Electrochemical Characterization of Salicylaldehyde Anils[1]

James E. Kuder,* Harry W. Gibson,[1b] and Darlene Wychick
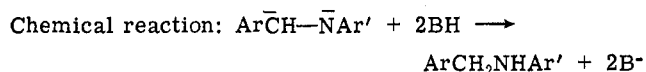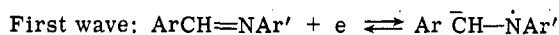
Xerox Corporation, Webster Research Center, Webster, New York 14580

The polarographic half-wave potential in a series of 14 salicylaldehyde anils is a linear function of σ_x^- (except for the *m*- and *p*-NO$_2$ compounds in which the nitro group is electroactive); analyses of potential as a function of the currents indicate a one-electron process. The half-wave oxidation potential is directly proportional to σ_x^+ (except for *m*- and *p*-NMe$_2$ compounds in which the dimethylamino group is electroactive). Cyclic voltammetry reveals that the reduction process is irreversible. Oxidative cyclic voltammetry demonstrates that with the exception of the nitro and dimethylamino compounds the initial irreversible one-electron oxidation product undergoes chemical transformation to a tertiary product that forms a reversible one-electron couple; the average of the peak potentials, i.e., the half-wave potential, of the couple is directly proportional to the normal Hammett substituent constant, σ. In addition to the anils, the half-wave reduction and oxidation potentials of the isoelectronic series stilbene, benzaldehyde anil, and azobenzene were linearly correlated to the calculated energies of the lowest unoccupied and highest occupied molecular orbitals, respectively. The effects of anil substituent and intramolecular hydrogen bonding are rationalized on this basis.

The electrochemical behavior of Schiff bases[1c] has been extensively studied by polarography in both aqueous and nonaqueous solutions. Under aqueous conditions reduction has been shown[2] to consist of a two-electron, two-proton transfer which converts the C=N linkage to a CHNH group. In keeping with this, the half-wave potential of the first reduction wave shows a pronounced dependence on pH.[2-4] Such studies are complicated, however, by the hydrolysis of the azomethine compound into its constituent amine and carbonyl compounds.[2,3]

While hydrolysis is not a problem when electrochemical studies are carried out in nonaqueous solvents, the results of such studies have shown the possibility of a number of electrochemical mechanisms. Thus, the two reduction waves seen in dimethylformamide (DMF) were attributed by Scott and Jura[5] to two one-electron transfers followed by irreversible protonation of the dianion formed.

First wave: $ArCH{=}NAr' + e \rightleftharpoons Ar\,\dot{\overline{C}}H{-}\dot{N}Ar'$

Second wave: $Ar\overline{C}H{-}\dot{N}Ar' + e \longrightarrow Ar\overline{C}H{-}\overline{N}Ar'$

Chemical reaction: $Ar\overline{C}H{-}\overline{N}Ar' + 2BH \longrightarrow$

$$ArCH_2NHAr' + 2B^-$$

Remarkably, Bezuglyi and coworkers[6] concluded that the first reduction wave in azomethine compounds in DMF involves an irreversible two-electron transfer, although both these and the former workers used diffusion current constants and the Nernstian slope to reach their differing conclusions.
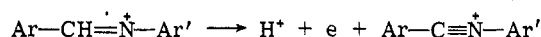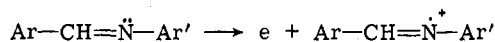
The results of single sweep voltammetry studies,[7] however, indicate that the reduction of anils in aprotic media proceeds via reversible one-electron transfer followed by an *irreversible one-electron transfer and chemical reaction*, in agreement with Scott and Jura. Cyclic voltammetry was used by Andrieux and Saveant[8] to study the reduction of several imines in both DMF and acetonitrile (AN). Depending on the solvent and the compound, it was possible to observe either a two-electron wave leading to the saturated amine or two one-electron waves associated with dimerization. In either case the reduction is irreversible.

Studies by Fry and Reed[9] on several imines in DMF indicated that reduction of these compounds occurs by way of an irreversible two-electron transfer. It was postulated on the basis of polarography and cyclic voltammetry that the overall two-electron reduction in fact consists of a one-electron transfer followed by rapid proton transfer and a second rapid electron transfer. It was further found that the stereochemistry of the electrochemical reduction prod-

uct was the same as that obtained upon reduction with sodium–ethanol.

