The Kinetics of Reduction of Azobenzenes by a Hydroquinone

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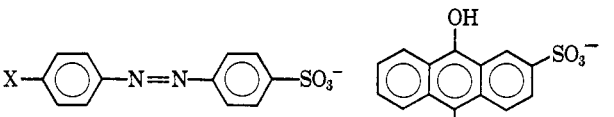
Abstract: The kinetics of reduction of *para*-substituted azobenzenesulfonates by 9,10-anthracenediol-2-sulfonate were measured in aqueous solution by a stopped-flow method. Substrates with electron-donating substituents were reduced to the aniline stage, whereas those with electron-withdrawing substituents were only reduced to the hydrazobenzene stage. The variation of the experimental second-order rate constant with acidity in the region H_0 0.0 to pH 7.5 indicates a rate law, $k_2 = k_0 + k_H a_{H^+} + k_B/a_{H^+}$. The acid-catalyzed reduction involves reaction between protonated azobenzene and un-ionized hydroquinone; the pH-independent reduction involves reaction between unprotonated azobenzene and un-ionized hydroquinone; and the base-catalyzed reaction involves unprotonated azobenzene and ionized hydroquinone. A general acid catalyzed path is observed with substrates having electron-withdrawing substituents, the extent of which increases with the electron-withdrawing power of the substituent. The constants k_0, k_H, and k_B do not vary greatly with structure and give nonlinear, free energy relationships. The effect of structure on k_H is due to opposing effects on the K_a's ($\rho^+ = +2.3$) and on the specific rate constants for reduction of the protonated azobenzenes ($\rho = +2.8$). Arrhenius plots of k_0 showed isokinetic points in the temperature range 33–50°. The variation in k_0 with structure is due to large differences in $\Delta H^{\ddagger}$ and in $\Delta S^{\ddagger}$. A kinetic deuterium isotope effect is found for the pH-independent reduction of one substrate ($k_0^H/k_0^D = 2.7$). The results are discussed in terms of possible electron-transfer mechanisms.

The nature of electron-transfer mechanisms between organic reactants is an intriguing area of study that is little understood. One source of difficulty arises from the fact that the products and reactants differ by hydrogen atoms as well as by electrons. Many of the questions regarding mechanism involve uncertainty as to the sequence of events during the transfer of the electrons and hydrogens, *i.e.*, whether the electrons are transferred singly or in pairs, whether they are transferred as electrons with protonation preceding or completing the process, or whether they are transferred along with the hydrogens, either as hydrogen atoms or as hydride ions.

One important class of redox reactions between organic reactants involves conjugated systems in which hydrogen atoms are attached to nitrogen or oxygen atoms. This class of reactants includes quinones and quinone imines, azines, flavins, dyes, and the respective reduced forms of the couples. In such systems the mechanism of electron or hydrogen transfer is difficult to determine for the following reasons. (1) The hydrogens exchange readily with hydroxylic solvents so that labeling experiments are not straightforward. (2) Many of the reactants in this class give stable intermediate radicals or ion radicals (semiquinones) by single electron tranfers at certain acidities, along with the products from transfer of two electrons. In these systems the various redox species are in mobile equilibrium so that identification of the reactive oxidation state becomes difficult. (3) Most reactants in this class are weak acids or bases so that the relative reactivities of the possible ionic species with respect to electron transfer are a question of mechanistic significance. Since formal analogies can be drawn between the transition states for redox reactions and for nucleophile–electrophile reactions, the question naturally arises as to how far our knowledge regarding the latter class of reactions can be extended to redox reactions. (4) Since many of the compounds in this class are readily oxidized or reduced by inert electrodes and by inorganic ions, as well as by organic redox reagents, we must consider the possibility of dual mechanisms for a given substrate, *i.e.*, consecutive electron and hydrogen ion transfers for some reagents[1] and hydrogen atom or hydride transfer for others.

In this study we have investigated the kinetics of reduction of a series of ionic azobenzenes (**1–6**) by the

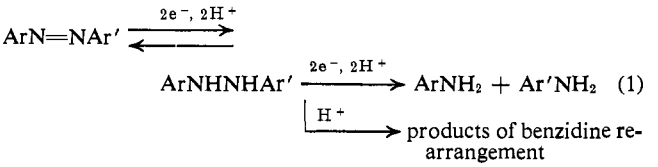


1, X = H
2, X = OH
3, X = OMe
4, X = NMe_2
5, X = Cl
6, X = NMe_3^+

7

soluble hydroquinone **7** in aqueous acid and neutral solutions. The azobenzenes seemed ideal because (1) they are very weak bases,[2] and each except one (**4**) exists as a single predominant ionic species in the range of acidities of interest; (2) they undergo clean 2- or 4-equiv reduction to hydrazobenzenes or to anilines; and (3) intermediate oxidation states are not stable. The anthracene-9,10-diol **7** seemed ideal as a reducing agent for our initial study because its oxidation potential is sufficiently negative (European sign convention) to reduce all the azobenzenes (**1–6**) and because it exists predominantly as the un-ionized species in acid and neutral solution. Semiquinone formation is not very significant in the neutral and acid solutions used in this study.[3]

The reactions that must be considered in the reduction of azobenzenes are summarized as follows in eq 1.



(1) Here we make the simple approximation that a cathode is a reagent that supplies electrons.
(2) R. L. Reeves, *J. Am. Chem. Soc.*, **88**, 2240 (1966).
(3) R. Gill and H. I. Stonehill, *J. Chem. Soc.*, 1845 (1952).

