trostatic) is increased by the addition of other solvents to methanol. These results support the hypotheses that methanol is depolymerized by addition of other solvents and that selective solvation of ions can occur.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Kinetics of the Diazotization of Anilines

BY MASAYA OKANO AND YOSHIRO OGATA

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The rates of diazotization of aniline and substituted anilines in aqueous sulfuric acid at 0° have been estimated by coupling of the diazonium salts with β-naphthol. From *p*H 0.6 to 3.3 the rate of diazotization was first-order with respect to aniline concentration and second-order with respect to nitrous acid. The relation between *p*H and the rate constant indicated that $HN_2O_3^+$ is the attacking agent. Substituted anilines were studied in competitive diazotizations at *p*H 0.6 with sulfanilic acid as a standard, and the relative rates satisfied a Hammett equation with a ρ-value of −1.96.

The rate of reaction of amines with nitrous acid has generally been expressed as *k*[amine][nitrous acid]^2.[1] In a recent study of the reaction of methylamine or ammonia with nitrous acid, Dusenbury and Powell[2] have suggested that the rate is first-order with nitrous acid, implying an attack by NO^+ ion. Early studies on aromatic diazotization[3] led to a rate law *k*[amine][nitrous acid], but Schmid[1d,4] and Ingold and his collaborators[5] have found the rate to be second-order with respect to nitrous acid over a comparatively wide *p*H range. This means that either the formation of, or the attack by, N_2O_3 or $HN_2O_3^+$ is rate-determining, but it is not clear which is the more probable. Moreover, although a rough comparison of the apparent rates of diazotization of substituted anilines has been made,[6] no decisive data on the effect of substituents on the rate are available. The present study was undertaken in order to supply this information.

I. Kinetics of the Diazotization of Aniline

Experimental

Materials.—Commercial aniline and β-naphthol were purified by duplicate vacuum distillations. Sodium nitrite, sulfuric acid and sodium sulfate were of the best grade available.

General Procedure for Rate Measurements.—A mixture of 150 cc. of 0.02 *N* aniline sulfate solution, 150 cc. of 0.2 *N* sulfuric acid–sodium sulfate buffer[7] and 240 cc. of distilled water was placed in a 1-l. three-necked flask equipped with thermometer and stirrer, and thermostated at 0° by immersion in an ice-bath. Now 60 cc. of 0.05 *N* sodium nitrite solution, previously cooled to 0°, was added. Five 100-cc. aliquots were withdrawn by means of a calibrated pipet and the time of each withdrawal was noted. Each aliquot was added to about 150 cc. of water, which contained 0.000625 mole (at least 25% excess) of β-naphthol, about 1 g. of sodium acetate and a quantity of sodium hydroxide sufficient to leave a slight excess after neutralization of the sulfuric acid present.[8] The azo compound was immediately formed. The mixture was allowed to stand overnight, heated, cooled and filtered through a sintered glass funnel. The collected azo compound was dried at 80° for 3 hours and weighed. This method of estimation is believed to be nearly quantitative because after complete consumption of the nitrous acid the yields of azo compound obtained always exceeded 98% of the theoretical amount.

Experimental Results and Calculations.—Table Ia summarizes the effect on the rate of the molar ratio and of the concentration of the reactants, and the *p*H effect is shown in Table Ib. The *p*H was determined at 15° by means of a glass electrode. The rate constants were calculated from (2) which arises on integration of (1), where *a* and *b* are the initial concentrations of aniline and nitrous acid, respectively, and *x* is the concentration of the diazonium salt present after *t* seconds.

$$\mathrm{d}x/\mathrm{d}t = k(a - x)(b - x)^2 \qquad (1)$$

If $a = b$

$$k = \frac{1}{2t}\left\{\frac{1}{(a - x)^2} - \frac{1}{a^2}\right\}$$

if $a \neq b$

$$k = \frac{1}{t(a - b)}\left\{\frac{1}{b - x} - \frac{1}{b} + \frac{1}{a - b}\ln\frac{a(b - x)}{b(a - x)}\right\} \qquad (2)$$

Discussion of Results

The order with which the reactants appear in the rate equation lead us to assume a rate-determining step involving an electrophilic attack by

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[1] (a) The reaction of ammonia with nitrous acid: E. Abel, H. Schmid and J. Schafranik, *Z. physik. Chem.*, *Bodenstein Festband*, 510 (1931); (b) the reaction of aliphatic amines with nitrous acid: T. W. J. Taylor, *J. Chem. Soc.*, 1099, 1897 (1928); T. W. J. Taylor and L. S. Price, *ibid.*, 2052 (1929); (c) the reaction of amino acid with nitrous acid: E. Abel and H. Schmid, *Z. Elektrochem.*, **39**, 863 (1933); (d) the reaction of aromatic amine with nitrous acid: H. Schmid and G. Muhr, *Ber.*, **70**, 421 (1937).

