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Salt Effects on the Kinetics of the Proton-Transfer Reactions in the 3,5-Dinitrohydroxybenzoic Acid/Ammonia System

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A T-jump study of the 3,5-dinitrohydroxybenzoic acid (DNSA)/ammonia system has been undertaken, as a function of the nature and concentration of the added salt. Rate constants for the different possible proton-transfer reactions have been obtained from the experimental relaxation curves. The mechanism has been analyzed with the aid of a theoretical model based on Marcus- like free energy surfaces for each elementary step. Despite possible uncertainties in the estimations and approximations used, two conclusions seem to be well founded: first, the stepwise character of the proton-transfer reactions involving DNSA, and second, the possible change in the mechanism connected with the change in the final proton acceptor in the deprotonation of DNSA. This result, not previously assessed in the literature, is relevant for analyzing the salt effects, as is discussed in this work, and also for the hypothetical application of such a system in a molecular protonic device, an area of current research interest. Finally, the use of the well-known plot of log(k) versus ΔpK_a for analyzing the negative or positive salt effects on the proton-transfer reactions is suggested.

Introduction

In previous papers we have studied the proton-transfer equilibria and kinetics of the title system and its dependence on the nature of an added supporting electrolyte.[1,2] The study of salt effects on proton-transfer reactions is of interest not only because proton-transfer reactions appear ubiquitously enough in nature[3] but also because they take place in ionic environments.[3] It has been shown that salt bridges may accelerate or slow charge-transfer processes by 2 orders of magnitude.[4]

They are usually very fast processes, controlled by diffusion; thus, their rates can be estimated with Smoluchowski equations, but sometimes they are even faster.[5] The proton mobility in water and in ice is several orders of magnitude faster than expected based on the Smoluchowski equations for diffusion, due to the special mechanism of proton mobility.[6] According to this mechanism, the enlarged conductivity of the proton in solution is due to the concerted vibration of adjacent water molecules, which allows an extremely fast proton transfer from one place to another in the solution.

Consequently, proton-transfer reactions are usually investigated with the help of ultrafast techniques. However, due to different factors, proton-transfer rate constants may be lowered by several orders of magnitude, such as when the transferred proton is embedded in an intramolecular cavity as in proton criptates[7] or when the proton is involved in an intramolecular hydrogen bond. Here, first the hydrogen bond must be broken, and in a second step, the proton transfer may take place or a concerted mechanism could be favored due to a smaller activation energy through this way. As a result, the process is slower than when no intramolecular hydrogen bond is involved and can be studied by conventional relaxation techniques. Since in these techniques an equilibrium situation is perturbed and the relaxation to the new equilibria is observed, the system must be reversible. This also means that the experiment can be repeated, resulting in the same relaxation curve, thus meeting the requirements of reproducibility and repeatability needed for a possible application in molecular protonic devices.[8,9]

In this paper we report a T-jump study of the title system and analyze the concerted or stepwise character of the mechanism, as well as the salt effects on this system. The control of the proton-transfer reactions is of interest for its hypothetical use in a molecular protonic device.[9] Even if electromagnetic radiation is used as a wire to connect the different components of a molecular computer,[10] these are located on a supporting material, providing an environment, which should be considered in the design of such devices.

Experimental Section

Reactants. 3,5-Dinitro-2-hydroxybenzoic acid (3,5-dinitrosalicylic acid, DNSA) was purchased from Fluka and used as received.

Sodium perchlorate was from Merck, quality P.A., and used as received. Lithium perchlorate was purchased from Aldrich, quality P.A., and used also without further purification.

Deionized water was employed throughout the study. NH_4^+/NH_3 was used as a buffer to stabilize the pH and to act as a donor/acceptor in the proton-transfer equilibria. The desired concentration was prepared with a diluted ammonium hydroxide standarized solution. The pH of the solutions were always in the range 7.8−8.2. These pH values were obtained by neutralizing the ammonium hydroxide solution with perchloric acid.