Before the details of electron transfer can be considered in such a system, the relative rates of the three reactions must be determined for each substrate in a series of azo compounds to ensure that one is comparing rates for the same step. In an earlier study of the reduction of azobenzene and some derivatives containing electron-donating substituents by $TiCl_3$, Hinshelwood and his co-workers[4] found that, in several cases, the two stages of reduction proceed at comparable rates.

In the present investigation we have established the stoichiometry of the reductions with the hydroquinone **7**, the rate-controlling steps, the effect of acidity on the rates, activation parameters for one of the paths, and a deuterium kinetic isotope effect. The results indicate that both the protonated and unprotonated forms of the azobenzenes and the undissociated and dissociated forms of the hydroquinone can participate in the reduction reaction, depending upon the acidity. At least one of the paths appears to proceed by a hydrogen-transfer mechanism. The complex dependence of the rate on structure has been partially dissected.

Experimental Section

Materials. The azobenzenes were the same as those described previously.[2] Eastman Grade anthraquinone-2-sulfonic acid sodium salt was recrystallized from water. Baker and Adamson Reagent Grade sulfuric acid and glacial acetic acid were used to prepare the dilute acid and acetic acid–acetate buffers, respectively. Phosphate buffers were used for the pH range 5–7.5.

Anthracene-9,10-diol-2-sulfonate (**7**) was too susceptible to aerial oxidation to be isolated and stored, so it was prepared *in situ* as needed by reduction of the corresponding quinone with sodium borohydride. In a typical run, 0.40 g of the quinone (1.2×10^{3} mole) was dissolved in 150 ml of water in a three-necked flask equipped with a gas dispersion tube, a 100-ml pipet, and a magnetic stirrer. A polyethylene boat containing 0.025 g (6.6×10^{-4} mole) of 99% sodium borohydride made by Metal Hydrides, Inc., was suspended above the solution while the solution was deaerated. About 10 min at room temperature was required for complete reduction, as indicated by a change in color from brown to a clear red orange. The pipet was filled by nitrogen pressure, and the aliquot was transferred to 1900 ml of deaerated 0.1 *N* sulfuric acid. This solution was constantly bubbled with pure nitrogen and could be maintained for a day as a stock solution for several kinetic runs with very little change. It was analyzed immediately before each run. Although the quinone is reduced quantitatively by this procedure, the yield of the hydroquinone was consistently about 70% of the theoretical. No other reduced species were found.

Analytical Methods. The anthraquinone-2-sulfonate and the corresponding hydroquinone **7** were determined polarographically in dilute sulfuric acid (0.1–0.2 *N*) with a 3-sec drop time and a Ag|AgCl reference electrode. Both materials gave linear relationships between concentration and diffusion current over the range of concentrations studied (up to 1.0 m*M* for the quinone and 0.65 m*M* for **7**). The calibration constant for the hydroquinone was determined by measuring the diffusion current of an unknown sample, bubbling the solution with oxygen until oxidation to the quinone was complete, purging with nitrogen, and determining the quinone. The fact that the measured diffusion currents for both species were similar indicates that the aerial oxidation was essentially quantitative. The calibration constants for the quinone and hydroquinone in 0.2 *N* sulfuric acid are 113 and 118 $M\ amp^{-1}$, respectively. All solutions were transferred in hypodermic syringes that had been thoroughly flushed with nitrogen.

Measurement of the Stoichiometry. Solutions of the hydroquinone were prepared and analyzed in 0.2 *N* acid, as already described. Deaerated solutions of the azobenzenes in the same medium were added to the hydroquinone solutions in the polarographic cell, with the hydroquinone in excess. The reductions were rapid and complete and the final polarograms showed only the wave for the reversible quinone–hydroquinone couple in cases where reduction proceeded to the aniline stage, or that wave plus the slowly disappearing hydrazobenzene wave in those cases where reduction stopped at the 2-equiv stage. The quinone formed in the reaction was determined as the difference between the initial (if any) and the final cathodic diffusion current; the corresponding difference in anodic diffusion current was used to measure the amount of hydroquinone consumed. The loss of hydroquinone and formation of quinone agreed quite closely (Table I), which further supports the validity of the method used to calibrate the analytical procedure.

Kinetic Measurements. Since most of the reactions were too fast to be measured by conventional means, flow methods were employed. The flow apparatus has been described.[5] In most cases the stopped-flow method could be used. For a few very rapid runs the continuous-flow method was used and the reaction time was varied by insertion of machined spacers of varying length between the mixing chamber and the observation cell. The rates were measured by following the decrease in absorbance of the azo compounds. In some cases the absorption maximum of the azo compound[2] was at a wavelength at which the hydroquinone has low absorptivity; in this case the latter material could be used in sufficient excess that pseudo-first-order conditions obtained. With some of the azo compounds, however, the absorption maxima were too close to that of **7** and the initial concentration of **7** had to be decreased until it was in small excess. Most runs were made under initial concentration conditions where a second-order rate expression was appropriate. The second-order rate constants were computed from the equation

$$k_2 t = \frac{2.3}{na - b} \log \frac{b(a - x)}{a(b - nx)} = \frac{2.3}{na - b} \log \left[\frac{(b/a)(D_t - D_\infty)}{(b/a)(D_0 - D_\infty) - n(D_0 - D_t)} \right] \quad (2)$$

