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Structure−Reactivity Correlation of Anilines in Acetic Acid

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The oxidation of aniline in glacial acetic acid with percarbonate, a dry carrier of hydrogen peroxide, is a second-order reaction conforming to the isokinetic relationship. The hitherto followed method of correlation of the reaction rates in terms of the structure−reactivity relationships is unsatisfactory and erroneous. But the reaction rates of molecular anilines, obtained for the first time, conform to the structure−reactivity relationships.

Introduction

Studies on the structure−reactivity relationships of anilines are numerous, and the reaction rates conform to the usual Hammett equation (reaction constant: ρ), its modified form (reaction constant: ρ^-), or the Brown−Okamoto equation (reaction constant: ρ^+). The oxidation by chloramine-T (aqueous ethanol, $[OH^-] = 0.10$ mol dm^{-3}, $\rho = -1.0$),[1] peroxodisulfate (aqueous 2-propanol, $[OH^-] = 0.48$ mol dm^{-3}, $\rho = -1.3$),[2] aqueous *tert*-butyl alcohol, $[OH^-] = 0.25$ mol dm^{-3}, $\rho = -1.5$),[3] carbonate radical (pH 8.5, $\rho^+ = -1.0$),[4] borate radical (pH 11.4, $\rho^+ = -0.9$),[5] and hexacyanoferrate(III) (aqueous ethanol, $10^2[OH^-] = 2.5$ mol dm^{-3}, $\rho^+ = -4.1$)[6] were studied in basic medium and by *N*-chloroacetamide (aqueous ethanol, $\rho = -3.3$),[7] *N*-bromoacetamide (aqueous methanol, $\rho = -0.8$),[8] periodate (aqueous methanol, $\rho = -2.4$),[9] peroxodisulfate (aqueous ethanol, $\rho^+ = -1.4$),[10] (aqueous ethanol, pH 7, $\rho^+ = -0.8$),[11] and peroxomonophosphoric acid (aqueous acetonitrile, pH 5.4, $\rho = -1.4$, $\rho^+ = -1.3$, $\rho^- = -1.4$)[12] at neutral pH. The oxidations by hydrogen peroxide catalyzed by methylrhenium trioxide (methanol, $\rho = -1.2$),[13] peracetic acid (ethanol, $\rho = -1.9$),[14] iodosobenzene (chloroform, $\rho = -1.6$; manganese(III)salen complex-catalyzed, methylene chloride, $\rho^+ = -0.8$),[15] lead(IV) acetate (chloroform−acetic anhydride, $\rho = -2.4$),[16] and pyridinium chlorochromate (chlorobenzene−nitrobenzene, $10^3[Cl_2CHCOOH] = 3 \pm 0.5$ mol dm^{-3}, $\rho^- = -3.8$)[17] were in nonaqueous media. Similar studies in acid medium include chloramine-T (aqueous acetic acid, $10^2[HClO_4] = 0.62-5.0$ mol dm^{-3}),[18] *N*-chlorosuccinimide (acetic acid, $\rho = -1.5$),[19] bromate ion (aqueous acetic acid, $\rho = 1.7$),[20] iodate catalyzed by ruthenium(III) (aqueous acetic acid, $10^2[HClO_4] = 1.0$ mol dm^{-3}, $\rho = -2.8$),[21] periodate (aqueous acetic acid, $\rho^+ = -2.3$),[22] peroxodisulfate (aqueous acetic acid, $\rho = 1.9$),[23] thallium(III) (aqueous acetic acid, $[HClO_4] = 1.0$ mol dm^{-3}, $\rho = -3.0$),[24] thallium(III) catalyzed by ruthenium(III) (aqueous acetic acid, $[HClO_4] = 1.0$ mol dm^{-3}, $\rho = -0.8$),[24] and iron(III)-bipyridyl (aqueous methanol, $10^2[HClO_4] = 1.2$ mol dm^{-3}, $\rho^+ = -3.1$).[25] But the present study reveals that the hitherto followed method of correlation of the reaction rates in acidic solution is erroneous and presents a modified approach. Sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$), a dry carrier of hydrogen peroxide,[26−29] is an inexpensive, innocuous, crystalline salt used extensively in the detergent industry as a bleaching or antiseptic agent. Its use as an effective reagent in organic synthesis

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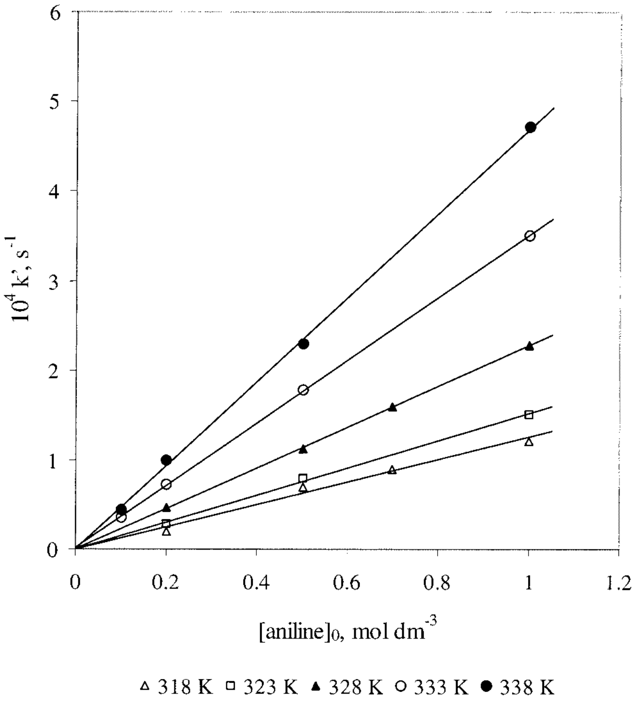

Figure 1. Rate dependence on [aniline].

is beginning to emerge,[30−40] and this is the first report on the kinetics of the oxidation; the reaction was carried out in glacial acetic acid, a solvent suitable for the oxidation.

