'s with the samples from the first two procedures gave no depression.

Finally, 2-amino-2-methylpropyl benzoate hydrochloride was converted by the Schotten–Baumann reaction to the benzamido benzoate XA in a quantitative yield of crude material, m.p. 100–105°. Three recrystallizations from 95% ethanol raised the m.p. to 109.6–110.2°. Boyd and Hansen[11] report the m.p. 111–112°.

Benzoic Acid Salt of 2-Amino-2-methylpropyl Benzoate (XIII Benzoate).—To a reaction mixture containing 0.23 g. of 2,2-dimethylethylenimine and 1.16 g. of benzoic acid in 10 ml. of chloroform which had been refluxed for 2 hours and allowed to stand 45 hours, a few drops of ether was added. A precipitate of the benzoate salt of 2-amino-2-methylpropyl benzoate formed at once, yield 0.74 g. (74%). A sample sublimed at 100° (0.4 mm.) gave an analytical sample m.p. 143.5–144.0°.

Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.63; H, 6.80; N, 4.61.

2-Aminobutyl Benzoate Hydrochloride (VIIIB).—The B series of compounds (Chart I) were obtained by procedures similar to those just described. The hydrochloride of 2-aminobutyl benzoate was obtained from 2-benzamido-1-chlorobutane[9,15] in 59% yield; m.p. 161.0–163.2° (from acetone). Ullyot[14] gives m.p. 161–163.5°. The compound was also obtained from 2-amino-1-butanol hydrochloride[14] by Cope's[7] method in 78% yield; m.p. 161–163°. A Schotten–Baumann reaction on the benzoate ester hydrochloride gave a quantitative yield of 2-benzamidobutyl benzoate, m.p. 103.2–103.6° (from ethanol followed by sublimation).

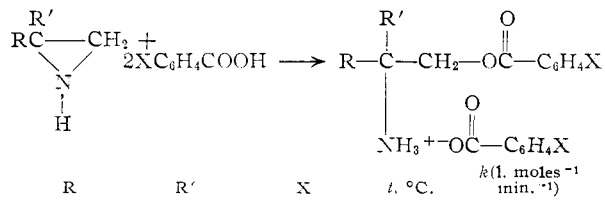
Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44. Found: C, 72.69; H, 6.30.

Purification of Materials.—For the kinetic experiments in dioxane, the benzoic acids were recrystallized from methanol–water mixture to constant melting points as follows: benzoic, 121.2–122.0°; *p*-toluic, 178.5–179.5°; *p*-anisic, 183.5–184.5°; *p*-bromobenzoic, 251–252°; *p*-nitrobenzoic, 241–242°. The ethylenimines were freshly distilled from sodium before each run: 2,2-dimethylethylenimine, b.p. 70.5–71.0°; 2-ethylethylenimine, b.p. 88.5–89.0°. Dioxane was purified by the method of Hess and Frahm[17] as outlined by Fieser[18] and distilled under nitrogen directly into the reaction flask containing a benzoic acid.

Kinetic Method.—A solution of 2.533 g. of benzoic acid in about 400 ml. of pure dioxane was allowed to come to ther-

TABLE II

RATES OF THE REACTIONS OF 2-ETHYLETHYLENIMINE AND 2,2-DIMETHYLETHYLENIMINE WITH SUBSTITUTED BENZOIC ACIDS IN DIOXANE



R	R′	X	t, °C.	k(l. moles^{-1} min.$^{-1}$)
C_2H_5	H	H	25	0.00130
C_2H_5	H	H	35	.00392
C_2H_5	H	H	45	.00740
CH_3	CH_3	H	45	.0204
C_2H_5	H	NO_2	25	.0223
C_2H_5	H	NO_2	35	.0379
C_2H_5	H	NO_2	35	.0409
C_2H_5	H	NO_2	35	.0338
C_2H_5	H	NO_2	45	.132
CH_3	CH_3	NO_2	45	.222
C_2H_5	H	Br	45	.0260
CH_3	CH_3	Br	45	.0517
C_2H_5	H	CH_3	45	.00374
C_2H_5	H	CH_3O	45	.00293
CH_3	CH_3	CH_3O	45	.00891

(10) For a leading reference, see E. E. van Tamelen, *ibid.*, **73**, 5773 (1951).

(11) R. N. Boyd and R. H. Hansen, *ibid.*, **75**, 5896 (1953).

(12) Melting points given to tenths of a degree are corrected. Analyses by S. M. Nagy, Microchemical Laboratory, M.I.T., Cambridge, Massachusetts.

(13) P. F. Tryon, U. S. Patents 2,372,409–10 (1945).

(14) G. E. Ullyot, U. S. Patent 2,463,831 (1949).

(15) V. B. Schatz and L. B. Clapp, THIS JOURNAL, **77**, 5113 (1955).

(16) J. H. Jones, *J. Assoc. Official Agr. Chem.*, **27**, 467 (1944); *C. A.*, **38**, 6275 (1944).

(17) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

(18) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, Ed. 2, p. 368.

mostat temperature (constant to ±0.05°). A 25-ml. portion of the solution was withdrawn, added to 25 ml. of standard sodium hydroxide at the same temperature, and titrated conductometrically in an erlenmeyer cell[19] against standard hydrochloric acid in 50% dioxane.

A sample of 2,2-dimethylethylenimine weighing 1.3319 g. was diluted with dioxane to 50 ml. A 25-ml. portion of this solution was added to the remaining solution of benzoic acid in dioxane and the time recorded. At appropriate intervals 25-ml. samples of the reaction mixture were withdrawn and treated as the benzoic acid solution had been. The time of withdrawal was considered to be when half the sample was added to the sodium hydroxide solution. The accuracy was ±0.5 minute. The reaction mixture was kept under a slight nitrogen pressure and samples were taken by increasing the nitrogen pressure to fill the pipet.