According to the conditions employed by other authors,[11] the concentrations of DNSA and ammonia were varied in the ranges $(1-5) \times 10^{-4}$ and $(2.5-30) \times 10^{-3}$ mol dm^{-3}, respectively.

pH Measurements and Determination of the Proton Concentrations. To obtain proton concentrations in the different electrolyte solutions, the following procedure was used, since the solutions had rather large salt concentrations. Thus, the pH reading does not correspond to the pH in the solution, due to the liquid junction potential. Besides, the pH cannot

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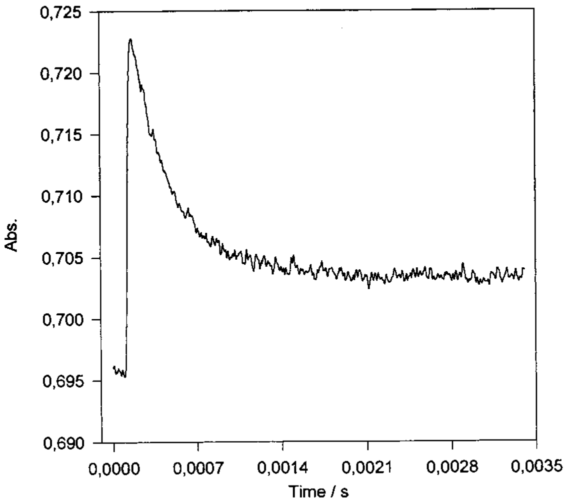


Figure 1. Experimental relaxation curve with $LiClO_4$ as supporting electrolyte: $[LiClO_4] = 0.3$ mol dm^{-3}, $[NH_3] = 7.5 \times 10^{-3}$ mol dm^{-3}, [DNSA] $= 5 \times 10^{-4}$ mol dm^{-3}, pH = 8.0.

easily be converted into H^+ concentrations, because the activity coefficients are not unity under these conditions. Therefore, a correction is needed to convert the pH-meter readings into proton concentrations.

This was done by measuring the pH of solutions containing a known concentration of a strong acid (perchloric acid was used). For each salt concentration a linear correlation was found between the log of the concentration of acid and the pH reading of the pH meter. The slope was always close to unity, while the ordinate was not zero, due to the liquid junction potential. These correlations were then used to interpolate the H^+ concentration. The pH was measured with a Crison 2000 pH meter previously calibrated with Merck buffer solutions in the range 4−10.

T-Jump Experiments. For the T-jump experiments a Hi-Tech TJ-64 apparatus was employed. The cell was thermostated at 20 °C with a Techne C-400 thermostat and a TECAM 1000 heat exchanger. The T-jump unit achieved, according to the technical specification, a 5 °C temperature jump with a heating time constant smaller than 5 μs by discharging two 0.02 μF capacitors loaded with 11 kV. Thus, relaxation times of about 30 μs are the shortest one that can be measured with our equipment. The heating time is directly related to the resistance of the solution and capacitance through

$$\tau_h = RC/2 \tag{1}$$

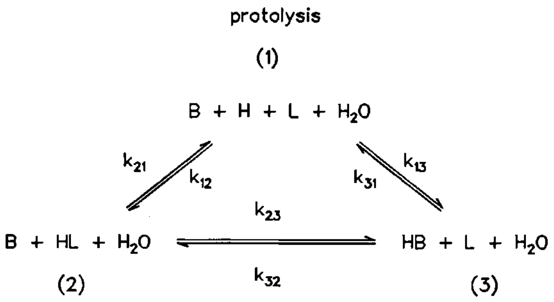
Thus, a supporting electrolyte is required to lower the resistance of the solution. To achieve the heating time mentioned above, an ionic strength of about 0.3 mol dm^{-3} is always needed. Measurements with a lower ionic strength were not intended because of this limitation. The result of a T-jump experiment is a relaxation curve, where the absorbance changes are recorded versus time, as shown in Figure 1.

Since the absorbance changes in relaxation experiments are not large, the measurements for a given concentration were repeated and averaged over 20 repetitions to improve the signal-to-noise ratio. This way the uncertainty in the determined relaxation times is lower than 5%.