Shifts in the reduction potential caused by changes in the Ar groups attached to either side of the C=N bond have been discussed in terms of Huckel molecular orbital theory for aromatic rings of different size.[3,5] The effect of substituents on the half-wave potential follows the Hammett relationship, reduction being facilitated by electron-withdrawing substituents.[4,10,11] The presence of an intramolecular hydrogen bond, as would be present in the condensation product of an ortho-hydroxy aldehyde with an amine, was found to facilitate reduction by 0.2–0.3 V.[12,13]

The electrochemical oxidation of imines has been less well studied. The results of linear sweep voltammetry studies[14] on a number of aromatic imines in AN indicated that anodic oxidation occurs via two one-electron steps with the loss of a proton accompanying the second charge transfer.

$$Ar{-}CH{=}\ddot{N}{-}Ar' \longrightarrow e + Ar{-}CH{=}\overset{\cdot}{\underset{}{N}}{}^{+}{-}Ar'$$

$$Ar{-}CH{=}\overset{\cdot}{\underset{}{N}}{}^{+}{-}Ar' \longrightarrow H^+ + e + Ar{-}C{\equiv}\overset{+}{N}{-}Ar'$$

The use of anils in liquid crystal display devices has given fresh impetus to studies of their electrochemical behavior, and a number of reports on just this aspect have recently appeared.[15-17]

Our own interest in the electrochemistry of anils arises from studies of substituent effects on molecular orbital energies[18] and the relationship between solution and solid state charge exchange.[19,20] This report, then, is less concerned with electrochemical pathways than with trends in reduction and oxidation potentials caused by substitution and deviations from the general trends. Polarography and cyclic voltammetry were used to study the electrochemistry in AN of 14 salicylaldehyde anils (1) bearing various substituents on the aniline ring. In addition, the effect of the bridging group was also examined in the series stilbene (2), benzaldehyde anil (3), and azobenzene (4).
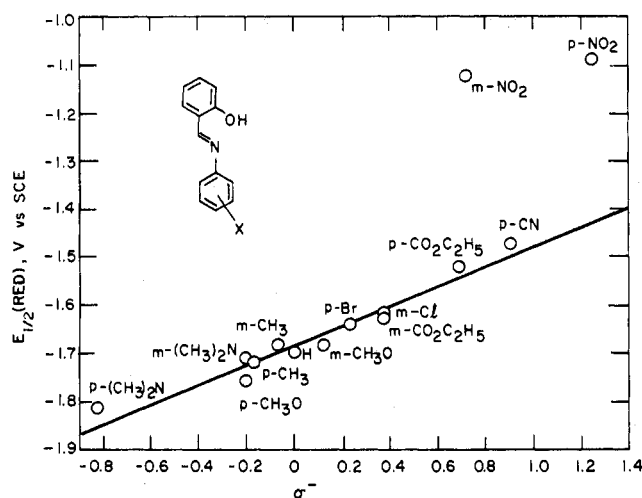

1

2

3

4
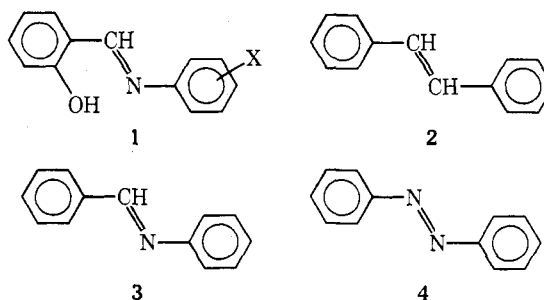
Figure 1. Half-wave reduction potentials of a series of salicylaldehyde anils (1) vs. nucleophilic substituent constant, σ^-.

Results and Discussion

Reduction at the Dropping Mercury Electrode (DME). The polarography of the salicylaldehyde anils (1) was performed at sample concentrations of 4×10^{-4} M, since at higher concentrations the reduction waves are distorted by maxima. Typically the polarograms consist of two waves, the first at about -1.7 V vs. a saturated calomel electrode (SCE) and the second at about 0.6 V more negative potential. The height of the second wave is typically 1–1.5 times that of the first. Beyond this observation, our attention focused mainly on the first reduction process, however.