[2] J. H. Dusenbury and R. E. Powell, THIS JOURNAL, **73**, 3266, 3269 (1951). And also A. T. Austin, E. D. Hughes, C. K. Ingold and J. H. Ridd, *ibid.*, **74**, 555 (1952). Recently Abel suggested another mechanism which involves an attack of NO on ammonium or aminium ion in this case [E. Abel, *Monatsh.*, **83**, 1103 (1952)], but this seems less probable in view of present electronic theory.

[3] A. Hantszch and H. Schümann, *Ber.*, **32**, 1691 (1899); E. Tassilly, *Bull. soc. chim.*, **27**, 19 (1920); J. Böeseken, W. F. Brandsma and H. A. J. Schoutissen, *C. A.*, **15**, 1023 (1921).

[4] H. Schmid and A. Wappmann, *Monatsh.*, **83**, 346 (1952).

[5] E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950).

[6] S. Ueno and T. Suzuki, *J. Soc. Chem. Ind., Japan*, **36**, 615B (1933).

[7] No effect of ionic strength on the rate was observed on addition of sodium sulfate. In weakly acidic media, an increase of *p*H was recognized during the reaction; therefore, we employed sulfuric acid–sodium sulfate solution with constant ionic strength as a buffer. Rate measurements in other buffers (for example, biphthalate-hydrochloric acid or citric acid–citrate buffer) were also carried out at *p*H *ca.* 3; the data, however, did not agree with those in sulfuric acid–sulfate buffer. Perhaps this is due to a catalytic action of the anions as observed in the case of chloride ion in the diazotization in hydrochloric acid.[1d]

[8] Although coupling is faster in the presence of a substantial excess alkali, the danger of losses due to solubility of the product argued against the use of higher *p*H. Too low a *p*H leads to uncertain data because the rate of coupling falls below that of diazotization.

TABLE I

RATE CONSTANTS OF THE DIAZOTIZATION OF ANILINE AT 0°

(a) Effect of the Molar Ratio and Concentration

Initial concentration Aniline, (*a*) *M*	Initial concentration HNO$_2$, (*b*) *N*	*p*H^a	$k_{av} \times 10^{-2}$, l.^{2} mole^{-2} sec.$^{-1\,b}$
0.0050–0.0075	0.0050–0.0075	2.2	3.13 ± 0.04
.0050	.0025– .0075	3.0	1.84 ± .03
.0050–0.0075	.0050– .0075	3.3	1.10 ± .04

(b) Effect of *p*H^c

*p*H^a	$k \times 10^{-2}$, l.^{2} mole^{-2} sec.$^{-1\,b}$	*p*H^a	$k \times 10^{-2}$, l.^{2} mole^{-2} sec.$^{-1\,b}$
3.3	1.11 ± 0.04	2.0	3.11 ± 0.02
3.15	1.38 ± .04	1.8	2.98 ± .03
3.0	1.83 ± .03	1.6	2.54 ± .03
2.6	2.42 ± .02	1.3	1.86 ± .03
2.3	2.95 ± .03	1.0	1.27 ± .02
2.15	3.07 ± .02	0.6	0.64 ± .02

[a] H_2SO_4–Na_2SO_4 buffer was employed at *p*H 2.0–3.3, and H_2SO_4 alone at the lower values. [b] The probable error for each constant is given. [c] Initial concentration: aniline, 0.0050 *M;* HNO$_2$, 0.0050 *N*.