Results and Discussion

The kinetics of the oxidation, studied in glacial acetic acid under the condition [aniline] ≫ [oxidant], were followed by iodometric estimation of the unreacted oxidizing agent. The reaction is sluggish at room temperature but is smooth at 45−65 °C; the decomposition of the oxidant is large above 65 °C. The reaction is first order with respect to the oxidant. The reaction rates were measured from 15 to 75% consumption of the oxidant, and the plot of log [oxidant] versus reaction times is linear. The pseudo-first-order rate constant (k'), obtained from the least-squares slope of the pseudo-first-order plot, remains constant at different initial concentrations of the oxidant ($10^2[\text{oxidant}]_0 = 0.40-1.80$ mol L^{-1}, $[\text{aniline}]_0 =$ 0.50 mol L^{-1}; $10^4 k' = 2.3$ s^{-1} at 60 °C). The reaction rate is reproducible to ±4%. The oxidation is also first order with respect to aniline. The reaction rate increases with the concentration of aniline, and the plot k' versus [aniline] is a straight line passing through the origin (Figure 1). Glacial acetic acid is a suitable solvent for percarbonate oxidation. At 65 °C, on decreasing the composition of acetic acid to 70% by the addition of methanol, the reaction rate decreases to one-third. The oxidation is not through radical pathway; addition of vinyl monomer, acrylonitrile to the reaction solution (0.10 mol L^{-1}) fails to suppress the reaction. Also, the added vinyl monomer does not polymerize during the course of the reaction.

Sodium percarbonate is a dry carrier of hydrogen peroxide.[26−29] Chemical tests confirm the presence of hydrogen peroxide and the absence of peracetic acid in fresh solutions of percarbonate in glacial acetic acid; formation of peracetic acid from commercial hydrogen peroxide and glacial acetic acid requires a catalytic amount of mineral acid.[41] Further, kinetic experiments with peracetic acid as the oxidant show that the peracetic acid oxidation under identical conditions is fast, too fast to follow by titrimetry. The oxidation mechanism is classical.[42] The electrophilic attack of the peroxide oxygen on the amine nitrogen leading to formation of phenylhydroxylamine is slow and rate limiting. Phenylhydroxylamine is further oxidized to nitrosobenzene, which in turn couples with aniline, present in large excess, to yield azobenzene; the latter two reactions are fast. Methanol is a nucleophile, and association of methanol with the electrophilic peroxide oxygen atom may be a reason for the suppression of the oxidation with the addition of methanol.

The structure−reactivity relationships in the oxidation of anilines in glacial acetic acid were studied with 31 anilines. The activation parameters were calculated from the measured rates at 45, 55, and 65 °C using the Eyring relationship (Table 1). The oxidation is neither isoentropic nor isoenthalpic but conforms to the compensation law also known as isokinetic relationship, a linear relationship between the enthalpy of activation and the entropy of activation (Figure 2: correlation coefficient, r = 0.98, standard error, sd = 3.0). The maximum possible errors in activation enthalpy (δ) and activation entropy are 3.6 kJ mol^{-1} and 11.6 J K^{-1} mol^{-1}, respectively. The error criterion is satisfied in the present study, that is, $\Delta\Delta H^{\ddagger}$ (74.4 kJ mol^{-1}) $\gg 2\delta$ (7.2 kJ mol^{-1}), and hence the correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is significant. However, this relationship is to be viewed with skepticism, as these parameters are mutually interdependent.[43,44] But the existence of the Exner relationship, the linear double logarithmic relationship between the rates at two different temperatures, confirms the isokinetic relationship and reveals that all the anilines, the reaction rates of which were measured, are oxidized through a common mechanism (Figure 3: r = 0.99, sd = 0.09, number of data points, n = 29, slope = 1.21).[43,44] The isokinetic temperature, obtained from the Exner plot, is −25 °C, which is far from the experimental temperature, justifying the structure−reactivity correlation. However, it is possible that anomalous behavior of one or two substituents of very high or very low reactivity (points at the extremes of the Exner plot, and here it is *o*-phenylenediamine) may lead to error in slope and hence in the isokinetic temperature. Inclusion of *o*-phenylenediamine in the Exner plot involves extrapolated values; this

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Table 1. Pseudo-First-Order Rate Constants (k'), Activation Parameters, and Specific Oxidation Rates of Molecular Anilines (k) in Glacial Acetic Acid[a]