The polarographic half-wave potentials, $E_{1/2}$ (redn), for the first reduction wave of the 14 salicylaldehyde anils vary from -1.81 V vs. SCE for the p-dimethylamino compound to -1.09 V for the p-nitro compound. Zuman has shown[21] that the effect of a substituent in a given series on the position of the half-wave potential is given by a relationship analogous to the Hammett equation.

$$\Delta E_{1/2} = E_{1/2,\mathrm{X}} - E_{1/2,\mathrm{H}} = \rho\sigma$$

A plot of the reduction potentials for the present series against the corresponding substituent constants[22] σ^- is shown in Figure 1. With the exception of the m- and p-NO_2 compounds, an excellent correlation ($R = 0.967$) of the form $\Delta E_{1/2} = (0.20 \pm 0.02)\sigma^-$ is obtained. It was found that a better fit was obtained with σ^-, the value appropriate to reactions in which electron density is released to the substituent, than with the ordinary σ constant.

The shape of the polarographic reduction waves may be described in terms of the so-called "log plot",[23] i.e., a plot of E against log $[i/(i_\mathrm{d} - i)]$ where i is the current at potential E and i_d is the diffusion limited current. The slopes of the log plots, with the exception of the two nitro compounds, are in the range -0.045 to -0.056 V, close to the value of -0.059 V expected for a one-electron process.[23] The m- and p-nitro compounds have log plot slopes of -0.040 and -0.029 V, respectively.

The polarograms of the two nitro compounds are characterized by a well-defined wave at -1.1 V, followed by a very broad, ill-defined wave which leads into a second well-defined wave near -1.6 V. Evidently the reduction of the two nitro compounds is quite complex and distinct from that occurring with the other members of the series. Based on the deviation of the half-wave potentials from the Hammett plot and the essential identity of the first reduction potentials for both compounds with that of nitrobenzene

(-1.15 V vs. SCE in AN),[24] it seems reasonable to consider that in these examples the nitro group is the electroactive moiety responsible for the observed reduction wave rather than the azomethine group.

Oxidation at the Rotating Platinum Electrode (RPE). The oxidative behavior of the salicylaldehyde anils (1) is characterized without exception by a single wave located at about $+1.2$ V vs. SCE. Plots of E vs. log $[(i_\mathrm{d} - i)/i]$ have slopes in the range -0.061 to -0.086 V, in satisfactory agreement with that expected for a one-electron process. The slope for the cyano compound (-0.108 V) is unexpectedly large, but its voltammetry is otherwise undistinguished. Those of the p- and m-dimethylamino compounds (-0.058 and -0.050 V, respectively) are lower than for the series as a whole and, as will be seen, are reflective of a difference in the mechanism of oxidation.

The half-wave oxidation potentials, $E_{1/2}$ (oxidn), range from $+0.70$ V for the p-dimethylamino compound to $+1.32$ V for the p-nitro compound. The trend in $E_{1/2}$ (oxidn) with substituent may be expressed by the least-squares expression ($R = 0.981$) $\Delta E_{1/2} = (0.12 \pm 0.01)\sigma^+$. This is illustrated in Figure 2, where it is seen that the two nitro compounds fit the correlation, but the two dimethylamino compounds are oxidized at less anodic potentials than would have been expected. However, the similarity of the $E_{1/2}$ (oxidn) values to that of N,N-dimethylaniline in AN ($+0.68$ V vs. SCE)[25] suggests that it is the amino nitrogen atom which is the electroactive center rather than the azomethine group.