Results

T-jump experiments provide experimental relaxation curves. From these curves, through a mathematical analysis involving irreversible thermodynamics considerations, rate constants and enthalpy for the different equilibria involved can be obtained. The present system has been investigated by several authors. From the general scheme for proton-transfer reactions between a donor and an acceptor in water, which includes direct proton transfer between donor and acceptor and hydrolytic and protolytic pathways,[5] the direct proton transfer and the protolytic pathways explain the experimental findings, as summarized in Scheme 1.[1,11,15]

SCHEME 1



In this scheme L stands for the completely unprotonated DNSA molecule, a species with two negative charges; B represents ammonia, and H represents the proton. The charges have been omitted throughout, for simplicity.

This scheme produces the following expression for the experimentally determined relaxation time, τ:

$$1/\tau = k_f F \tag{2}$$

$$k_f = \left[k_{23} + \frac{k_{21}k_{13}}{k_{12}[L] + k_{13}[B]}\right] \tag{3}$$

$$F = [B] + [HL] + (K_{HB}/K_{HL})([HB] + [L])$$

where B stands for ammonia and L represents unprotonated DNSA; the k_{ij} are the rate constants for the corresponding proton-transfer reactions shown in Scheme 1. K_{HB} and K_{HL} are the acid dissociation constants of ammonia and DNSA in the different electrolyte solutions. The acid dissociation constants of ammonia were found in the literature,[12] and those for DNSA were measured in a previous work.[2]

The rate constants for the different reactions have been calculated by fitting the experimentally determined relaxation times with several ammonia and DNSA concentrations to eqs 2 and 3. The rate constants obtained this way are given in Table 1 for the two salts employed. Notice that similar salt effects are observed with both electrolytes, although as the salt concentration increases some specific effects were found. So k_{21} shows a decrease in both cases, but in $LiClO_4$ solutions this decrease is more marked than with $NaClO_4$. Also, k_{32} shows different trends, with a larger decrease in $NaClO_4$ solutions than in $LiClO_4$. Curiously enough, the salt effects on k_{21} and k_{23} show opposite trends, although both processes imply breaking of an intramolecular hydrogen bond and transfer to water or ammonia, respectively. We will deal with this in the discussion.

Much care must be taken in a study of salt effects on the DNSA/ammonia system, because of the possible complexation of DNSA with cations. This is, in fact, the situation found with different transition-metal ions such as Ni(II), Fe(III), Mn(II), Cu(II), and Zn(II).[13] So the UV−vis spectra of DNSA in the different salt solutions were recorded. Remarkable changes were not observed, suggesting that with the salts used in this study no such complexation occurred. Perchlorates of bivalent

TABLE 1: Rate Constants with Different Ionic Strengths at 298.15 K

I	$k_{12} \times 10^{-10\,a}$	$k_{21} \times 10^{-3\,b}$	$k_{13} \times 10^{-10\,a}$	$k_{31}{}^{b}$	$k_{23} \times 10^{-6\,a}$	$k_{32} \times 10^{-3\,b}$
			$LiClO_4$			
0.3	4.9	5.9	3.3	19.1	3.1	12.9
1.0	3.3	7.0	2.6	9.2	4.3	7.0
1.5	2.3	4.7	2.2	6.2	5.1	7.1
2.0	1.2	2.1	1.7	3.6	6.1	7.2
2.5	1.0	1.4	1.2	1.9	6.7	7.5
3.0	0.7	0.7	0.9	1.0	7.1	8.1
			$NaClO_4$			
0.3	5.6	5.4	3.8	19.0	3.3	17.1
1.0	5.3	5.1	3.6	11.9	3.1	10.7
1.5	2.7	3.2	2.2	5.7	4.4	9.4
2.0	2.6	3.5	1.8	3.6	5.2	7.5
2.5	1.3	3.0	1.2	1.9	7.3	4.9
3.0	0.6	2.1	0.4	0.5	8.1	2.5

[a] Rate constant in units of $mol^{-1}\ dm^3\ s^{-1}$. [b] Rate constants in units of s^{-1}.

cations (Ca^{2+} and Ba^{2+}) were also tried, but precipitation of salicylates prevented further investigations.[14]