or

$$k_2 t = \frac{2.3}{na - b} \log \left[\frac{(a/b)(D_0 - D_\infty) - (1/n)(D_0 - D_t)}{(a/b)(D_t - D_\infty)} \right] \quad (3)$$

where a = initial molarity of the azobenzene, b = initial molarity of **7**, n = the molar stoichiometric factor (1 or 2), D_0 = the initial optical density, D_∞ = the final density, and D_t = the density at any time t. Equation 2 was used when **7** was in excess, and eq 3 was used when the azobenzene was in excess. The initial concentration of the azobenzene was 2.5×10^{-5} *M* or 5.0×10^{-5} *M*. Since the stock solution of the hydroquinone was always in dilute acid (0.1 or 0.2 *N*), the acidity of the kinetic run had to be controlled by the acidity of the stock solution of azobenzene. The approximate acidity of the mixed solutions was predetermined by calculation or experiment, and the exact acidity was determined by analysis of the effluent from the flow apparatus. In those runs involving acetic acid–acetate buffers, the amounts of acetic acid and sodium acetate needed to give a desired pH and concentration were dissolved in 0.10 *N* potassium hydroxide instead of in water. The dye solution in this mixture was then mixed in the flow apparatus with the hydroquinone in 0.10 *N* acid. The resulting pH was always very close to that intended. In cases where the concentrations of acetic acid and sodium acetate were varied, potassium chloride or sodium perchlorate was added to bring the ionic strength to 0.1 *M* in the mixed solutions.

The acidity of the dilute sulfuric acid solutions was determined by titration. The Hammett acidity function was used as a measure of acidity over the concentration range, 0.05–0.6 *M*, since all the azobenzenes but **2** and **3** behave strictly as H_0 indicators, whereas **2** and **3** show only slight deviation from H_0 behavior.[2] The appropriate value of H_0 was obtained from a plot of H_0 *vs.* acid concentration by using values from the literature.[6] All other acidities are based on the pH scale and were determined with a glass electrode.

Reaction in D_2O. The acetate buffer consisted of 0.750 g of glacial acetic acid, 1.025 g of anhydrous sodium acetate, 2.80 g of potassium chloride, 1.40 g of potassium hydroxide, and 6.95

(4) (a) N. R. Large, F. J. Stubbs, and C. N. Hinshelwood, *J. Chem. Soc.*, 2736 (1954); (b) N. R. Large and C. N. Hinshelwood, *ibid.*, 620 (1956).

(5) (a) W. R. Ruby, *Rev. Sci. Instr.*, **26**, 460 (1955); (b) C. A. Bishop, R. F. Porter, and L. K. J. Tong, *J. Am. Chem. Soc.*, **85**, 3991 (1963).

(6) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

mg of the azo compound **2** in 250 ml of 99.8% Bio-Rad deuterium oxide. A 0.111 *N* solution of sulfuric acid was prepared by adding 0.77 ml of 96% acid to 250 ml of 99.8% D_2O. The anthraquinone (50 mg) in 37.5 ml of D_2O was reduced with 3.3 mg of sodium borohydride, and 25 ml of the resulting solution was diluted with 225 ml of the dilute acid in D_2O. The pD of the reaction solution was 4.44. Although the acids and reagents used were the protium compounds, calculations showed that the final mole % of deuterium in the solutions was at least 99%. The identical procedure and amounts were used in the water solution employed for the rate comparison.

Results

Solutions of the hydroquinone **7** were conveniently prepared *in situ* by reduction of the corresponding anthraquinone with sodium borohydride in neutral solution. Subsequent addition of dilute acid destroyed any excess borohydride and gave a solution that was quite stable under a nitrogen atmosphere. No other species that are oxidizable at a mercury electrode could be detected; the stoichiometry and kinetic data show that no active reducing agent other than **7** was present in the solutions.

The over-all stoichiometry of the reduction by **7** was determined by measuring the loss of **7** and the formation of the quinone (Q) upon adding known concentrations of the azobenzenes to solutions containing excess hydroquinone (H_2Q) in 0.2 *N* acid. The results are shown in Table I.

Table I. Stoichiometry of the Reduction of Azobenzenes in 0.2 *N* H_2SO_4[a]

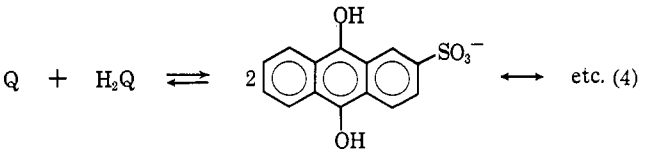
Structure	$\Delta[H_2Q] \times 10^4$	$\Delta[Q] \times 10^4$	Moles of H_2Q/mole of azo
2	2.56	2.41	2.0
3	2.40	2.35	1.9
4	2.44	2.38	1.9
1	(1.18, 1.28)	(1.25, 1.21)	1.0
5	1.26	1.33	1.0
6	...	...	1.0[b]

[a] $[AZO]_0 = 1.25 \times 10^{-4}$ *M*. [b] Determined indirectly from the adherence of kinetic runs to eq 2 with $n = 1.0$.

In the cases of the 4-equiv reductions, polarographic analysis of the final solutions showed that only Q and unreacted H_2Q were present. In the 2-equiv cases, the polarograms showed the additional anodic wave due to the hydrazobenzene. The height of this wave diminished with time as the hydrazobenzene rearranged to polarographically inert products. There was no change in the wave heights of Q and H_2Q during the decomposition of the hydrazobenzene from **1**, proving that the hydrazobenzene was not being reduced by unreacted H_2Q at a slow rate. The hydrazo form of **5** appeared to undergo slight additional reduction, along with the rearrangement. This reaction was too slow and too minor in extent to complicate the kinetic study of the fast first stage in the reduction.