It may be noted that a better correlation of $E_{1/2}$ (oxidn) values was obtained using σ^+, the value appropriate for reactions requiring large electron demand from the substituent, than that obtained using ordinary σ constants. Furthermore, the ρ value for oxidation is smaller than that for reduction, in agreement with an observation made in a similar study of substituted azo compounds.[19]

Cyclic Voltammetry. A. Reduction. For all of the anils investigated except the two nitro compounds the cyclic voltammetry (CV) curves consist of a single cathodic peak; no anodic peak is seen on reversal of the potential scan, thereby demonstrating that the reduction is irreversible under these conditions. The development of a yellow layer next to the cathode was observed during each CV experiment and was undoubtedly due to the irreversibly formed products. The peak potentials become more negative on increasing scan rate, with an average cathodic shift of 40 mV/tenfold increase in scan rate, as expected[26] for an irreversible charge transfer process.

As indicated from the polarographic results, the two nitro compounds do not fit the general pattern for reduction, and this difference is clearly seen in their CV behavior. Thus, the CV curve of the m-NO_2 anil (Figure 3) is characterized at high scan rates by a reduction peak at -1.18 V which undergoes a cathodic shift of 19 mV per decade increase in scan rate. No additional peaks are seen on scanning out to -1.8 V. On reversal of the scan the corresponding anodic peak is seen at -1.09 V, the separation in peak potentials being in agreement with a reversible one-electron transfer. However, on repetitive scan a new cathodic peak at -1.27 V appears together with its corresponding anodic peak at -1.17 V. The sequence of events is thus

$$\mathbf{1,\ X\ =\ }\textit{m}\text{-NO}_2\ \underset{-e}{\overset{e}{\rightleftharpoons}}\ A\ \longrightarrow\ B\ \underset{-e}{\overset{e}{\rightleftharpoons}}\ C$$
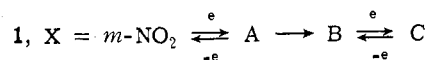
That is, we have two reversible electrochemical steps separated by an irreversible chemical step. The time required for a detectable amount of species B to be formed from reduced species A is 0.5–1.0 sec.
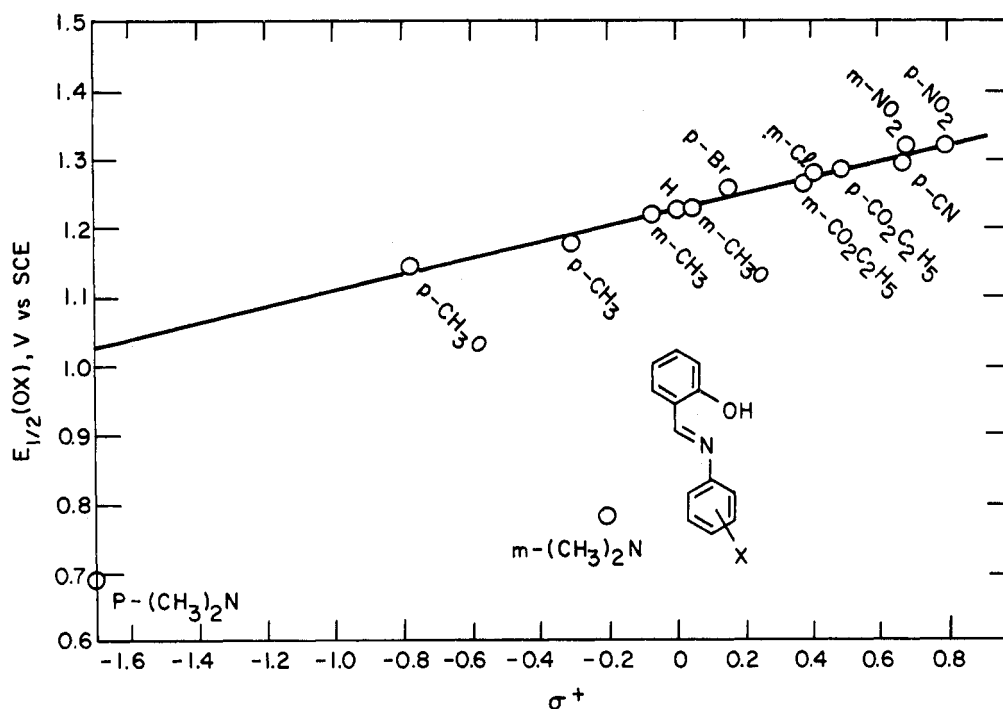
Figure 2. Oxidation half-wave potentials of a series of salicylaldehyde anils (1) vs. electrophilic substituent constant, σ^+.
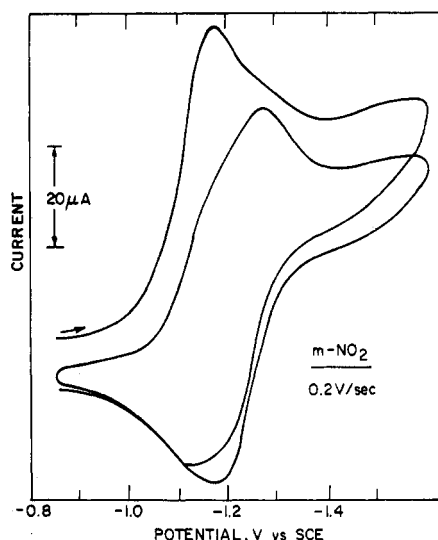