Discussion

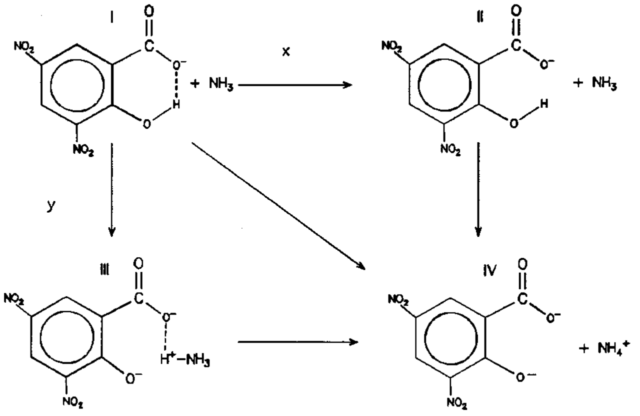
Mechanism. According to Scheme 1, processes 2−1 and 2−3 are very similar in the sense that, in both equilibria, the intramolecular hydrogen bond present in the protonated DNSA molecule is broken in the proton-transfer process. To analyze the salt effects on the proton-transfer reactions involved in the present system, a mechanistic analysis is needed to identify the elementary steps, since the question of whether the proton-transfer reactions involving DNSA occur in a stepwise or concerted fashion “is not clear, so far”.[15] Attempts to analyze the mechanism based on Eigen’s plots,[5] where logarithms of the rate constants are plotted versus ΔpK_a ($\Delta pK_a = pK_a^{Acceptor} - pK_a^{Donor}$),[15] need experimental data in the region of the crossing point of the two expected lines (see ref 5 for full details), as the deviation of this crossing point from the position where $\Delta pK_a = 0$ is the basis of the mechanistic analysis.[16] This in turn is a difficult experimental task.[17] Besides, all the reactions considered in the analysis of the mechanism must be between reactants of the same charge, since otherwise the experimental results are not expected to lie on the same lines. Thus, an analysis not relying on these plots could be very helpful.

The mechanistic analysis developed by Guthrie[18] can be useful in assessing the stepwise or concerted character of the processes involving DNSA. This analysis assumes Marcus parabolas for reactants and products in each possible step. However, these parabolas for reactants and products can be substituted by one parabola where the reactants and the products are points in this parabola and the transition state corresponds to the maxima.[19] It can be shown that this simplified picture is equivalent to the traditional Marcus model, since the energies of reactants and transition states are correctly given within this model. The proton-transfer dynamics in the wells is, however, not considered. Thus, possible dynamic solvent effects are not taken into account.[20] Equations 4 and 5 represent these parabolas for a proton-transfer reaction occurring in two steps:

$$G = \alpha x + \beta x^2 \tag{4}$$

$$G = \gamma y + \delta y^2 \tag{5}$$

SCHEME 2



The concerted reaction is represented by eq 6,

$$G = \alpha x + \beta x^2 + \gamma y + \delta y^2 + \epsilon xy \tag{6}$$

where an additional parameter ϵ represents the coupling between the two coordinates. Thus, as in Marcus theory, two magnitudes are needed for each coordinate, namely, α and β (for the x coordinate) and γ and δ (for the y coordinate). These magnitudes are related to the free energy change for each independent step, $\Delta G°$, and the intrinsic barrier to the proton transfer if $\Delta G°$ values were zero. This intrinsic barrier is the well-known reorganization energy in the Marcus model.

The following relations can be derived to calculate the different parameters:

$$\Delta G°_x = \alpha + \beta$$

$$\Delta G^{\neq}_x = -\alpha^2/4\beta \tag{7}$$

$$\Delta G°_y = \gamma + \delta$$

$$\Delta G^{\neq}_y = -\gamma^2/4\delta \tag{8}$$

The two possible steps are shown in Scheme 2, where x and y are two unitless variables that define the reaction coordinate for each step of the reaction. This scheme shows the initial (**I**) and final situations (**IV**), which are equivalent to states 2 and 3 in Scheme 1, when ammonia is the species involved, or states 2 and 1, if the proton transfer occurs to a water molecule. When ammonia is the acceptor, the two possible intermediates are states **II**, where the intramolecular hydrogen bond is broken, and **III,** where the proton is first transferred, and in a second step (going from **III** to **IV**), the hydrogen bond is broken. So the relation from Scheme 2 to Scheme 1 is clear: as the proton transfer is not a simple direct process, the rate constants k_{21} and k_{23} are not elementary rates, and Scheme 2 provides the detailed mechanism for these two reactions.