		$10^4k'$ (s^{-1})					10^3k ($dm^3\ mol^{-1}\ s^{-1}$)		
entry	substituent	45 °C	55 °C	65 °C	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$-\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	45 °C	55 °C	65 °C
1	H	0.795	1.58	3.11	58.2	141	4.60	9.14	18.0
2	*m*-CH_3	1.01	2.69	5.30	71.5	96.8	7.41	19.7	38.9
3	*m*-OH	1.60	4.17	8.66	72.9	88.9	5.04	13.1	27.3
4	*m*-Cl	0.594	1.27	2.23	56.5	149	0.474	1.01	1.78
5	*m*-NO_2	0.348	0.596	1.24	54.0	161	0.108	0.185	0.384
6	*m*-COOH	0.942	2.33	6.06	80.5	69.7	0.447	1.11	2.88
7	*m*,*p*-$(CH_3)_2$	0.679	1.65	3.52	70.9	102	13.9	33.7	71.9
8	*m*,*p*-Cl_2	0.419	0.801	1.59	56.9	151	0.180	0.345	0.685
9	*p*-CH_3	0.702	1.64	3.52	69.4	107	11.7	27.3	58.7
10	*p*-OCH_3	0.811	2.15	6.10	87.4	49.1	25.5	67.6	192
11	*p*-OC_2H_5	0.755	1.87	4.63	78.3	78.2	18.5	45.8	113
12	*p*-Cl	0.721	1.59	3.59	69.0	108	1.23	2.70	6.10
13	*p*-Br	0.774	1.72	3.82	71.3	52.1	1.08	2.41	5.34
14	*p*-NO_2	0.217[b]	0.408	0.746	52.9	168	0.0472	0.0887	0.162
15	*p*-COOH	0.283	0.555	1.58	74.0	101	0.0856	0.168	0.478
16	*p*-$COOC_2H_5$	0.295	0.686	1.38	66.3	124	0.185	0.429	0.863
17	*p*-$NHCOCH_3$	0.721	1.71	4.38	77.9	80.1	4.17	9.89	25.3
18	*o*,*m*-Cl_2	0.267	0.514	0.921	52.6	168	0.0650	0.125	0.224
19	*o*-CH_3	1.10	2.33	4.74	62.6	125	4.63	9.80	19.9
20	*o*-OCH_3	0.976	2.46	4.42	64.9	118	4.86	12.3	22.0
21	*o*-OC_2H_5	1.04	2.65	5.41	71.1	98.0	4.56	11.6	23.7
22	*o*-Cl	0.295	0.613	2.19	86.6	60.6	0.101	0.210	0.749
23	*o*-NO_2	0.129	0.288	0.472	65.0	135	0.0263	0.0587	0.0962
24	*o*-COOH	0.408	0.877	1.99	68.1	116	0.109	0.234	0.531
25	*o*-$COOCH_3$	0.320	0.647	1.20	56.4	154	0.0947	0.191	0.355
26	*o*-$COCH_3$	0.226	0.456	0.854	56.7	156	0.0631	0.127	0.238
27	*o*-NH_2	104[c]	457[c]	1920[c]	127	−114	670	2940	12400
28	-$NHCH_3$	4.74	11.2	26.9	74.9	73.9	47.3	112	269
29	-$N(CH_3)_2$	1.82	4.47	8.04	63.8	116	35.5	87.3	157
30	*o*-OH	fast							
31	*o*-SH	very fast							

[a] $[\text{oxidant}]_0 = 0.010$ mol dm^{-3}; $[\text{aniline}]_0 = 0.50$ mol dm^{-3}. [b] Extrapolated using Arrhenius plot: 0.576 at 60 °C. [c] Extrapolated using Arrhenius plot: 1.42, 10.7, and 43.1 at 20, 30, and 40 °C, respectively.

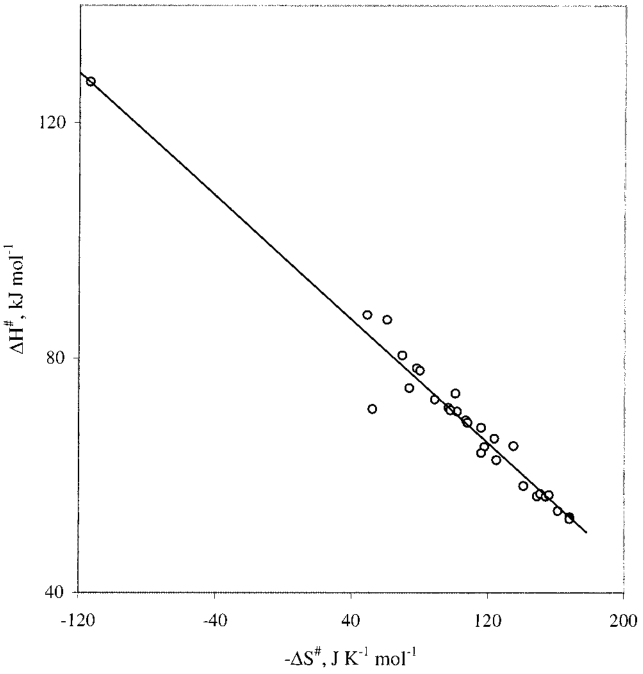

Figure 2. Isokinetic plot.