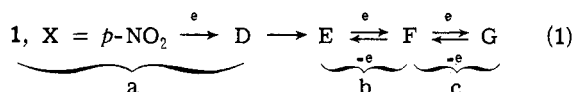Figure 3. Cyclic voltammogram of salicylaldehyde m-nitroanil (1, X = m-NO$_2$) at 200 mV sec^{-1}.

The CV behavior of the p-NO$_2$ compound is illustrated in Figure 4. Here again the initial reduction (E_{pc} = -1.12 V) is followed by the irreversible formation of a new electroactive species but at rate much greater than observed for the m-NO$_2$ compound. The events observed in Figure 5 may be represented by the following sequence.

$$1, \ X \ = \ p\text{-NO}_2 \ \xrightarrow{\text{e}} \ D \ \longrightarrow \ \underbrace{E \ \underset{-e}{\overset{e}{\rightleftarrows}} \ F}_{b} \ \underset{-e}{\overset{e}{\rightleftarrows}} \ \underbrace{G}_{c} \qquad (1)$$

$$\underbrace{\phantom{1, \ X \ = \ p\text{-NO}_2 \ \xrightarrow{\text{e}} \ D}}_{a}$$

The initial reduction (eq 1, step a) is not reversible on the time scale employed for these experiments and a detectable amount of species E is found to be present as soon as 0.1 sec after initial reduction of 1, X = p-NO$_2$. The product of the irreversible chemical reaction is found to undergo two reversible one-electron transfers characterized by peak potentials (on the second scan) of E_{pc} = -1.31 V and E_{pa} = -1.23 V for the first (eq 1, step b) and E_{pc} = -1.64 V and E_{pa} = -1.51 V for the second step (eq 1, step c).
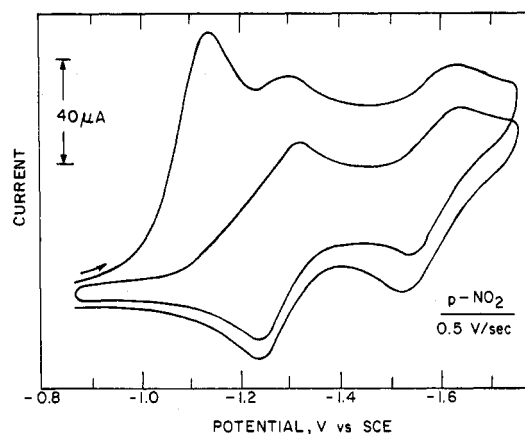

Figure 4. Cyclic voltammogram of salicylaldehyde p-nitroanil (1, X = p-NO$_2$). Sweep rate 500 mV sec^{-1}.
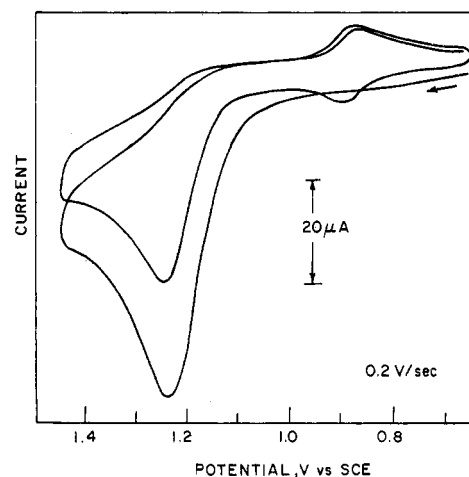

Figure 5. Cyclic voltammogram of salicylaldehyde anil (1, X = H). Sweep rate 200 mV sec^{-1}.