The rates of reduction of all the azobenzenes gave good fits to the appropriate integrated second-order rate expressions (eq 2 and 3), when neither of the reactants was in large excess. Data were obtained through 80% reaction and were fitted by least squares to eq 2 or 3. The mean value for the standard errors for the slopes was 1.1% of the value of the slope; the largest error observed for any given run was 2% of the value of the slope. The mean per cent deviation of rate constants for replicate runs was 2%. When H_2Q was in large excess, the pseudo-first-order rate constants for reduction of **1** were directly proportional to the concentration of H_2Q for a sixfold variation in $[H_2Q]$. The molar stoichiometric factors determined in 0.2 *N* acid for the over-all reductions were used in the second-order rate expressions (2 or 3) over the acidity range, H_0 0.0 to pH 7.5. There were no significant deviations from linearity of the appropriate second-order plots that might indicate that the stoichiometry changed with acidity or that the relative rates of the two stages of reduction (eq 1) change with acidity. All the data indicate that the hydrazobenzenes from **1**, **5**, and **6** are reduced very slowly or not at all by **7**, whereas the hydrazobenzenes from **2**, **3**, and **4** are reduced at rates much faster than the rates of the reduction of the corresponding azobenzenes. Our results are consistent with the assumption that, in every case, the rates being measured are the rates of reduction of the azo compounds to the hydrazo form.

The rate of reduction of **1** in 0.19 *N* acid was unchanged by the addition of an eightfold excess of the quinone. This shows that the position of equilibrium in the reversible first stage of reduction is not perturbed to a measurable extent by the products. It also shows that the intermediate oxidation state (semiquinone) that could be formed by equilibrium 4 is not kinetically important.



The effect of changing acidity on the reduction rates is shown by the log k_2–pH (H_0) profiles in Figure 1. The pH scale is used for the region pH 2 to 7.5. The H_0 scale is used for the higher acidities, since it has been shown[2] that all the substrates but **2** and **3** behave as H_0 indicators, whereas **2** and **3** give only slight deviation from H_0 behavior. The data conform to the rate expression given by eq. 5. The values of the three

$$k_2 = k_0 + k_H a_{H^+} + k_B/a_{H^+} \quad (5)$$

parameters required for each substrate are given in Table II. The solid lines in the profiles for all substrates but **4** were calculated from eq 5, by using the parameters in the table.

Table II. Summary of Rate Constants at 25°

X	k_0, M^{-1} sec^{-1}	k_H, M^{-2} sec^{-1}	k_B, sec^{-1}	$k_{AH^+ \cdot H_2Q}$ M^{-1} sec^{-1}	$k_{A \cdot HQ^-}$ M^{-1} sec^{-1}
NMe_2	...	...	...	4.0×10^4	...
OH	250	6.2×10^4	1.0×10^{-4}	1.7×10^6	8.2×10^3
OMe	250	6.2×10^4	1.0×10^{-4}	1.9×10^6	8.2×10^3
H	42	4.3×10^3	9.5×10^{-6}	6.1×10^6	7.9×10^2
Cl	90	4.3×10^3	2.5×10^{-5}	1.4×10^7	2.1×10^3
NMe_3^+	100	1.5×10^4	5.8×10^{-4}	1.3×10^9	4.8×10^4

Methyl orange (**4**) was the only azobenzene whose rates could be measured at pH values near the pK_a (+3.49). These rate constants are also shown in

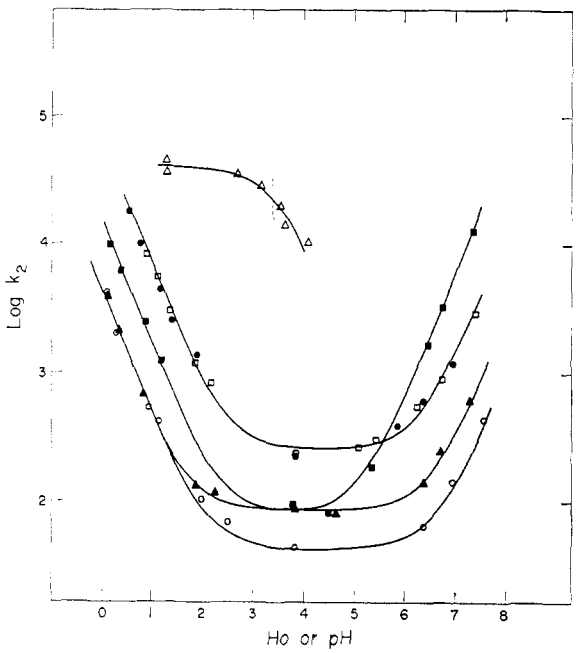


Figure 1. Plots of log second-order rate constants for reduction of azobenzenes against pH or H_0 at 25°: O, X = H; ▲, X = Cl; ■, X = NMe_3^+; ●, X = OH; □, X = OMe; △, X = NMe_2. Solid lines for X = H, Cl, NMe_3^+, OH, and OMe were calculated from eq 5; the solid line for X = NMe_2 is log $k_{AH^+,H_2Q}[AH^+]/([AH^+] + [A])$.