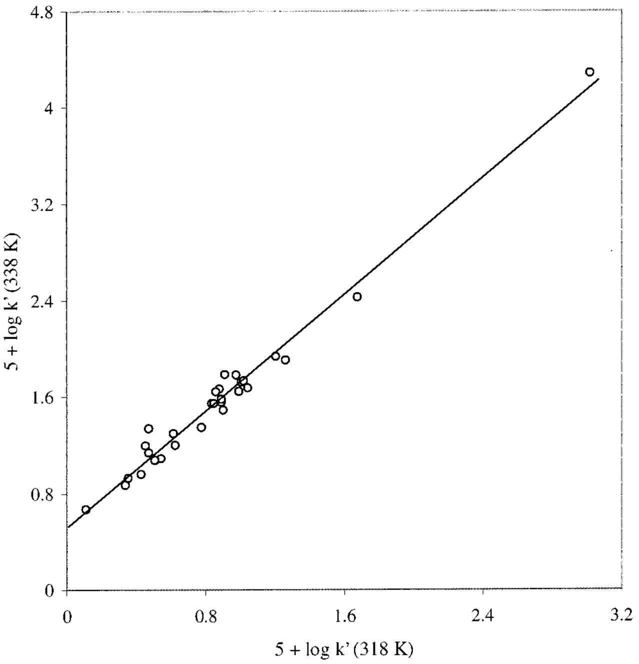

Figure 3. Exner plot.

substrate is highly reactive and may largely define the plot. However, even if *o*-phenylenediamine is omitted, the correlation is satisfactory ($r = 0.97$, sd $= 0.09$, $n = 28$, slope $= 1.12$; figure not given); the isokinetic temperature drops to −58 °C. The spread of the k' values increases with temperature and is in accordance with the fact that the isokinetic temperature is lower than the experimental temperature. Current views do not attach much significance to the isokinetic temperature, though linear correlation is usually a necessary condition for the validity of the Hammett equation.

The rates of oxidation of para- and meta-substituted anilines in acetic acid do not conform to the usual Hammett equation at any of the temperatures studied

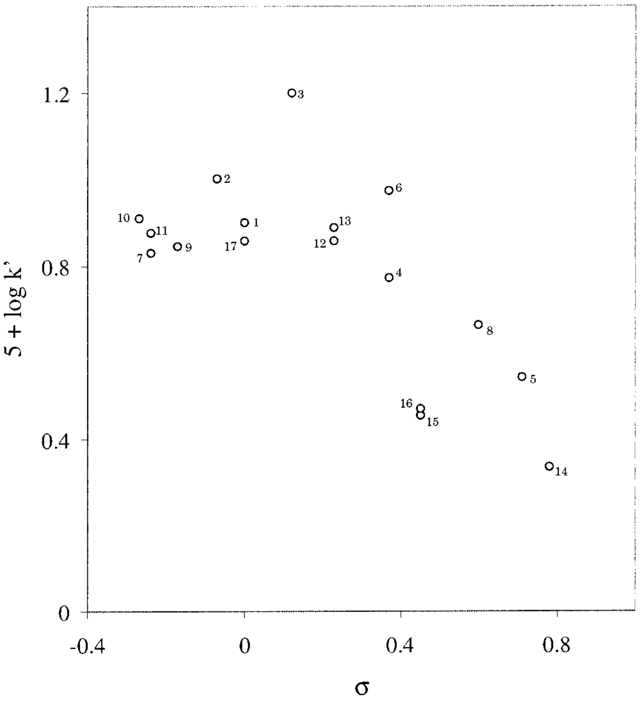

Figure 4. Hammett plot with the rate constants obtained by the hitherto reported method at 45 °C.

(e.g., Figure 4). In anilines, the reaction site may conjugate with the para substituent, but correlation of the oxidation rates of para- and meta-substituted anilines separately with the usual Hammett substituent constants or the Brown−Okamoto substituent constants or the modified Hammett substituent constants (para: σ_p, σ_p^+, σ_p^-, meta: σ_m, σ_m^+) was also unsuccessful. The reaction rates at all the temperatures measured were analyzed in terms of the dual substituent parameter (DSP) equations (para: σ_I, σ_R; σ_I, σ_R^+; σ_I, σ_R^-; F, R; meta: σ_I, σ_R; σ_I, σ_R^+; σ_I, σ_R^-; F, R) but with failure. The σ values of H, *m*-CH_3, *m*-OH, *m*-Cl, *m*-NO_2, *m*-COOH, *p*-CH_3, *p*-OCH_3, *p*-Cl, *p*-Br, *p*-NO_2, *p*-COOH, σ_p^+ of CH_3, OCH_3, Cl, Br, σ_p^- of NO_2, COOH, and σ_I, σ_R, σ_R^+ of OH used were those compiled by Shorter;[45] for the meta substituents (*m*-CH_3, *m*-Cl, *m*-NO_2, *m*-COOH), σ_m^+ values of Brown were employed.[46] Taft's σ_I, σ_R, σ_R^+, and σ_R^- values[47] of H, CH_3, OCH_3, Cl, Br, NO_2, $COCH_3$, $COOC_2H_5$, and $NHCOCH_3$ were used in the DSP equations. The values of σ of *p*-OC_2H_5, *p*-$COOC_2H_5$, *p*-$NHCOCH_3$, σ_p^+ of H, OC_2H_5, NO_2, COOH, $COOC_2H_5$, $NHCOCH_3$, σ_p^- of H, CH_3, OCH_3, OC_2H_5, Cl, Br, $COOC_2H_5$, $NHCOCH_3$, σ_R^- of OH, and σ_I, σ_R, σ_R^+, σ_R^- of OC_2H_5, COOH, and $COOCH_3$ employed were those compiled by Hansch.[48] The F and R values used were those of Swain.[49] The Hammett equation and its different modified forms are applicable to para- and meta-substituted benzene derivatives but not to the ortho compounds; besides the well-known inductive and resonance effects associated with the para and meta substituents, the ortho substituents cause steric effects. In the present study, the activation enthalpies and activation entropies of all the para-, meta-, and ortho-substituted anilines conform to the isokinetic relationship. So are the rates at 65 and 45 °C to the Exner relationship. This indicates that the mechanism of oxidation of the ortho-substituted anilines is the same as that of para- and meta-substituted anilines and justifies the analysis of the reaction rates of the ortho-substituted anilines in terms of the structure−reactivity relationships. The rates of oxidation of ortho-substituted anilines also fail to conform to Charton's LDS equations; the carboxy-, nitro-, and methoxycarbonyl groups individually take either planar or orthogonal orientations requiring appropriate steric substituent constants, the acetyl substituent was excluded due to nonavailability of the steric substituent constant. The values of the steric substituent constants (υ) used were those of Charton.[50]