B. Oxidation. The oxidative behavior of the anils, with the exception of the two nitro compounds and the two dimethylamino compounds, is typified by the CV curve
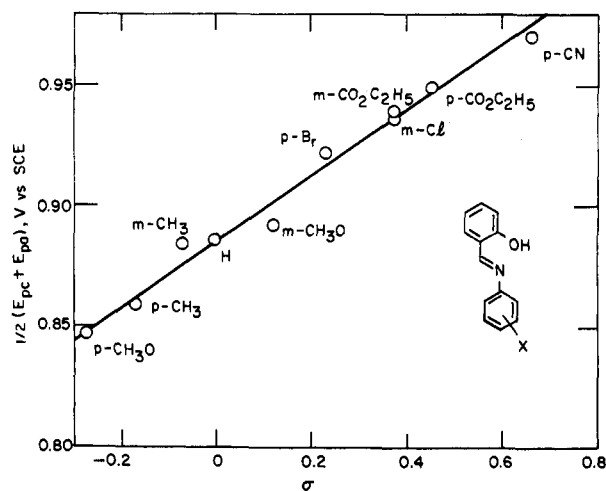
Figure 6. Average of peak potentials for reversible couple formed following CV oxidation of salicylaldehyde anils (1) vs. Hammett σ.

shown in Figure 5. The anodic peak potentials undergo an average positive shift of 32 mV per tenfold increase in scan rate and there is no corresponding cathodic peak seen on reversal of the scan direction. These observations characterize the oxidation as an irreversible one-electron charge transfer. The oxidized species apparently undergoes chemical reaction to form an electroactive product whose reversible redox couple is seen between 0.8 and 1.0 V in the reverse portion of the first scan and in both forward and reverse portions of the second scan. The processes occurring are then

$$1 \xrightarrow{-e} H \xrightarrow{-e} I \underset{\underbrace{}_{a}}{\overset{-e}{\rightleftarrows}} J \qquad (2)$$
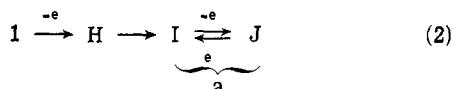
The initial oxidation undoubtedly involves the nitrogen atom and hence $H = ArCH=N^+Ar'$ in accord with previous findings.[14] This intermediate could then lose a proton to form I, which is a neutral radical stabilized by resonance interaction between O and N. Species I is involved in the redox couple with J, which is presumably a resonance-stabilized cationic species. The mean separation of the peak potentials for the reversible couple (eq 2, step a) produced after initial oxidation is 0.05 V. The average of these $\frac{1}{2}(E_{pc} + E_{pa})$, may be taken as being equal to the half-wave potential for the system of eq 2, step a. As shown in Figure 6, $\frac{1}{2}(E_{pc} + E_{pa})$ shows a linear dependence ($R = 0.981$) on the Hammett substituent constant σ, the actual relationship being $\Delta(E_{pc} + E_{pa})/2 = 0.14\sigma$. It will be noted that in the case of this reversible charge transfer the best correlation was found with the ordinary σ constant.

The two nitro compounds do not show the presence of the reversible couple following their initial irreversible oxidation. The same is true for the two dimethylamino compounds, but here there is an additional feature of interest. At low scan rates the initial oxidation of the p-dimethylamino anil is irreversible, but as the scan rate increases a cathodic peak appears corresponding to the anodic peak of the forward scan. At 0.5 V/sec the separation between the two peaks is 0.09 V. The m-dimethylamino anil behaves similarly, so that the observed CV curves correspond to the following processes.

$$1, \ X = N(CH_3)_2 \underset{e}{\overset{-e}{\rightleftarrows}} K \longrightarrow L$$
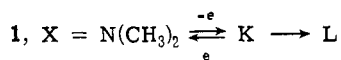
The Effect of the Bridging Group. Additional information regarding the nature of the charge transfer process in anils may be obtained by consideration of the isoelectro-