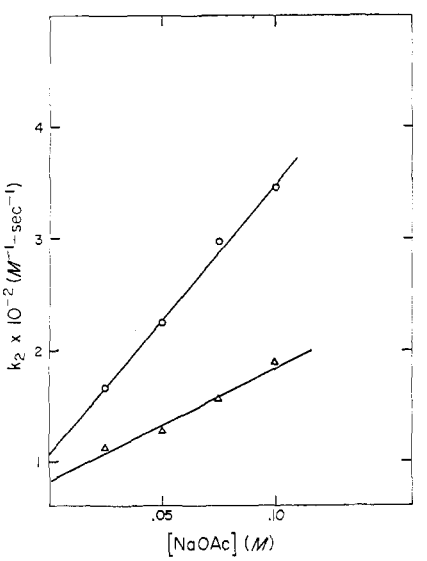


Figure 2. Effect of acetate buffer concentration on the second-order rate constant for reduction of **6** at 25° and ionic strength of 0.1 M: O, pH 3.8; △, pH 4.6.

Figure 1 and, although the precision of the runs is not as good as with the slower runs, the data indicate that the rates tend to level off as the azobenzene becomes protonated. The solid line in this plot is log $k_{AH^+,H_2Q} \cdot [AH^+]/([AH^+] + [A])$ *vs.* pH, calculated from the acid dissociation constant for the azonium tautomer[2] of monoprotonated **4** (+3.40, dashed vertical line).

The rates of reduction of the azobenzenes possessing electron-withdrawing substituents showed general acid catalysis in the region of the log k_2–pH profiles where the reduction rate is independent of pH. The rates for **2** and **3** were unaffected by increased buffer concentration in this pH region. Figure 2 shows the rate data for **6**. The variation in acetate ion concentration is the same for both plots (0 to 0.10 M), but the pH and hence the acetic acid concentration are different. The active catalytic species is clearly the acetic acid. Figure 3 shows how the acetic acid catalysis increases upon changing the substituent from H to Cl to NMe_3^+. The values of the rate constants for acetic acid catalysis are 22, 1.3 × 10^2, and 5.0 × 10^2 M^{-2} sec^{-1} for X = H, Cl, and NMe_3^+, respectively. The data points in Figure 1 and the k_0 values in Table II are those obtained by extrapolation to zero acetic acid concentration. Substitution of sodium perchlorate for potassium chloride as the inert salt in the buffers did not alter the rates.

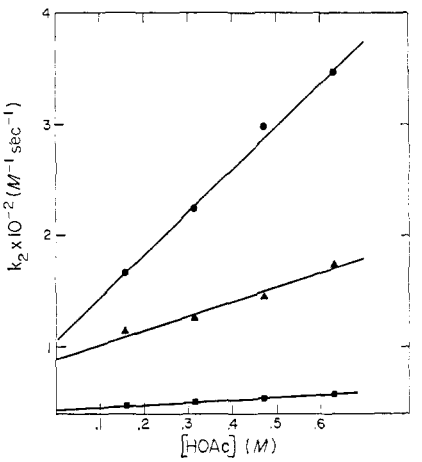


Figure 3. Catalysis of the reduction of azobenzenes by acetic acid at pH 3.8, 25°, and ionic strength 0.1 M: ●, X = NMe_3^+; ▲, X = Cl; ■, X = H.

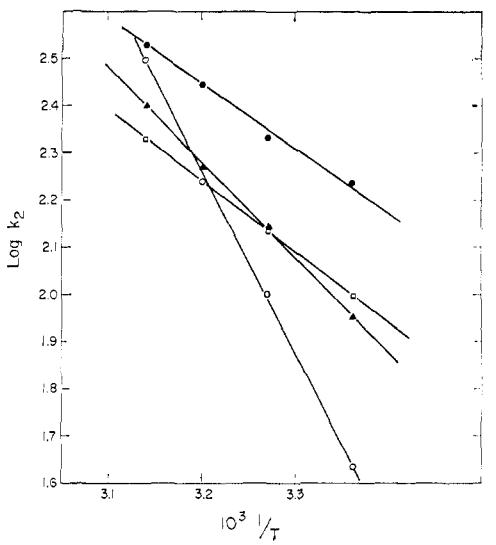


Figure 4. Temperature coefficients of the rate constants for the uncatalyzed reductions at pH 3.8, ionic strength 0.1 M, temperature range, 25–45°: O, X = H; ▲, X = Cl; □, X = NMe_3^+; ●, X = OH.

The temperature coefficients of the pH-independent rates were measured in pH 3.8 acetic acid–acetate buffers over the temperature range 25–45°. The Arrhenius plots are shown in Figure 4 and the derived activation parameters are listed in Table III. In the case of **6**, rates were measured at several buffer levels at each

temperature and extrapolated to zero buffer concentration to obtain the uncatalyzed rate for that temperature. Acetic acid catalysis of the reduction of **1** and **5** was not experimentally significant at the higher temperatures.

Table III. Activation Parameters for the Uncatalyzed Reduction of Substituted Azobenzenes at 25°

X	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
OH	5.61 ± 0.01[a]	-29.2 ± 0.1[b]
H	17.0 ± 0.2	$+6.2 \pm 0.2$
Cl	9.18 ± 0.01	-18.7 ± 0.1
NMe_3^+	6.26 ± 0.01	-28.3 ± 0.1

[a] 95% confidence limits calculated from the standard error of the slope of the Arrhenius plot and the appropriate t factor. [b] 95% confidence limits calculated from the pooled standard errors for $\Delta H^{\ddagger}$ and for the predicted value of log k at 25°.