Anilines in basic and neutral media are present as free bases but in acid medium exist in dual forms, the free bases and the conjugate acids. And, the ratio of the concentrations of the free base to the conjugate acid ($[XC_6H_4NH_2]/[XC_6H_4NH_3^+]$) depends on the p$K_a$ of the aniline and the acidity of the medium. The reported oxidations of anilines (vide supra) were carried out under pseudo-first-order conditions ([anilines] $\gg$ [oxidant]), and the concentration of the oxidants at different reaction times were determined by titrimetry or spectrophotometry. The pseudo-first-order rate constants (k') were obtained from the least-squares slopes of log [oxidant] versus time plots, and the second-order rate constants are $k'/[\text{aniline}]_T$ where $[\text{aniline}]_T$ is the total concentration of aniline. Since the pK_a varies from 5.36 (*p*-OCH_3) to −0.28 (*o*-NO_2) and molecular anilines are the reactive species (nucleophile), the reported $k'/[\text{aniline}]_T$ values are not the rate constants of the oxidant−molecular aniline reactions. And, the analysis of $k'/[\text{aniline}]_T$ in terms of the Hammett, Brown−Okamoto, DSP, and LDS equations is erroneous. Now, for the first time, the specific reaction rates of molecular anilines with the oxidant (k) have been obtained and correlated in terms of the structure−reactivity relationships. In the reactions of anilines in acid medium, as the free bases are the nucleophiles, the specific reaction rates of anilines are to be obtained using the concentrations of the free bases but not the total concentrations of anilines. The concentrations of the free bases may be deduced from the acid strength of the medium and the pK_a values of the anilines and acetic acid.[51−55] Although the pK_a values correspond to aqueous solutions, detailed examination reveals that they may be used to obtain the concentrations of the free bases in glacial acetic acid. Coupling the ionization equilibrium of acetic acid with that of anilinium ion results in the elimination of $[H_2O]$ and $[H_3O^+]$. The ratio of the ionization constant of acetic acid to that of

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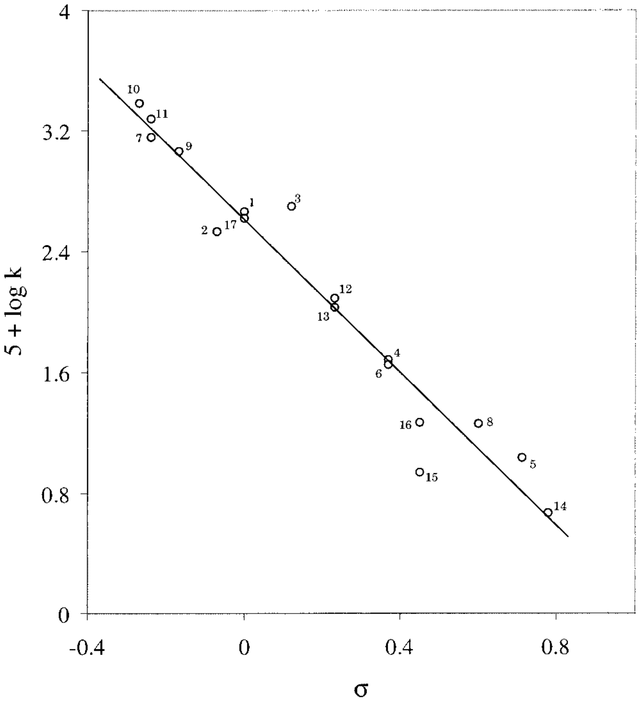

Figure 5. Hammett plot with the rate constants obtained by the modified method at 45 °C.