Table I
Reduction and Oxidation Half-Wave Potentials in the Isoelectronic Series Stilbene, Benzaldehyde Anil, Azobenzene Together with Hückel Frontier Orbital Energies

Compd	$E_{1/2}$ (redn)[a]	$E_{1/2}$ (oxidn)[a]	Energy of LUMO[b]	Energy of HOMO[b]
2	−2.32	+1.45	−0.544	+0.544
3	−1.96	+1.58	−0.447	+0.642
4	−1.38	+1.72	−0.301	+0.701

[a] AN solution. Potentials vs. SCE. [b] Energies in β units. The following parameters were used: $h_N = 0.5$, $k_{CX} = 0.9$ for the bond connecting the phenyl ring to the bridging group, all other $h_X = 0$, $k_{XY} = 1.0$.

nic series stilbene (2), benzaldehyde anil (3), azobenzene (4), in which methine groups of the bridge are successively replaced by more electronegative nitrogen atoms. Half-wave potentials for reduction (DME) and oxidation (RPE) for these compounds are given in Table I.

The results of the electrochemical investigation may be compared with the results of Hückel molecular orbital (HMO) calculations. It is usually assumed[27] that the energy of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) may be linearly related to the electrochemical reduction and oxidation potentials, respectively. This is borne out for the present series by the data in Table I, which lead to the excellent correlation ($R = 0.999$)

$$E_{1/2}(\text{redn}) = 3.88E_{\text{LUMO}} - 0.22$$

where E_{LUMO} is the energy of the LUMO expressed in β units. A similar relation is obtained for the oxidation potentials, described by the equation ($R = 0.987$)

$$E_{1/2}(\text{oxidn}) = 1.68E_{\text{HOMO}} + 0.53$$

Since examination of the eigenvectors obtained in the HMO calculation reveals that both LUMO and HOMO are concentrated on the bridging moiety, it is not surprising that increasing the electronegativity of the atoms located there should have a pronounced effect on the reduction and oxidation potentials in this series. Furthermore, since the effect of hydrogen bonding may be considered to be due in large extent to an increase in the effective electronegativity of the acceptor atom,[28] one might expect similar shifts in half-wave potentials upon comparison of benzaldehyde anil (3, no H bond) with salicylaldehyde anil (1, X = H; internal OH···N bond). Indeed, the presence of an ortho OH group is found to shift the reduction potential, $E_{1/2}$ (redn), 0.26 V more positive, in agreement with the findings of Bezuglyi and coworkers.[12,13] At the same time the oxidation potential, $E_{1/2}$ (oxidn), is shifted 0.28 V, also in the positive direction. It will be noted that the shifts in $E_{1/2}$ (redn) and $E_{1/2}$ (oxidn) (0.26–0.28 V) are the same magnitude as the hydrogen bond energy obtained from a variety of chemical situations.[29]

Mechanisms. Thus, both reduction and oxidation of salicylaldehyde anils occur by charge transfer involving molecular orbitals centered on the bridge between the two rings. The energies of these MO's may in turn be perturbed by altering the effective electronegativity of the bridging group atoms (as by internal hydrogen bonding), and (as demonstrated in the preceding section) by transmission of electronic effects from substituents located distant from the azomethine bridge.

Beyond this, an attempt to elucidate the details of the electrochemical mechanism on the basis of our voltammetric studies was not made. The present results do indicate,

however, that the initial reduction of salicylaldehyde anils in AN takes place by an irreversible one-electron step (a second reduction step not being examined in any detail), in contrast to the conclusions of both Scott and Jura[5] and Bezuglyi et al.[6] Further, in contrast to the results of Martinet, Simonet, and Tendil,[14] however, only a single irreversible one-electron step was observed for the initial oxidation, followed by a chemical reaction whose product forms a reversible redox couple. If the chemical reaction involves loss of a proton from a phenolic group, this would be expected to occur at a rate greater than loss from a methine group as postulated in earlier work.[14]

