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BENZIDINE REARRANGEMENTS IN MODERATELY CONCENTRATED AQUEOUS ACID

C. A. Bunton* and R. J. Rubin

Department of Chemistry, University of California, Santa Barbara, California 93106

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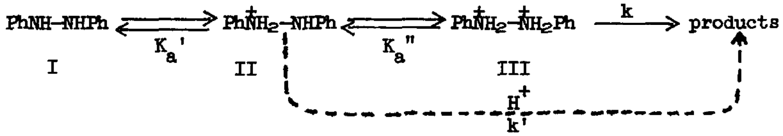
To date the acid catalyzed benzidine rearrangement has generally been followed in aqueous organic solvents.[1] Both one and two proton mechanisms can be observed, and sometimes the order with respect to hydrogen ions is fractional or variable. In a two proton rearrangement of, say 1,2-diphenylhydrazine (I), the first proton transfer should be an equilibrium step. Our aim was to carry out the reaction in moderately concentrated aqueous acid under conditions in which there should be extensive monoprotonation, so that K_a' (Scheme I) could be estimated in terms of protonating power of the medium as measured by Hammett's acidity function, H_0', because to date the kinetic evidence has not permitted separation of the rate and equilibrium constants in the postulated multistep reactions. The rearrangement is rapid under these conditions, but can be followed using a stopped flow spectrophotometer. Scheme I involves diprotonation on nitrogen,[2,3] but it has also been suggested that the second protonation is on the ring.[4,5] This hypothesis is consistent with the kinetics and with evidence for ring protonation of some aromatic amines and ethers, but then aromatic deuterium exchange should compete with rearrangement, whereas none is observed in the rearrangement of 1,2-diphenylhydrazine in D_2O.[4]

Scheme I



It is generally assumed that both proton transfers are preequilibria, at least for the simple diaryl hydrazines, based on the kinetic solvent deuterium isotope effect $k_{H_2O}/k_{D_2O} <$ 0.25,[2,6] but we could also assume that the second protonation is rate limiting with the proton essentially fully transferred in the transition state, so that zero point energy is conserved in the transition state.[7,8]

Rearrangement of some halogen substituted diphenyl hydrazines have $k_{H_2O}/k_{D_2O} > 0.25$, suggesting that here the second proton is not fully transferred in the transition state.[3]

The reaction scheme involving two proton preequilibria leads to equation (1), provided that H_0' is the appropriate measure of protonating power, as it is for these reactions in aqueous dioxane.[2,6]

$$\log k_\psi + H_0' = \log k/K_a'' - H_0' - \log(h_0 + K_a') \qquad (1)$$

(If the second proton transfer is rate limiting, as shown by the broken line in Scheme I, the term k/K_a'' would be replaced by k'.)

The experimental results for reaction of (I) in aqueous $HClO_4$ can be fitted to equation (1) $K_a' = 5$ and $\log k'/K_a''$ (or $\log k'$) $= 1.55$ (Figure 1). The deviations are not unexpected because of errors in k_ψ and H_0' and the uncertainty in the use of H_0' as the appropriate acidity function for these reactions. The value of K_a' is reasonable in terms of the basicity of hydrazine and the -I effect of phenyl groups.

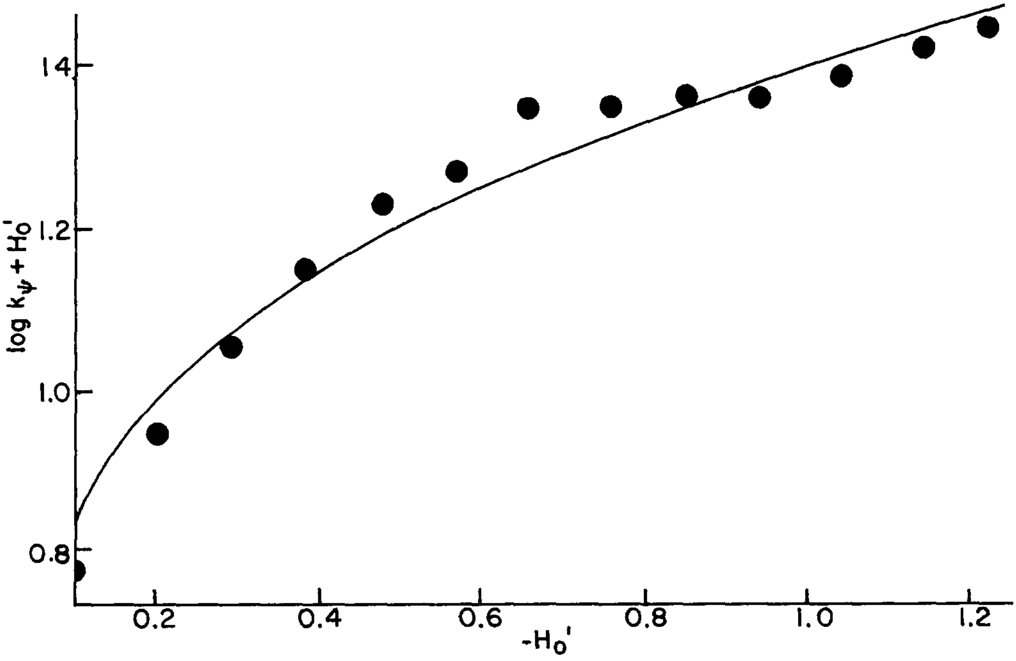
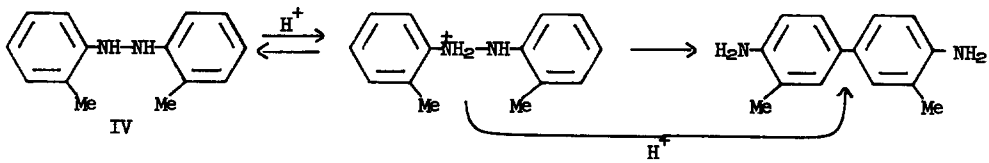