anilinium ion yields the equilibrium constant of the equilibrium $PhNH_2 + HOAc \rightleftharpoons PhNH_3^+ + OAc^-$. In the absence of water, self-ionization of acetic acid is unlikely, and hence, $[PhNH_3^+] = [OAc^-]$. Also, $[PhNH_3^+] + [PhNH_2] = [PhNH_2]_T$. Solving the quadratic expression on $[PhNH_2]$ yields $[PhNH_2]$. Examination of the pK_a and pK_b values of acetic acid and ammonia in water reveals that the variation of these values with temperature is small; the pK_a of acetic acid varies between 4.76 and 4.79 in the temperature range 0−50 °C, and the pK_b of ammonia decreases from 4.78 to 4.72 on raising the temperature from 15 to 50 °C.[53,56] As the pK_a values of anilines at the experimental temperatures are not available, as an approximation, the pK_a values at 25 °C[51−55] were used in the calculation. The specific reaction rates of molecular anilines in glacial acetic acid (k) thus obtained conform to the usual Hammett equation at all the temperatures studied; Figure 5 is the Hammett plot at 45 °C ($r = 0.98$, sd = 0.20, number of data points, $n = 17$, $\rho = -2.7 \pm 0.1$ at 45−65 °C). The Hammett plots reveal some noteworthy features. The plots involve the ordinary benzoic acid-based σ values throughout and include p-nitro, p-ethoxycarbonyl, and p-carboxy substituents. In anilines, these substituents enter into cross-conjugation with the reaction center and withdraw electrons strongly through resonance, necessitating the use of σ_p^-. But the plots, e.g., Figure 5, show that the p-nitro and p-ethoxycarbonyl substituents fit the Hammett line with the usual Hammett σ values; use of σ_p^- values lead to deviations. This is not uncommon. Examination of the literature of the oxidation of anilines provides many satisfactory correlations using benzoic acid-based σ values or the Brown−Okamoto σ_p^+ values rather than σ_p^- (vide supra). Although p-aminobenzoic acid could be brought into the line using the σ_p^- value, it is illogical. The large deviation of the p-carboxy substituent is probably due to complication of zwitterion formation not allowed for in the calculation of the concentration of the molecular form of the aniline. The meta acid does not deviate significantly, and a possible explanation is that the zwitterion formation is insignificant.

The specific reaction rates of ortho-substituted anilines were analyzed in terms of Charton's LDS equations. The oxidation of o-mercaptoaniline is very fast. The UV−vis spectra of the reaction solution during and after the completion of the reaction show no formation of azo compound; the reaction is not the oxidation of amino group but that of thiol. The oxidation of o-aminophenol is also too fast; o-aminophenol enters into intramolecular hydrogen bonding. o-Phenylenediamine in glacial acetic acid may exist in three forms, viz., o-$^+NH_3C_6H_4NH_3^+$, o-$NH_2C_6H_4NH_3^+$, and o-$NH_2C_6H_4NH_2$. Calculation of the individual concentrations, using the pK_a values, reveals that o-phenylenediamine exists predominantly as o-$NH_2C_6H_4NH_3^+$; the other two forms exist in trace amounts. The protonated amino group (NH_3^+−) is highly electron withdrawing ($\sigma_p = 0.60$), and the free energy of activation for the oxidation of the conjugated acid is likely to be large; hence, the free base is the probable reactive species; the reported k values correspond to this species. The oxidation of molecular o-phenylenediamine encounters two identical reaction sites; one acts as the substituent and the other is the reaction center. This requires that only half of the rate to be considered for the correlation analysis. Because of these complications and also that the reported reaction rates are only the extrapolated values, o-phenylenediamine was omitted from the regression. Correlation analysis of the specific rates of the ortho-substituted molecular anilines in terms of the LDS equations gave fairly satisfactory results. The electronic parameters used were the σ_I values of Taft,[47] along with σ_R, σ_R^+, or σ_R^-; for ethoxy, carboxy, and methoxycarbonyl substituents, the values employed were those compiled by Hansch.[48] Alternatively, the field F and resonance R parameters of Swain[49] were employed. The steric parameters used were the υ values of Charton.[50] Each data set involved eight points (methyl, methoxy, ethoxy, chloro, nitro, carboxy, methoxycarbonyl, and hydrogen), acetyl being excluded due to the unavailability of the steric parameter. Table 2 reveals that σ_R^- is less satisfactory in explaining the variation of the rate with the substituent. This is in accordance with the literature of the oxidation of anilines (vide supra); most of the satisfactory correlations involve either σ or σ_p^+. Better results were found when it was assumed that the carboxy, nitro, and methoxycarbonyl groups were in the orthogonal orientation, and the results obtained by using σ_I and σ_R^+ were fairly better. One of the most satisfactory correlation equations was as follows:

$$-\log k = 2.28(\pm 0.15) + 2.90(\pm 0.28)\sigma_I + 1.15(\pm 0.12)\sigma_R^+ + 1.18(\pm 0.35)\upsilon$$

$$45\ °C,\ n = 8,\ 100R^2 = 98.6,\ sd = 0.156$$

The regression coefficients yield the percentages of inductive (σ_I), resonance (σ_R^+), and steric (υ) terms as 55, 22, and 23, respectively, at 45 °C.

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(56) Weast, R. C., Selby, S. M., Hodgman, C. D., Eds. *Handbook of Chemistry and Physics*, 45th ed.; The Chemical Rubber Co.: Clevelan, OH, 1964; p D-79.