The rates gives in Table II were determined by plotting $1/(a - 2b) \ln (a - 2X)/(b - X)$ against time in minutes where a is the original acid concentration, b is the original imine concentration and X the amount of benzoic acid used in forming the benzamide. A value for the rate was calculated for each recorded interval of time from the equation

$$kt = \frac{1}{a - 2b} \ln \frac{a - 2X}{b - X} - \frac{1}{a - 2b} \ln \frac{a}{b}$$

where the value for the second term is the intercept of the curve as calculated by the method of least squares. Average deviations from the calculated rates were determined and the slopes were calculated by the method of least squares.

The ρ-values were then obtained by plotting the accepted σ-values[20] for the various substituents against log k (Fig. 1). The slopes of these curves are the respective ρ-values + 1.66 and +1.50.

Acknowledgment.—The authors are indebted to John O. Edwards for valuable suggestions and discussions on the kinetic studies reported here.

(19) C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

(20) Ref. 3, p. 188.

PROVIDENCE, R. I.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Rate of Ferrous–Ferric Exchange in D_2O[1]

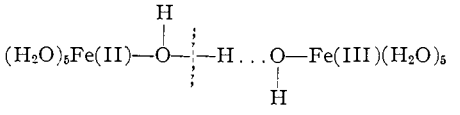
BY J. HUDIS AND R. W. DODSON

RECEIVED OCTOBER 25, 1955

The rate of the ferrous–ferric electron exchange reaction has been measured in heavy water solvent as a function of perchloric acid concentration at constant ionic strength. As in light water, the acid dependence indicates two reaction paths involving ferric ion and hydrolyzed ferric ion, respectively. The specific rate constants are each lowered by a factor of *ca.* 2 in D_2O. The result supports the idea of a hydrogen "atom transfer" mechanism for electron exchange.

Introduction

Previous measurements[2] of the rate of the ferrous–ferric electron exchange in aqueous perchlorate media have shown that the rate law is expressible as $R = k_1(Fe^{++})(Fe^{+++}) + k_2(Fe^{++})(FeOH^{++})$, and that the specific rate constant, k_2, for the path involving hydrolyzed ferric ion is about 1000 times that for the path involving unhydrolyzed ferric ion. In order to account for the exceptionally high rate of the Fe^{++}–$FeOH^{++}$ reaction it has been suggested[3] that a mechanism of hydrogen atom transfer might be particularly favorable in this case.



It has also been found[2,4] that $FeCl^{++}$, $FeCl_2^+$, FeF^{++}, FeF_2^+ and FeF_3 all exchange with ferrous ion at rates equal within an order of magnitude to that of the (Fe^{+++}) reaction. Hydrogen atom transfer has been suggested[4] as a feature common to all these reactions.

To investigate the hypothesis of a hydrogen transfer mechanism we have studied the rate of the ferrous–ferric exchange in heavy water solvent under conditions which were otherwise comparable to those of some of the earlier experiments.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 869 (1952).

(3) R. W. Dodson, *ibid.*, **56**, 852 (1952); R. W. Dodson and N. Davidson, *ibid.*, **56**, 866 (1952), remarks in discussion at the 1952 ACS Symposium at Notre Dame.

(4) J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

Experimental

The experimental procedure followed was similar to that used in previous iron exchange work.[2,4] α,α'-Dipyridyl was used to complex the Fe(II), thereby stopping the reaction. The Fe(III) fraction was then removed immediately by precipitation of $Fe(OH)_3$ with NH_4OH. Fe^{55} obtained from the Atomic Energy Commission at Oak Ridge was the radioactive tracer used, and the 5.9 kev. Mn X-rays emitted were detected either by means of a scintillation counter or a Geiger–Mueller counter. All reagents, including the radioactive tracer, were purified as earlier described.[4] The heavy water (~99% D_2O) was obtained from the Stuart Oxygen Co., San Francisco.

Each exchange solution was prepared by the addition of small volumes of the relatively concentrated reagent solutions (H_2O) to a sufficient volume of D_2O to bring the final volume to 10.0 ml. The ionic strength was adjusted to 0.55 *f* with weighed amounts of sodium perchlorate. Eight 0.8-ml. samples were withdrawn from the reaction mixture for exchange points; two 1.0-ml. aliquots were taken for iron analyses; and the remaining solution was used to check the D_2O/H_2O ratio present at the end of the experiment. The sample taken for the determination of the D_2O/H_2O ratio was doubly vacuum distilled and the refractive index of the purified sample measured with an Abbe type refractometer.[5] All D_2O/H_2O analyses indicated that at the end of the experiment the mole fraction of D_2O was greater than 0.90 ± 0.05. The refractive index measurements were reproducible to ±3% and the difference between the refractive indices of pure D_2O and pure H_2O agreed with the literature value to ±5%. Any error in the refractive index analysis due to H_2O^{18} enrichment of the D_2O would be small, since the samples measured were high in D_2O content and were analyzed by comparison with 99% D_2O. No correction was applied to the rate data to normalize results to 100% D_2O.

The reaction mixtures were made up in such a way that the ferrous concentration was approximately twice the ferric concentration. The exact concentration of total iron was determined by reducing an aliquot of the mixture, adding α,α'-dipyridyl, and measuring the optical density with a Beckman spectrophotometer. Since the reaction has been

(5) G. N. Lewis and D. B. Luten, *ibid.*, **55**, 5061 (1933).