N_2O_3 or $HN_2O_3^+$ upon the amino nitrogen. Since the reaction is acid-catalyzed we prefer the more reactive species $HN_2O_3^+$, and the sequence is suggested

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^- \text{ (mobile)} \quad (3)$$

$$2HNO_2 + H_3O^+ \rightleftharpoons HN_2O_3^+ + 2H_2O \text{ (mobile)} \quad (4)$$

$$C_6H_5NH_2 + H_3O^+ \rightleftharpoons C_6H_5NH_3^+ + H_2O \text{ (mobile)} \quad (5)$$

$$C_6H_5NH_2 + HN_2O_3^+ \longrightarrow C_6H_5N_2^+ + H_2O + HNO_2 \text{ (slow)} \quad (6)$$

The rate equation for this sequence is

$$dx/dt = k_6[C_6H_5NH_2][HN_2O_3^+] \quad (7)$$

where k_6 is the rate constant pertaining to step 6. The stoichiometric concentration of aniline may be expressed[9] as

$$a - x = [C_6H_5NH_2] + [C_6H_5NH_3^+] \backsimeq [C_6H_5NH_3^+]$$

and

$$[C_6H_5NH_2] = \frac{[H_2O]}{K_5[H_3O^+]}(a - x) \quad (8)$$

In expressing the stoichiometric concentration of nitrous acid one considers its feeble proton acceptor properties—equilibrium 4 lies to the left-hand side—and arrives at

$$b - x = [HNO_2] + [NO_2^-] + 2[HN_2O_3^+] \backsimeq [HNO_2] + [NO_2^-]$$

whence

$$[HN_2O_3^+] = \frac{[H_3O^+]^3K_4}{[H_2O]^2\{[H_3O^+] + K_3[H_2O]\}^2}(b - x)^2 \quad (9)$$

where *K*-values are the equilibrium constants of the subscripted reactions. By substitution from (8) and (9) into (7), we obtain the rate constant *k* as a function of $[H_3O^+]$, *i.e.*, equation 10.

$$\frac{dx}{dt} = \frac{k_6K_4[H_3O^+]^2}{K_5[H_2O]\{[H_3O^+] + K_3[H_2O]\}^2}(a - x)(b - x)^2 = k(a - x)(b - x)^2$$

$$k = C\frac{[H_3O^+]^2}{\{[H_3O^+] + K_3[H_2O]\}^2} = Cf([H_3O^+]) \quad (10)$$

where $C = k_6K_4/K_5[H_2O]$ = constant.

The value of K_3 at 0° has been reported[10] to be 0.64×10^{-5}; thus relative rates at various *p*H values may be computed from (10). For mechanisms involving attack by N_2O_3[11] or NO^+ rather than $HN_2O_3^+$, the relationships 11 and 12, respectively, are derivable.

$$k' = C'\frac{[H_3O^+]}{\{[H_3O^+] + K_3[H_2O]\}^2} = C'f'([H_3O^+]) \quad (11)$$

$$k'' = C''\frac{[H_3O^+]}{\{[H_3O^+] + K_3[H_2O]\}} = C''f''([H_3O^+]) \quad (12)$$

where C' and C'' constants and rate equation: $dx/dt = k''_6[C_6H_5NH_2][NO^+]$.

In Table II are listed relative rates, at varying *p*H, as predicted from relations 10, 11 and 12 in columns I, II and III, respectively. The values listed in column I agree best with the observed data.

TABLE II

COMPARISON OF OBSERVED RELATIVE RATES WITH RATES PREDICTED FROM THREE DIFFERENT MECHANISMS

		Calcd.						
		(I) Attack by $HN_2O_3^+$		(II) Attack by N_2O_3		(III) Attack by NO^+		Obsd.
*p*H	*M* $[H_3O^+] \times 10^3$	$f([H_3O^+])$	Rel. rate	$f'([H_3O^+]) \times 10^{-3}$	Rel. rate	$f''([H_3O^+])$	Rel. rate	Rel. rate
3.3	0.50	0.35	1.0	0.69	1.0	0.59	1.0	1.0
3.0	1.00	.55	1.6	.55	0.8	.74	1.3	1.7
2.6	2.50	.77	2.2	.31	.45	.88	1.5	2.2
2.3	5.00	.88	2.5	.17	.25	.93	1.6	2.7
2.0	10.00	.93	2.7	.09	.13	.97	1.6	2.8