Table 2. Correlation Analysis of the Rates of Ortho-Substituted Anilines[a]

explanatory variables	45 °C		55 °C		65 °C	
	$100R^2$	sd	$100R^2$	sd	$100R^2$	sd
σ_I, σ_R	94.0	0.286	93.5	0.303	98.0	0.230
σ_I, σ_R, υ^b	94.6	0.303	93.9	0.327	97.1	0.224
σ_I, σ_R, υ^c	94.1	0.316	93.6	0.336	96.7	0.237
σ_I, σ_R, υ^d	96.5	0.243	95.8	0.270	98.1	0.178
σ_I, σ_R, υ^e	96.4	0.249	95.8	0.271	98.5	0.160
σ_I, σ_R, υ^f	94.0	0.318	93.6	0.335	96.2	0.255
σ_I, σ_R, υ^g	94.9	0.295	94.5	0.310	96.5	0.245
σ_I, σ_R, υ^h	95.2	0.287	94.5	0.311	96.6	0.240
σ_I, σ_R, υ^i	97.0	0.227	96.4	0.253	98.0	0.186
σ_I, σ_R^-	90.9	0.352	89.8	0.379	94.0	0.287
σ_I, σ_R^-, υ^b	91.2	0.388	89.9	0.421	94.2	0.314
σ_I, σ_R^-, υ^c	91.2	0.387	90.1	0.418	94.8	0.299
σ_I, σ_R^-, υ^d	92.6	0.354	91.4	0.389	95.0	0.292
σ_I, σ_R^-, υ^e	93.5	0.333	92.4	0.366	96.5	0.246
σ_I, σ_R^-, υ^f	91.5	0.381	90.6	0.406	94.8	0.298
σ_I, σ_R^-, υ^g	91.5	0.379	90.5	0.408	94.2	0.315
σ_I, σ_R^-, υ^h	91.3	0.385	90.0	0.418	94.0	0.321
σ_I, σ_R^-, υ^i	93.7	0.327	92.5	0.364	95.7	0.271
σ_I, σ_R^+	94.6	0.271	94.3	0.282	96.3	0.225
σ_I, σ_R^+, υ^b	96.0	0.263	95.5	0.283	98.3	0.172
σ_I, σ_R^+, υ^c	95.0	0.291	94.7	0.306	97.5	0.207
σ_I, σ_R^+, υ^d	97.9	0.188	97.5	0.209	99.2	0.118
σ_I, σ_R^+, υ^e	97.6	0.204	97.3	0.217	99.4	0.103
σ_I, σ_R^+, υ^f	94.6	0.303	94.3	0.316	96.3	0.251
σ_I, σ_R^+, υ^g	95.0	0.293	94.8	0.302	96.3	0.250
σ_I, σ_R^+, υ^h	96.3	0.251	95.9	0.269	97.2	0.218
σ_I, σ_R^+, υ^i	98.6	0.153	98.3	0.172	99.0	0.130
F, R	93.9	0.287	93.6	0.299	96.5	0.220
F, R, υ^b	94.7	0.301	94.2	0.320	97.6	0.205
F, R, υ^c	94.0	0.321	93.7	0.334	96.3	0.234
F, R, υ^d	96.8	0.233	96.3	0.254	98.8	0.140
F, R, υ^e	95.9	0.264	95.6	0.277	98.5	0.159
F, R, υ^f	94.0	0.321	93.6	0.334	96.5	0.245
F, R, υ^g	95.0	0.292	94.8	0.301	96.9	0.229
F, R, υ^h	95.9	0.265	95.3	0.286	97.5	0.207
F, R, υ^i	97.4	0.213	97.0	0.231	98.6	0.155

[a] $n = 8$ (*o*-NH_2 and *o*-$COCH_3$ excluded); $100R^2$: the percentage of variation explained. [b] COOH: planar, NO_2: planar, $COOCH_3$: planar. [c] COOH: orthogonal, NO_2: planar, $COOCH_3$: planar. [d] COOH: planar, NO_2: orthogonal, $COOCH_3$: planar. [e] COOH: orthogonal, NO_2: orthogonal, $COOCH_3$: planar. [f] COOH: planar, NO_2: planar, $COOCH_3$: orthogonal. [g] COOH: orthogonal, NO_2: planar, $COOCH_3$: orthogonal. [h] COOH: planar, NO_2: orthogonal, $COOCH_3$: orthogonal. [i] COOH: orthogonal, NO_2: orthogonal, $COOCH_3$: orthogonal.

Figures 4 and 5 clearly show that the values of k', although obtained under identical conditions, are incapable of yielding a meaningful Hammett plot, and this is because they involve a highly variable concentration of free aniline. Similarly, an Exner plot involving k', even though reasonably linear, is not meaningful to afford the isokinetic temperature. Hence, as a rough approximation, an Exner plot with the tabulated k values at 45 and 65 °C was made (Figure 6); it is satisfactorily linear yielding an isokinetic temperature of −133 °C ($r = 0.997$, sd = 0.087, $n = 28$, slope = 1.05). *o*-Phenylenediamine was omitted, as its inclusion involves extrapolated values and also complication of the reactive species (i.e., either *o*-$NH_2C_6H_4NH_3^+$ or *o*-$NH_2C_6H_4NH_2$ or both). The statistical parameters of the fit remain unaltered even on inclusion of *o*-phenylenediamine ($r = 0.996$, sd = 0.115, $n = 29$, slope = 1.08, figure not given), and the isokinetic temperature raises to −89 °C. Although it appears that the reported thermodynamic properties correspond to the combined process of ionization of anilinium ions and the reaction of molecular anilines with hydrogen peroxide they are not so as the combination is not in any simple form; hence, they lack any physical significance.