The deuterium kinetic isotope effect for the uncatalyzed reduction of **2** was determined by comparison of reduction rates in H_2O and D_2O buffers prepared in identical ways. The pH and pD values were 4.62 and 4.44, respectively. The deuteriohydroquinone was prepared by reduction of the quinone with sodium borohydride in D_2O and dilution with dilute acid in D_2O. The mole % of deuterium in the final medium was calculated to be about 99%. Duplicate rate measurements were made on the same D_2O solutions at different times with no change in rate, establishing that the exchangeable hydrogens of the hydroquinone had assumed the isotopic composition of the medium by the time the measurements were made. The experimental value of k_0^H at pH 4.6 was a little lower than the k_0^H value used to obtain the log k_2–pH profile for **2** in Figure 2. The ratio $k_0^H/k_0^D = 2.7$ is based on the measured rates. The ratio has the value of 3.9 if the rate measured in D_2O is compared with the "best-fit" value of k_0^H in Table II. The lower value is probably more reliable.

The rate of reduction of **1** was also measured in dilute hydrochloric acid solution over the concentration range 0.1–1.9 N ($H_0 = +0.98$ to -0.65). A plot of log k_2 *vs.* H_0 for this medium was linear but had a slope of 1.4 instead of the slope of 1.0 observed for sulfuric acid solutions. Addition of potassium chloride at constant acid *concentration* increased the rate. Large, Stubbs, and Hinshelwood[4a] have noted a similar specific effect from added chloride ion in the reduction of azobenzenes by titanous chloride in aqueous ethanolic hydrochloric acid solutions. These workers found that a given increase in Cl^- concentration increased the rate by about the same amount as did the same increase in H^+ concentration. On the other hand, it is known that alkali halide salts have pronounced and specific effects on the H_0 values of fairly dilute hydrochloric acid solutions.[7] We therefore measured the effect of varying the potassium chloride concentration from zero to 1.6 M at the constant HCl *concentration* of 0.10 M. This corresponds to a change in H_0 from +0.98 to +0.75.[8] The plot of log k_2 against H_0 for this narrow range of acidity also had a slope of 1.4. These results indicate that, with our system, the principal effect of added potassium chloride is a salt effect on H_0. The fact that the rate increases more steeply with acidity in hydrochloric acid solutions than in sulfuric acid solutions may be caused either by failure of the activity coefficient postulate[9] for **1** or the activated complex in the former medium, or by a specific chloride effect on the reduction rate.

(7) M. A. Paul, *J. Am. Chem. Soc.*, 76, 3236 (1954).

(8) The exact salt effect on H_0 depends to a small degree on the indicator used to measure H_0.[7] We have used the data based on *p*-nitroaniline as the indicator.

Discussion

The results of the kinetic and stoichiometric studies show that the rates of reduction of the intermediate hydrazobenzenes are considerably more sensitive to changes in substituents than are the rates for the parent azobenzenes. Although no quantitative measure of the reduction rates of the hydrazobenzenes was made, it is evident that those intermediates with electron-withdrawing substituents are reduced at very slow rates, so that, in dilute acid, the benzidine rearrangement is the main path for their decomposition. In sharp contrast, the introduction of electron-donating substituents causes the intermediate hydrazobenzenes to be reduced at greater rates than their parent azobenzenes.

It is to be expected that some substituted azobenzenesulfonate with a substituent constant lying between that of OH and H might have comparable reduction rates for the azo and hydrazo species.

The interpretation of the effect of acidity on the reduction rates turns out to be much simpler in our system than in the study[4a] of the reduction of azobenzene in hydrochloric acid solutions with $TiCl_3$. With the inorganic reducing agent, the effect of changing HCl concentration on the complex ion equilibrium of the reducing agent has to be separated from the effect on the azobenzene protonation. Large, Stubbs, and Hinshelwood found that the effect of changing acidity in their system could best be expressed by a rate law involving a power series in acid concentration in the range of 0.5 to 3.5 N acid. From this they concluded that doubly protonated azobenzene must be an important reactive species.

Our results show that, if the acidity is expressed by the appropriate acidity function, the rate of the acid-catalyzed reduction is proportional to a_{H^+} and higher-order terms are not indicated. Our results in HCl solutions gave a strictly linear plot of log k_2 against H_0 in a region of acidity where the plot of log k_2 against $-\log C_{H^+}$ curves upward significantly, as observed by Large, Stubbs, and Hinshelwood. Our additional observation that the rate of reduction of **4** is strictly proportional to $[AH^+]/([AH^+] + [A])$ at pH values near the pK_a convinces us that the only protonated species of kinetic significance in our system is the monoprotonated azobenzene. Our failure to find evidence for the addition of a second proton to the simple azobenzenes up to very high acidities[2] indicates that such a species would be in very low concentration at the acidities of our kinetic studies. We suggest that the previous results could also be interpreted in terms of the monoprotonated azobenzene if an appropriate acidity function were determined and used in the interpretation of the kinetic data.

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 275.

