Structure-reactivity correlation of anilines in acid medium

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Received 20 June 2001; accepted (revised) 11 April 2002

Studies on the structure-reactivity relationships of anilines are numerous and the reaction rates conform to the usual Hamnett equation (reaction constant: $\rho$), or its modified form (reaction constant: $\rho^+$) or the Brown-Okamoto equation (reaction constant: $\rho^+$). The oxidation by chloramine-T (aqueous ethanol, $[OH] = 0.10$ mol dm$^{-3}$, $\rho = -1.0^{19}$), peroxodisulfate (aqueous 2-propanol, $[OH] = 0.48$ mol dm$^{-3}$, $\rho = -1.3^{25}$), (aqueous t-butyl alcohol, $[OH] = 0.25$ mol dm$^{-3}$, $\rho = -1.48^{32}$), N-chlorosuccinimide (aqueous acetic acid, $pH 7$, $\rho = -2.5^{31}$), thallium(III) catalyzed by ruthenium(III) (aqueous acetic acid, $[HClO_4] = 1.0$ mol dm$^{-3}$, $\rho = -3.0^{25}$), thallium(III) catalyzed by ruthenium(III) (aqueous acetic acid, $[HClO_4] = 1.0$ mol dm$^{-3}$, $\rho = -0.76^{25}$), iron(III)-bipyridyl (aqueous methanol, $10^3[HClO_4] = 1.2$ mol dm$^{-3}$, $\rho = -3.10^{28}$) and pyridinium chlorochromate (chlorobenzene-nitrobenzene, $10^3[Cl_2CHCOOH] = 0.5$ mol dm$^{-3}$, $\rho = -3.75^{29}$). But this study reveals that the hitherto followed method of correlation of the reaction rates in acidic solution is erroneous and presents a modified approach. Chromium(VI) oxidation in acidic solution is a well studied one and imidazolium dichromate (IDC) is the chromium(VI) reagent for the title study; recently we have shown that oxidation of a substrate by chromium(VI) and its complexes occur via a common mechanism$^{26-29}$.

Experimental Section

Imidazolium dichromate (IDC) was prepared as reported$^{26}$. The anilines were purified by distillation or recrystallization. Acetic acid was refluxed with chromium(VI) oxide for 4 hr and distilled through a column. Solution of IDC was prepared and standardized iodometrically. The kinetics of the reaction at fixed temperature was studied by mixing solutions of IDC and aniline and estimating the unreacted chromium(VI) at suitable time intervals iodometrically.

IDC was reacted with aniline in aqueous acetic acid at 50°C, diluted with water after 4 hr, the separated solid filtered, recrystallized and identified by its IR spectrum (3237, 3057, 1589, 1504, 1295 cm$^{-1}$) as 2,5-dianilino-p-benzoquinone. The reduction product of IDC was identified as hexaaquachromium(III) radical by the UV-visible spectrum (576, 408 nm) of the re-
action solution after completion of the reaction under the condition: [Cr(VI)] << [aniline].

Results and Discussion

Reaction order: The IDC oxidation of anilines in aqueous acetic acid, studied under the condition: [anilines] >> [IDC], is first order with respect to chromium(VI). Plot of log [Cr(VI)] vs reaction time is a straight line, the least squares slope yields the pseudo-first order rate constant ($k'$) and $k'$ remains constant for a 10-fold increase of [IDC]$_0$ (10$^3$[IDC]$_0$ = 2.0 - 20.0 mol dm$^{-3}$; [aniline]$_0$ = 0.21 mol dm$^{-3}$; pH = 2.56, 50% (v/v) aq. HOAc, 40°C, 10$^4$$k'$ = 5.2 ± 0.2 s$^{-1}$). The reaction rate increases with [aniline]$_0$ but the increase is only marginal (Table I). Further, the increase of [aniline]$_0$ leads to a raise of pH of the medium, measured using a digital pH meter. Hence the variation in rate is due to the combined effect of [substrate] and pH of the medium. Plot of (log $k' + pH$) vs log [aniline] yields a straight line with a slope of near unity (correlation coefficient, $r$ = 0.99, standard error, sd = 0.08). This clearly demonstrates that the reaction is first order with respect to aniline and hydrogen ion. Measurement of pH during and after the completion of the reaction shows that the pH of the medium does not change with the progress of the reaction. The reaction rate was determined at different solvent compositions; the variation of solvent composition leads to the variation of dielectric constant (D) as well as pH of the medium. Hence the variation of rate is due to the combined effect of dielectric constant and pH of the medium. Since the reaction is first order in H$^+$ the acid independent rate constant ($k'$/[H$^+$]) reveals the influence of dielectric constant of the medium; Table II presents that the reaction is less susceptible to dielectric constant of the medium.