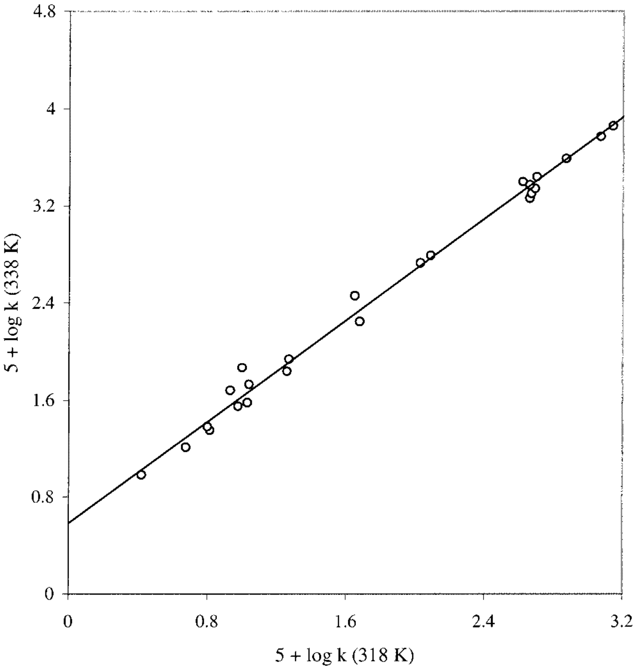

Figure 6. Exner plot with the rate constants obtained by the modified method (*o*-phenylenediamine excluded).

Conclusions

The hitherto followed correlation of the reaction rates of anilines in acid medium is erroneous, found to be unsatisfactory in the reaction in glacial acetic acid. But the specific reaction rates of molecular anilines, obtained for the first time, conform to the structure−reactivity relationships.

Experimental Section

General Procedure. Sodium percarbonate, $Na_2CO_3 \cdot 1.5H_2O_2$ (Fluka), was used as received. The anilines (AR or LR) were redistilled or recrystallized before use; the experimentally determined physical constants confirm the identity of the anilines employed. Percarbonate was dissolved in glacial acetic acid, standardized iodometrically, and used afresh. The kinetics of the oxidation, at fixed temperature, was followed by mixing required volumes of the oxidant and aniline in glacial acetic acid and estimating the unreacted oxidant at different reaction times iodometrically. Percarbonate (0.01 mol) was added to aniline (0.015 mol) in acetic acid at 60 °C and diluted with water after 4 h, and the separated solid was filtered, recrystallized from petroleum ether (40−60), and identified as azobenzene by its mp, mixed mp, and IR spectrum. Formation of azobenzenes in the reaction of all the anilines listed, except *o*-mercaptoaniline, *N*-methylaniline, and *N*,*N*-dimethylaniline, was confirmed by the UV−visible spectra of the reaction solutions, during and after the completion of the reaction. For the experiments with peracetic acid, solution of peracetic acid in glacial acetic acid was prepared by standard method,[41] standardized iodometrically, and used afresh.

Physical Constants and Solvents of Recrystallization of Anilines. Aniline, bp 183 (184) °C; *m*-methylaniline, bp 201 (203) °C; *m*-aminophenol, mp (water) 126 (124−6) °C; *m*-chloroaniline, bp 229 (230) °C; *m*-nitroaniline, mp (water) 114 (114) °C; *m*-aminobenzoic acid, mp (water) 177 (178) °C; *m*,*p*-dimethylaniline, mp (petroleum ether 40−60) 50 (51) °C; *m*,*p*-dichloroaniline, mp (ligroin) 71 (72) °C; *p*-methylaniline, mp (water) 42 (42) °C; *p*-methoxyaniline, mp (petroleum ether 40−60) 57 (57) °C; *p*-ethoxyaniline, bp 254 (253) °C; *p*-chloroaniline, mp (petroleum ether 40−60) 70 (70−1) °C; *p*-bromoaniline, mp (aqueous ethanol) 65 (66) °C; *p*-nitroaniline, mp (water) 147 (148) °C; *p*-aminobenzoic acid, mp (water) 188 (188) °C; ethyl *p*-aminobenzoate, mp (ethanol) 90 (92) °C; *p*-aminoacetanilide, mp (water) 163 (162−3) °C; *o*, *m*-dichloroaniline, bp 250 (252) °C; *o*-methylaniline, bp 198 (200) °C; *o*-methoxyaniline, bp 223 (225) °C; *o*-ethoxyaniline, bp 228 (230) °C; *o*-chloroaniline, bp 207 (209) °C; *o*-nitroaniline, mp (water) 71 (72) °C; *o*-aminobenzoic acid, mp (water) 145 (144−8) °C; methyl *o*-aminobenzoate, bp 256 (256) °C; *o*-aminoacetophenone, bp 249 (250−2) °C; *o*-phenylenediamine, mp (water) 102 (104) °C; *N*-methylaniline, bp 194 (196) °C; *N*,*N*-dimethylaniline, bp 191 (193) °C; *o*-aminophenol, mp (water) 173 (174) °C; *o*-aminothiophenol, bp 232 (234) °C; given in parentheses are the literature values.

Supporting Information Available: The method of calculation of the concentration of free aniline base and the pK_a values used. This material is available free of charge via the Internet at http://pubs.acs.org.

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