An increase of the observed rate constant with falling *p*H is expected from equation 10 and verified experimentally (Table I). However, whereas equation 10 predicts approximations of *k* to a constant value, the observed rate constant passes through a maximum at *p*H 2.0. This reversal may be due to the approximation made in deriving expression 9. At low *p*H the term $[HN_2O_3^+]$ may no longer be negligible in the expression for $(b - x)$ and, instead, $[NO_2^-]$ may become negligibly small, so that

$$b - x = [HNO_2] + [HN_2O_3^+]$$

Development of this expression leads to an approximation for $[HN_2O_3^+]$ which, when combined with (8), gives a differential equation $dx/dt = k(a - x)(b - x)^2$ where *k* now has the form (when C_1, etc., are constants)

$$k = \frac{C_3}{C_1 + C_2[H_3O^+](b - x)}$$

This expression accounts qualitatively for the inverse relationship between the observed rate constant and acid concentration at low *p*H, but accurate consideration is difficult since the term $(b - x)$ is a variable.

II. Competitive Diazotization of Substituted Anilines

Experimental

Materials.—Commercial substituted anilines were purified by vacuum distillation or recrystallization and their

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(9) Even at *p*H 3.3 98% of the aniline present is ionized and the concentration of free aniline becomes negligible.

(10) H. Schmid, R. Marchgraber and F. Dunkel, *Z. Elektrochem.*, **43**, 337 (1937). Calcd. from $K_A = 3.5 \times 10^{-4}$.

(11) The detailed calculations of Schmid and Wappmann[4] appear unsuitable because the value of K_5 for diazotization in nitrate-buffered medium was derived from the equilibrium constant for the reaction $C_6H_5NH_2 + HNO_2 \leftrightarrows C_6H_5NH_3^+ + NO_2^-$.

m.p. or b.p. agreed with the literature values. For the other materials see Part I.

General Procedure.—A solution of 0.002 mole of sulfanilic acid and of 0.002 mole of a substituted aniline in 80 cc. of 0.625 *N* sulfuric acid was placed into a 200-cc. erlenmeyer flask and cooled to 0°. In another flask 20 cc. of 0.1 *N* sodium nitrite solution was cooled to 0°. The solutions were mixed, allowed to stand for 2 hours and run into an alkaline solution of β-naphthol as described in Part I. The coupling product of the diazotized sulfanilic acid (Orange II) remains in solution and the azo compound formed from the substituted aniline studied is collected and estimated as in Part I.

Experimental Results and Calculations.—The following rate equations apply to the case of competitive diazotization of a substituted aniline B in the presence of sulfanilic acid A

$$\begin{cases} \mathrm{d}x_A/\mathrm{d}t = (k_A/K_A)(a - x_A)(b - x_A - x_B)^2 \\ \mathrm{d}x_B/\mathrm{d}t = (k_B/K_B)(a - x_B)(b - x_A - x_B)^2 \end{cases} \qquad (13)$$

where K_A and K_B are equilibrium constants in equation 5, k_A and k_B are rate constants, and x_A and x_B are the diazonium salt concentrations at time t. Thus k_B may be expressed as a function of the other five variables.

$$\frac{\mathrm{d}x_A}{a - x_A} = \frac{k_A K_B}{k_B K_A}\frac{\mathrm{d}x_B}{a - x_B}$$

$$k_B = K_B \left\{\frac{\log(1 - (x_B/a)}{\log(1 - (x_A/a)}\right\} \frac{k_A}{K_A} \qquad (14)$$

Since K_A, K_B and x_B are known or measurable, and since upon complete consumption of nitrous acid the sum $(x_A + x_B)$ equals the total amount of nitrite added, k_B may be computed. Table III lists the results, where x_B/a and x_A/a represent the fractions diazotized of the two competing amines. From the rate relative to aniline the ρ-factor for Hammett's equation[12] was calculated as shown in the Table III.