The exceptions to the general pattern and the deviations from the Hammett plots occur for the reduction of the nitro anils and the oxidation of the dimethylamino anils. In these cases the effect of substitution can no longer be considered as a simple perturbation of the MO's of the azomethine group, and charge transfer now involves orbitals centered on the substituents themselves. The fate of the products of the initial charge transfer is then undoubtedly similar to that of aromatic nitro and amino compounds in general.[30]

Experimental Section

Chemicals. Elemental analyses are by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points are corrected. *trans*-Stilbene, zone refined from Aldrich, was used without further purification. Azobenzene (Eastman) was recrystallized from hexane before use. Benzaldehyde anil (mp 52°, lit.[31] mp 53°) was prepared by the condensation of benzaldehyde and aniline and recrystallized from low-boiling petroleum ether. The salicylaldehyde anils were synthesized by condensation of equimolar amounts of salicylaldehyde and substituted anilines in refluxing absolute ethanol for 2 hr. The crude products, which precipitated in 57–100% yields on cooling or after concentration of the solutions, were brought to analytical purity by several (at least three) recrystallizations from ethanol or ethanol–benzene. p-N(CH$_3$)$_2$: mp 135.0–136.0° (reported[32] 137°). Anal. Calcd for C$_{15}$H$_{16}$N$_2$O: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.17; H, 6.99; N, 11.80. m-N(CH$_3$)$_2$: mp 69–72° (reported[33] 72°). p-OCH$_3$: mp 82.0–83.5° (reported[34] 83–84°). m-OCH$_3$: mp 59.0–60.1° (reported 60°,[32] 61–62°[34]). p-CH$_3$: mp 90.0–91.5° (reported 94°,[32] 97°[34]). m-CH$_3$: bp 161 (1.2 mm), mp 39.0–40.5° (reported[34] 42°). H: mp 49.2–50.4° (reported[34] 49–50°). p-Br: mp 108.5–109.7° (reported[34] 110–111°). m-Cl: mp 94.0–96.5° (reported[34] 89.0–90.0°). m-COOC$_2$H$_5$: mp 70.0–71.0°. Anal. Calcd for C$_{16}$H$_{15}$NO$_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.16; H, 5.68; N, 5.16. p-COOC$_2$H$_5$: mp 85.0–86.5° (reported[35] 83°). p-CN: mp 122.5–124.0°. Anal. Calcd for C$_{14}$H$_{10}$N$_2$O: C, 75.66; H, 4.54; N, 12.61. Found: C, 75.53; H, 4.57; N, 12.54. m-NO$_2$: mp 127.0–128.0° (reported[34] 128°). p-NO$_2$: mp 158.5–159.0° (reported[34] 153°). The solvent for the electrochemical measurements was acetonitrile (Burdick & Jackson, distilled in glass) dried over 4-Å molecular sieves and percolated through a 55-cm column of grade I neutral alumina into a volumetric flask containing sufficient tetraethylammonium perchlorate (Southwestern Analytical Chemicals, dried for 16 hr under vacuum) to produce a 0.1 M solution of supporting electrolyte.

Electrochemistry. All measurements were made using the Princeton Applied Research Model 170 Electrochemistry System in the three-electrode mode. The working electrode for reduction was a DME using a 1-sec drop timer. For oxidations a Beckman RPE was used, while for cyclic voltammetry a stationary platinum disk electrode (Beckman) served for both reduction and oxidation studies. An isolated platinum wire was used as the auxiliary electrode, and potentials are referred to a SCE. All runs were made after a 15-min purge with purified nitrogen and within 30 min of preparing the solutions.

References and Notes

(1) (a) Presented in part at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, ORGN 107. (b) This contribution is part III of Linear Free Energy Relationships by H. W. G.; for part II, see *Tetrahedron*, **30**, 2043 (1974). (c) The literature contains several ways of naming compounds of general structure RR'C=NR'' obtained from the condensation of an aldehyde or ketone with ammonia or a primary amine. "Schiff base" refers to the general class of compounds and is used interchangeably with "imine". An "anil" is a Schiff base derived from aniline or a substituted aniline. "Azomethine compounds" are also imines, but the azomethine "group" CH=N is contained not only in imines, but also in such compounds as oximes, hydrazones, and the like.

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