Finally, ϵ can be obtained from the total free energy change. This change is just

$$\Delta G° = \alpha + \beta + \gamma + \delta + \epsilon \tag{9}$$

For the present system, the proton-transfer step, once the intramolecular hydrogen bond has been broken, is diffusion controlled when ammonia acts as acceptor, since ΔpK_a, as defined above, is positive. With water this second step is slower than diffusion controlled as shown below. In both cases, this hydrogen bond introduces an important stabilization of the protonated DNSA.[21] This stabilization can be estimated from

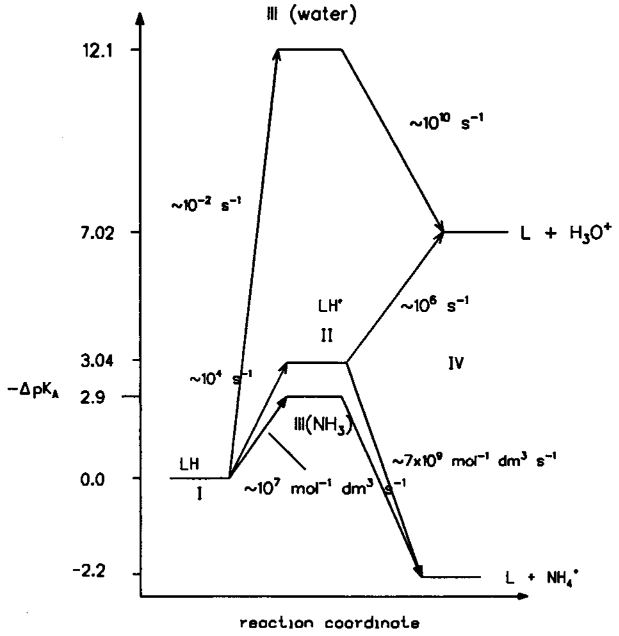


Figure 2. Free energy diagram showing, in pK_a units, the relative positions of the different intermediates and final products in the proton-transfer reactions 2−1 and 2−3.

the difference between the large second pK_a value of DNSA (7.02) and the pK_a of a similar phenol without intramolecular hydrogen bond stabilization,[22] as for example the 2,4-dinitrophenol (pK_a = 3.96[23]).

Thus, we have estimates based on experimental data for three of the possible structures proposed in Scheme 2. A sensible estimate of the free energy of the intermediate structure **III** is needed, to solve eqs 4−6. This is certainly a high-energy intermediate, since the less acidic group (the phenol group) is deprotonated and the proton interacts with the carboxylate group. To find experimental data in order to estimate the free energy of such a structure seems to be a difficult task; therefore, we have done a theoretical calculation of structure **III** with the program SPARTAN as follows: First, the original DNSA monoprotonated molecule, structure **I**, is calculated in water and the geometry fully optimized. This calculation has been done with the AM1 semiempirical Hamiltonian and SM2 model for the solvent (water). Then structure **III** is also optimized at the same level of calculation. This way the total energies of structures **I** and **III** in water have been obtained, and assuming that the free energies are not very different from the total energies, a value of +69 kJ mol^{-1} can be obtained as a rough estimate of this intermediate. Catalán et al.[24] have very recently done several theoretical calculations at the ab initio level, including electronic correlation corrections in their calculations on the keto−enol equilibria in 2-hydroxybenzoyl compounds. Their estimates for this process yield results with a mean value of ~60 kJ mol^{-1}, in good agreement with our calculations. (A rough experimental estimate could be made from the difference between the first and second pK_a values of DNSA and the addition of the energy of the intramolecular hydrogen bond, since this is broken in intermediate **III**. The resulting $\Delta G°$ is 55 kJ mol^{-1}.) These results are shown in Figure 2 in pK_a units ($\Delta pK_a = \Delta G°/2.3RT$). When the acceptor is ammonia, the stabilization due to the proton transfer to ammonia should be considered. Thus, in this case the free energy of intermediate **III** is $\Delta G = +69 - 2.3RT \times 9.2 = +16.5$, since the proton has been transferred to ammonia (pK_a = 9.2 for ammonia). Notice that, in contrast to the intermediate structure **II**, structure **III** is acceptor dependent. It is more stable when ammonia acts as the proton acceptor than when water is involved. This is due to the different sign of $\Delta G°$ for both processes.