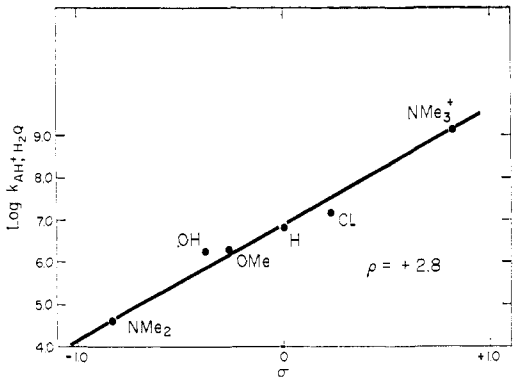


Figure 5. Effect of substituents on the specific second-order rate constant for reduction of protonated azobenzenes at 25°.

The base-catalyzed reduction that we observed at pH 6 to 8 is undoubtedly associated with the fact that the ionized hydroquinone (HQ^-) is oxidized more rapidly than the un-ionized species (H_2Q). This is logical if the reducing agent is regarded as a nucleophile. Ionized hydroquinones are known to be oxidized at higher rates than the un-ionized species.[10] If this interpretation is correct, base catalysis is peculiar to the system we have studied, and will not be a general phenomenon for the reduction of azobenzenes.

The pH-independent rate may either be associated with reduction of unprotonated azobenzene by undissociated hydroquinone (eq 8) or with the reduction of protonated azobenzene by ionized hydroquinone. In the first case, the experimental rate constant, k_0, is a direct measure of the specific rate constant of the indicated reaction, k_{A,H_2Q}, whereas, in the second case, it is a composite constant, $k_0 = k_{AH^+,HQ^-}(K_{H_2Q}/K_{AH^+})$. The acid dissociation constants for the protonated azobenzenes were measured earlier;[2] the pK_a for the loss of the first proton from **7** was measured spectrophotometrically in this study and found to be 7.92.[11] Using the experimental values of k_0, K_{H_2Q}, and K_{AH^+}, we calculated values for k_{AH^+,HQ^-} that vary from 6×10^{11} M sec^{-1} for **2** up to 6×10^{14} M sec^{-1} for **6**. All these calculated values exceed the rate constants for the fastest diffusion-controlled reactions,[14] so this mechanism need not be considered. The three paths for reduction are summarized in eq 6–10.

$$A + H \rightleftharpoons AH^+ \quad \text{(fast)} \quad (6)$$

$$K_{AH^+} = [A][H^+]/[AH^+]$$

$$H_2Q \rightleftharpoons HQ^- + H^+ \quad \text{(fast)} \quad (7)$$

$$K_{H_2Q} = [HQ^-][H^+]/[H_2Q]$$

$$A + H_2Q \xrightarrow{k_{A,H_2Q}} \text{products} \quad \text{(slow)} \quad (8)$$

$$k_0 = k_{A,H_2Q}$$

$$AH^+H_2Q \xrightarrow{k_{AH^+,H_2Q}} \text{products} \quad \text{(slow)} \quad (9)$$

$$k_H = k_{AH^+,H_2Q}/K_{AH^+}$$

$$A + HQ^- \xrightarrow{k_{A,HQ^-}} \text{products} \quad \text{(slow)} \quad (10)$$

$$k_B = k_{A,HQ^-}K_{H_2Q}$$

Two facts related to the effect of substituents on the rates are significant: (1) the experimental rate constants k_0, k_H, and k_B are not affected greatly by changing structure; and (2) the experimental constants show nonlinear substituent effects. Since k_H is a composite constant the effect of structure on K_{AH^+} and on the specific rate constant (k_{AH^+,H_2Q}) must be considered separately. It has already been shown[2] that all the pK_{AH^+} values give excellent correlation with σ^+. Figure 5 shows that values of log k_{AH^+,H_2Q} give good correlation with σ_p.[15] Failure of the composite constant, k_H, to give correlation can be ascribed to the fact that the two component constants are correlated by different substituent constants. The small net effect of substituents on the experimental rate of the acid-catalyzed reduction is the result of opposing effects on K_{AH^+} ($\rho^+ = 2.3$)[2] and on k_{AH^+,H_2Q} ($\rho = 2.8$). A positive value of ρ for the rate of reduction of the protonated azobenzenes is in accord with the concept of these oxidizing agents functioning as electrophiles.

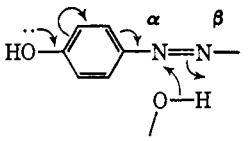
The effect of changing structure on k_{A,H_2Q} and on k_{A,HQ^-} cannot be disposed of so simply. Both these constants have minimum values for the unsubstituted derivative (Table II) at 25°. Whenever a curvilinear structure–reactivity relationship cannot be explained as we have explained it for the acid-catalyzed case, one suspects a change in mechanism as the structural series is traversed. The activation parameters (Table III) show that the entropies of activation are not constant through the series and that the value of $\Delta H^{\pm}$ is relatively high for the unsubstituted derivative. Of greater significance is the fact that four isokinetic points are found in the Arrhenius plots (Figure 4) in the temperature range 30–50°. This makes any interpretation of relative reactivities at one temperature meaningless since a different order of reactivity is found at a somewhat higher temperature.

The finding of a kinetic deuterium isotope effect for the uncatalyzed reduction of **2** is best interpreted in terms of a hydrogen-transfer mechanism for this particular substrate. A solvent deuterium isotope effect arising from the use of D_2O seems unlikely. In the first place, pH–pD differences should be negligible since the rate is independent of pH in the pH region where the effect is found. The difference $pK_a^H - pK_a^D$ for the buffer acid should be unimportant for the same reason and because **2** is not reduced by a path involving catalysis by buffer acid. The $pK_a^H - pK_a^D$ differences for **2** and **7** should not give rise to a solvent isotope effect since the reaction involves unprotonated **2** and undissociated **7**, both of which are the predominant species at the pH where the effect is found. Finally, it is unlikely that the kinetic isotope effect arises from a mechanism involving proton transfer from water in the transition state since the stronger acid, acetic acid, is not involved in such a mechanism.