Reactive species: In aqueous acetic acid IDC, an ionic complex, dissociates; solvents of high dielectric constant favour dissociation. In aqueous and partly aqueous solutions dichromate anion is hydrolyzed and the speciation of chromium(VI) are Cr$_2$O$_7^{2-}$, HCr$_2$O$_7^-$, H$_2$Cr$_2$O$_7$, CrO$_2^{2-}$, HCrO$_4^-$ and H$_2$CrO$_4$. Calculation of the concentration of dichromate anion reveals that 97 to 81% of the dimer is hydrolyzed in the concentration range 2x10$^{-2}$-2x10$^{-3}$ mol dm$^{-3}$. The UV-visible spectrum of IDC in aqueous acetic acid confirms the same; the absorbance at 440-450 nm is insignificant. Calculation of the relative concentration of chromate anion to acid chromate ([CrO$_2^{2-}$/[HCrO$_4^-$] = 1.1x10$^{-4}$ at pH 2.56), shows that the existence of chromate anion in the reaction solution is only in trace. The relative concentration of chromic acid to acid chromate, [H$_2$CrO$_4$]/[HCrO$_4^-$], calculated at pH 2.56 is 2.3 x 10$^{-4}$. These calculations reveal that the abundant chromium(VI) species in the reaction solution is acid chromate. Aniline is a base and in acid medium exists largely as anilinium ion. Calculation of the relative concentration of the free base to that of the conjugate acid ([PhNH$_2^-$]/[PhNH$_3^+$] = 0.01 at pH 2.56), using the $pK_a$-value of anilinium ion, shows that 99% of aniline is present as anilinium ion at the experimental pH. In the oxidation reactions aniline acts as a nucleophile and hence molecular aniline is the probable reactive species; removal of electron from anilinium ion requires high activation energy than from the free base. As the concentration of the free base is inversely related to the acidity of the medium and the reaction is acid catalyzed, protonated chromic acid (H$_2$CrO$_4^-$) is the probable oxidizing species. If chromic acid were to be the reactive species, contrary to the experimental observation, the reaction should be independent of acidity of the medium; [H$_2$CrO$_4$] is directly related to the acidity of the medium ([H$_2$CrO$_4$] = $K_i$[Cr(VI)][H$^+$]) whereas [H$_2$CrO$_4$] is related to the square of the acidity; [H$_2$CrO$_4^-$] = $K_i$$K_a$[Cr(VI)][H$^+$]$^2$ where $K_i$ is the reciprocal of the first ionization constant of chromic acid and $K_a$ is the protonation constant of chromic acid. The kinetic results suggest the reaction of protonated chromic acid with molecular

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aniline as slow and rate determining. The experimental results do not throw light on the reaction mechanism beyond the slow and rate limiting step and hence the mechanism in detail has not been attempted.