Figure 3. Dependence of k_ψ on $-H_0'$ at 25.0°. The line is calculated using eqn. 1.

If the monoprotonated species (II) is in equilibrium with the hypothetical diprotonated species (III), the latter must revert to (II) much more rapidly than it goes to products. An estimate of k requires a value of K_a'', and in order to estimate it for 1,2-diphenylhydrazine we measured the protonation of $PhNH\overset{+}{N}H_3$ in H_2SO_4 and $HClO_4$ in the H_0' range from the absorbance at 275 nm and obtained $pK_a \sim -2$. (Phenylhydrazine is diprotonated on nitrogen.[4]) The pK difference between ammonia or methylamines and the corresponding anilines is ca. 5 units suggesting $pK_a'' \sim -7$ for (III), and $k \sim 4 \times 10^8$ sec^{-1}. Proton loss from (III) to water cannot be faster than diffusion control, and is often much slower than it for protonated amines,[9] so that it may not be possible to reconcile our estimates of k and K_a'' with a mechanism involving two proton preequilibria. In that event we would have to assume that the second proton transfer is part of the rate limiting step with log k' ~ 1.55.

Our observation of a decrease in order with respect to acidity (Figure 1) is unusual in the benzidine rearrangement, although an increase in this order from 1 to 2 with increasing acidity is often observed for rearrangement in aqueous organic solvents when a two proton mechanism takes over from a one proton mechanism. However we have observed both these changes of kinetic order in the rearrangement of 1,2-di-*o*-tolylhydrazine (IV) in aqueous acid. (Rearrangement of (IV) has an order between 1 and 2 for reaction in aqueous organic solvents.[2])



IV

In aqueous acid with $C_{H^+} < 0.01$ M the reaction is first order with respect to C_{H^+} and a plot of k_ψ against C_{H^+} has a slope of 17 l. $mole^{-1}$ sec^{-1}. At higher acidities the order with respect to C_{H^+} gradually increases up to ca. 1.8 with respect to C_{H^+} in the range 0.05 - 0.3 M HCl because a two proton mechanism intervenes (c.f. ref. 2). With a further increase in acidity the order with respect to acidity reverts towards 1, and in the H_0' range, C_{HCl} or $C_{HClO_4} > 0.8$ M, a plot of k_ψ against $-H_0$ has a slope of approximately 1, suggesting that under these conditions the substrate is becoming fully protonated as was found with (I). In this range some representative values of k_ψ (sec^{-1}) are: 94 and 124 in 0.79 and 0.84 M HCl respectively, and 76, 204 and 303 in 0.79, 0.94 and 1.31 M HCl respectively. The faster reaction in $HClO_4$ is consistent with the larger value of $-H_0'$ for this acid than for HCl.[10]

These dissections of the rate and equilibria constants for benzidine rearrangements could not readily be made for reaction in aqueous organic solvents. The protonating power of moderately concentrated aqueous strong acids is reduced by addition of organic solvents such as dioxane,[10] so that it is difficult to monoprotonate the substrate completely, and then reaction of (I) or (IV) would be too fast to be followed by conventional methods.

It should be noted that our kinetic evidence is consistent with the second protonation being either on nitrogen[2] or carbon,[4,5] and with the various interactions which have been postulated as holding the rings together during the rearrangement.

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