The changing extent of general acid catalysis shows that the composition of the activated complex can

(10) T. H. James, J. M. Snell, and A. Weissberger, *J. Am. Chem. Soc.*, 60, 2984 (1938).
(11) Other estimates of this pK_a are 8.65,[3] 7.65,[12] and 8.[13]
(12) E. Burnstein and A. W. Davidson, *Trans. Electrochem. Soc.*, 80, 175 (1941).
(13) J. B. Conant, H. M. Kahn, L. F. Fieser, and S. S. Kurtz, *J. Am. Chem. Soc.*, 44, 1382 (1922).
(14) (a) G. Ertl and H. Gerischer, *Z. Elektrochem.*, 65, 629 (1961); (b) M. Eigen and L. DeMaeyer, *ibid.*, 59, 986 (1955).
(15) The σ_p values are those suggested by McDaniel and Brown.[16]
(16) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).

change systematically with changing substituents, and suggests a progressive change in mechanism. The more electrophilic substrates, **5** and **6**, probably undergo reduction by electron transfer from H_2Q with added assistance by concerted proton transfer from external acid. The less electrophilic, but more basic substrate, **2**, may react through a four-centered transition state in which the hydrogen from the reducing agent is transferred to the relatively basic β nitrogen, while electrons are being simultaneously transferred to the α nitrogen. Such a mechanism would account for the deuterium isotope effect being less than the maximum for a linear



transfer of a proton along the reaction coordinate, since the effect would arise largely from the difference in zero-point energy for a bending, rather than a stretching, vibration. It is also possible that the progressive change in structure of the azobenzenes leads to a change from attack by H_2Q at the α- to the β-azo nitrogen. The changes in the activation parameters can be interpreted in terms of a progressive change in the activated complex proceeding from **6** to **2** from one involving considerable orientation at a highly electron-deficient site where $\Delta H^{\pm}$ for electron transfer is low, to one requiring little orientation but a high $\Delta H^{\pm}$ for electron transfer, and finally to still another requiring considerable orientation at an electron-rich site but where $\Delta H^{\pm}$ is again low. Thus, in the case under study, where the oxidizing agent is both an electrophile and weak base and the reducing agent is a nucleophile and a weak acid, the nucleophile–electrophile interaction can become entangled with the acid–base interaction. A similar suggestion was advanced by Brown and Subba Rao to explain the fact that azobenzene is not reduced by borohydride ion, a Lewis base, but is readily reduced by diborane, a Lewis acid.[17]

Most of the other results that are not obscured by uncertainty regarding mechanism are interpretable in terms of the electrophile–nucleophile model for the oxidant–reductant interaction. Lowering the electron density at the reaction site in the azobenzene by protonation and by substituents, and increasing the electron density on the reactive functional group of the hydroquinone by ionization both facilitate electron transfer. The combined effect of protonation and two powerful electron-withdrawing substituents in **6** leads to a rate that is nearly diffusion controlled (Table II). The observed effect of substituents on the acid-catalyzed reduction rates shows remarkable parallelism with substituent effects in nucleophilic condensations with carbonyl compounds.[18]

Acknowledgment. We wish to thank Dr. S. G. Smith for helpful discussions of this work.

(17) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

(18) (a) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964); (b) R. L. Reeves in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, pp 567–619.

Acidity in Nonaqueous Solvents. IV. Hydrocarbon Acids in Dimethyl Sulfoxide[1,2]

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Abstract: By use of the glass electrode, we have measured the acidities of a number of weak acids in dimethyl sulfoxide solution relative to a standard state in the same solvent. The glass electrode is found to respond reversibly to changes of hydrogen ion activity over a range of 25 powers of ten. Surprisingly, for many of the hydrocarbon acids, the absolute values of the determined pK's are identical with those determined by acidity function techniques. The factors contributing to this behavior are discussed.

The acidities of hydrocarbon acids have been of interest to organic chemists in connection with a number of problems.[3] Both kinetic and equilibrium measurements have been used to estimate acidities of very weak acids, and a single scale covering an extremely wide range of acidities has recently been proposed.[3] Rather large discrepancies in the proposed scale, however, have been noted in a study of the acidity of hydrocarbons in dimethyl sulfoxide solution utilizing acidity function techniques.[4] Part of the discrepancy undoubtedly arises from the fact that measurements in a variety of solvents have been used in establishment of the single scale. A second contributing factor to the noted discrepancies is the complicating effect of ion pairing on some of the measurements which were made in solvents of extremely low dielectric constant.[5]

(1) For previous papers in this series, see: C. D. Ritchie and P. D. Heffley, *J. Am. Chem. Soc.*, **87**, 5402 (1965); C. D. Ritchie and G. H. Megerle, *ibid.*, **89**, 1447 (1967); **89**, 1452 (1967).

(2) This work was supported by Grant No. GP 2635 from the National Science Foundation, and by Grant No. GM 12832 from the Public Health Service.

(3) For an excellent discussion of the use and establishment of the acidities of a number of hydrocarbon acids, see: D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(4) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).

(5) A. Streitwieser, *Progr. Phys. Org. Chem.*, **3**, 44 (1965); see also ref 3, p 44.