**Structure-reactivity correlation:** The structure-reactivity relationship of the chromium(VI) oxidation of aniline in aqueous acetic acid was studied with a few electron withdrawing and releasing substituents. Rate measurements at 30-50°C afford the activation parameters. The oxidation of para-nitroaniline under the experimental conditions is sluggish; similar observation was made in the oxidation by pyridinium chlorochromate. The reaction conforms to the isokinetic relationship, confirmed with a linear Exner plot of log \( \frac{k'}{[\text{aniline}]} \) vs log \( \frac{k'}{[\text{aniline}]} \) at 30°C where \([\text{aniline}]\) is the total concentration of aniline \((r = 0.996, \text{sd} = 0.09, n = 6)\). The isokinetic temperature, calculated from the slope of the Exner plot, is 90 K. The isokinetic temperature is the temperature at which all the compounds of the series react at equal rate. Transgressing this temperature results in the reversal of the order of reactivity. The isokinetic temperature is far away from the experimental temperature and hence the observed effect of substituents is quite significant justifying the use of linear free energy relationships in the present study.

As the reaction center is likely to conjugate with the para-substituents the reaction rates were correlated in terms of the modified Hammett equation \((\sigma^-)\) as well as the Brown-Okamoto equation \((\sigma^+)\) but all without success. Failure of all the single parameter equations resulted in the analysis of the rates in terms of the dual substituent parameter (DSP) equations but also with failure. A possible reason for the lack of linear free energy relationships is error in the method of analysis. The reaction is acid catalyzed and the presence of anilines of varying \(pK_a\)-values could influence the \(pH\) of the reaction medium. The measurement of \(pH\) of the reaction solutions confirms the same. Hence acid independent rate constants \((k'/[\text{aniline}][H^+])\) were obtained using the measured \(pH\) and correlation was made in terms of the usual Hammett equation, its modified form and the Brown-Okamoto equation, all without success. The DSP equations also failed to explain the variation of rate with the substituent.

Anilines in basic and neutral media are present as free bases but in acidic solution the existence of substrates in dual forms, the free bases and the conjugate acids, leads to complication. For example, at \(pH 2.5\) the ratio of the concentrations of the free base to the conjugate acid \((\frac{[XC_6H_4NH_2]}{[XC_6H_4NH_2^+]}\) of \(p\)-methoxyaniline and \(p\)-nitroaniline are \(3.16 \times 10^{-3}\) and \(30.9\), respectively. This clearly shows that the concentration of the free base in acid medium depends on the \(pK_a\) of the substrate and the \(pH\) of the medium. The reported oxidations of anilines were carried out under pseudo-first order conditions \(([\text{anilines}] \gg [\text{oxidant}])\) and the concentration of the oxidants at suitable time intervals were determined by titrimetry or spectrophotometry. The pseudo-first order rate constants \((k)\) were obtained from the least-squares slopes of log [oxidant] vs 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 with the substituent (in the present case from 5.36 (p-OCH₃) to 2.41 (p-COOH)) and molecular aniline is the reactive species (nucleophile), the reported \( k' / [\text{aniline}]_T \) values are not the rate constants of the oxidant-molecular anilines reactions. And, the analysis of \( k' / [\text{aniline}]_T \) in terms of the Hammett, Brown-Okamoto and DSP equations is erroneous. In the reactions of anilines in acidic solution, as the free bases are the nucleophiles, the specific reaction rates in anilines are to be obtained using the concentrations of the free bases but not the total concentrations of anilines. The concentration of the free bases may be deduced from the measured \( pH \) of the reaction solutions and the \( pK_a\) of the anilines; \([\text{PhNH}_2] = K_a [\text{PhNH}_2]^+ / (K_a + [H^+])\) where \([\text{PhNH}_2]^+ = [\text{PhNH}_2] + [\text{PhNH}_3^+]\). The rate-determining step of the chromium(VI) oxidation of anilines in acid medium is the reaction between protonated chromic acid and molecular anilines. If \( k_3 \) is the specific rate of the rate-limiting step, the oxidation rate, \(-d[\text{Cr(VI)}]/dt = K_a K_C k_3[\text{Cr(VI)}][H^+][\text{PhNH}_2]\). Writing the rate law in terms of the total concentration of aniline, \(-d[\text{Cr(VI)}]/dt = K_a K_C k_3[\text{Cr(VI)}][H^+]^2[\text{PhNH}_2]/(K_a + [H^+])\) with a pseudo-first order rate constant of \( k = K_a K_C k_3[\text{PhNH}_2]/(K_a + [H^+])\). Hence correlation of the rates of chromium(VI) oxidation of anilines in acidic solution is be made with \( k' / [\text{aniline}]_T \) or \( k_3 / [\text{aniline}]_T \) (\( = k^* \), say) instead of \( k' / [\text{aniline}]_T \) or \( k_3 / [\text{aniline}]_T \) (\( = k' \)). Correlation analysis of \( k^* \) in terms of the Hammett, Brown-Okamoto and DSP equations confirm the proposition; Figure 2 is the Hammett plot at \( 40°C \) (Hammett plots: \( r = 0.98 \) and \( p = -6.2 \) to -6.1 at 30-50°C; \( \sigma_1, \sigma_2 \)-correlation: \( R = 0.98 \) and \( p_1 = -5.7 \) to -5.5; \( p_2 = -6.0 \) at 30-50°C). The \( \sigma \) and \( p \)-values reveal that the inductive and resonance effects operate equally in the reaction of molecular aniline with protonated chromic acid. Conformity of the rate data to the usual Hammett equation supports the same. Also, the \( \sigma \)-value concurs with the \( \rho \) and \( \rho_\sigma \)-values. The rate law based on the suggested rate-determining step is in agreement with the experimental rate law. In the case of the oxidation of aniline, \( K_a \) (2.5 \times 10^{-5} \text{ mol dm}^{-3} ; \ pK_a \ 4.60) \ll [H^+] \) (2.5 \times 10^{-5} \text{ mol dm}^{-3} ; \ pH 2.60) and the derived rate law reduces to the experimental rate law:

\[-d[\text{Cr(VI)}]/dt = K_a K_C k_3[\text{Cr(VI)}][H^+][\text{PhNH}_2]\). The \( pH \) of the medium seldom varies with the substituent. But in the present study the \( pH \) of the reaction solution varies with the substituent and this is because of the high concentration of aniline used. The fact that the chromium(VI) oxidation of p-nitroaniline in acid medium is sluggish is also in agreement with the observed experimental results. The oxidation conforms to the usual Hammett equation with a reaction constant (\( p \)) of -6.2. The value of the usual Hammett substituent constant of the \( p\)-NO₂ group (\( \sigma = 0.78 \)) implies the relative ratio of the reaction rates of the \( p\)-nitroaniline to aniline as \( 1.5 \times 10^{-5} \). This is on the expected lines; in \( p\)-nitroaniline, due to cross conjugation of the nitro and amino groups, the amino nitrogen acquires a positive charge making the removal of electron from the amino nitrogen by the protonated chromic acid difficult. This is the first report on the molecular aniline-protonated chromic acid reaction and the \( p \)-value which is highly negative could not be compared with similar reactions. But the reported \( p \)-value is not alarming, as the reaction constants of aromatic chlorination and bromination in acetic acid at \( 25°C \) are \(-10 \) and \(-12.1 \), respectively. 

Figure 2 — The Hammett correlation of the specific reaction rates of molecular anilines at \( 40°C \)

Conclusion

In acid medium anilines exist in dual forms, the conjugate acids and the free bases and in the oxidation of anilines the free bases (nucleophiles) are the reactive species. But the hitherto followed structure-reactivity correlation analysis did not take this into...
consideration and hence is erroneous. The specific rates of the reactions of molecular anilines with the oxidizing species, deduced from the $pK_a$s and $pH$ of the medium, correlate satisfactorily with the substituent constants.

References