TABLE III

RELATIVE RATES OF DIAZOTIZATION OF SUBSTITUTED ANILINES AT 0°

Initial concentration: 0.02 *M* for aniline and for sulfanilic acid; 0.5 *N* for sulfuric acid; 0.02 *N* for nitrous acid; *p*H 0.6; reaction time 2 hours

Substituent	x_B/a	x_A/a	$K_B \times 10^{-6}$ [a]	Relative rate: Based on sulfanilic acid,[b]	Relative rate: Based on aniline	ρ
m-CH_3	0.264	0.736	2.71	0.62	1.38	−2.12
p-CH_3	.209	.791	6.5	0.98	2.18	−1.99
p-OCH_3	.192	.808	10.8	1.39	3.10	−1.94
p-OC_2H_5	.223	.777	9.8	1.65	3.67	−2.26
None	.255	.745	2.10	0.450	1.00	....
m-Cl[c]	.421	.579	0.158	.100	0.222	−1.75
p-Cl	.340	.660	.47	.183	.407	−1.72
m-NO_2[c]	.518	.482	.022	.024	.053	−1.80
p-NO_2[c]	.867	.133	.0055	.0011	.0022	−2.08
					Av.	−1.96 ± 0.05[d]

[a] H. Landolt–R. Börnstein, "Physikalischen Chemische Tabellen," Eg. II, Eg. III, 5 Aufl., Julius Springer, Berlin, 1936. Calculated from the basicity constant K at 25°; $K_B = K[H_2O]/K_w = K \times 55 \times 10^{14}$. [b] Since the value of K_A was unavailable, these values were shown in $(K_A/10^6)$ unit, *e.g.*, the relative rate of *m*-toluidine is 0.62 × $10^{-6}/K_A$. [c] Became a little turbid during the reaction. [d] Probable error.

Apparently electron-releasing groups in the *p*-position facilitate the electrophilic attack by $HN_2O_3^+$ while with electron-withdrawing groups the reverse is true. The effect of substituents on the rate of the reaction may be expressed by a Hammett equation with an average ρ-value of −1.96 ± 0.05.

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KYOTO, JAPAN

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[12] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF GULF RESEARCH AND DEVELOPMENT COMPANY, MELLON INSTITUTE]

Fischer–Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Alcohols to the Synthesis Gas

BY J. T. KUMMER AND P. H. EMMETT

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When one of the radioactive primary alcohols, such as ethanol, *n*-propanol or isobutyl alcohol, is added to the extent of about 1.5 volume per cent. to a 1:1 hydrogen:carbon monoxide synthesis gas and passed over an iron catalyst at 235° and one atmosphere pressure, the hydrocarbon synthesis products in the C_2–C_{10}, C_3–C_{10} and C_4–C_{10} ranges, respectively, are found to have an approximately constant molal radioactivity equal to one-third to one-half the molal radioactivity of the original alcohol. These results show that primary alcohols adsorbed on iron catalysts can act as starting nuclei in building up higher hydrocarbons. Adsorbed methanol can also start reaction chains leading to higher hydrocarbons, but the efficiency of incorporation is only about one-fourth as great as with the other primary alcohols mentioned above. Isopropyl alcohol, a secondary alcohol, is extensively converted to isobutane and isobutene but only about one C_7 molecule in 15 and one C_9 molecule in 27 comes from the isopropyl alcohol. *t*-Butyl alcohol is apparently not capable of building up to higher hydrocarbons under the conditions of these experiments. In the runs in which radioactive normal propanol was added to the synthesis gas the *n*-C_4H_{10} formed was radioactive; the *i*-C_4H_{10}, non-radioactive. Conversely, when radioactive isopropyl alcohol was added, the *n*-C_4H_{10} was non-radioactive; the *i*-C_4H_{10}, radioactive. The results are interpreted as indicating that complexes resembling adsorbed alcohols are formed from carbon monoxide and hydrogen during synthesis and act as intermediates in the building up of higher hydrocarbons over iron catalysts.

When a small amount of radioactive ethanol is added to a 1:1 carbon monoxide–hydrogen synthesis gas mixture and passed over an iron catalyst at about 235°, the C_2 to C_{10} hydrocarbon synthesis product has been shown[1] to have an approximately constant radioactivity per mole. This has been interpreted as indicating that the complex formed by the adsorption of ethanol on the iron catalyst is capable of acting as an intermediate in the synthesis of higher hydrocarbons. Pyrolysis of the propane from these experiments showed, furthermore, that carbon atoms attach themselves preferentially

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[1] J. T. Kummer, W. B. Spencer, H. H. Podgurski and P. H. Emmett, THIS JOURNAL, **73**, 564 (1951).