TABLE 2: Estimation of Free Energies and Free Energies of Activation Used in Guthrie's Model[a]

acceptor	$\Delta G°_x$	$\Delta G^‡_x$	$\Delta G°_y$	$\Delta G^‡_y$	$\Delta G°_{total}$
H_2O	+17.5	+50.2	+69	+85	+40.1
NH_3	+17.5	+50.2	+16.5	+33	−13.0

[a] All data in kJ mol^{-1}. See text for details.

At this stage, kinetic data are needed to apply eqs 4−6 to our results.[25] For the process **I** → **II** the kinetic data were taken from the literature for a similar system involving salicylaldehyde, where only breaking and formation of the hydrogen bond can occur.[26] Accordingly, the rate constant for breaking the hydrogen bond is $k_1 \sim 10^4$ s^{-1}, as shown in Scheme 2. The rate constant for the step III → I is diffusion-controlled, as $\Delta pK_a \gg 0$.[5] Thus, using the Smoluchowski equation, this rate constant is estimated to be $k_{-2} \sim 10^{10}$ s^{-1}, and since $K_A = k_2/k_{-2}$, the value of k_2 is approximately 10^{-2} and ~10^6 s^{-1} when water and ammonia act as final acceptors, respectively. These results and estimates for the elementary rate constants of the second step with the two acceptors are summarized in Figure 2. The back rate constants can be easily obtained through the pK_a values of the different species. Assuming that the elementary rate constants have a preexponential factor given by conventional transition-state theory ($\upsilon = k_BT/h$), the activation free energies can be calculated and eqs 4−6 solved to obtain α, β, γ, δ, and ϵ values. The free energy results have been summarized in Table 2, and Figure 3a,b shows the free energy surfaces. $\Delta G^‡_x$ = 50.2 kJ mol^{-1} is a typical barrier for breaking an intramolecular hydrogen bond.[22] In both cases no concerted reactions are expected for the system studied in this work, as, in the framework of Guthrie's model, concerted pathways would require higher activation energies. The proton transfers to water and to ammonia show quite distinct features, despite the large uncertainty in the free energy of the intermediate structure **III**. The proton-transfer reaction to water occurs through intermediate **II**, where the intramolecular hydrogen bond is first broken, and then the proton is transferred to water. With ammonia intermediate **III** seems more likely, since the activation energy barrier to achieve this structure is smaller than through the other possible intermediate. However, the other possible pathway cannot be completely discarded, because of the rough estimate of this structure.

So, concluding the discussion in previous paragraphs, we expect the proton-transfer reaction to proceed through a two-step mechanism with both acceptors. With water, the first step is breaking the intramolecular hydrogen bond (which is the rate-determining one), and in the second step the proton is transferred to water. With ammonia, the mechanism may proceed through both possible intermediates. However, according to our calculations, the reaction pathway going through the intermediate **III** seems more likely, since the activation barrier is lower than for the other one. The second step is diffusion-controlled, if ammonia is the proton acceptor, when the reaction goes either through intermediate **II** or through intermediate **III**.

It is worth pointing out the main advantage of the present mechanism analysis, as compared to the classical one based on log(k) versus ΔpK_a.[5] In the classical analysis, all possible deviations from the simple direct proton transfer, despite its origin, cause the loss of the symmetry in these plots (see ref 5 for details). In the present analysis, as the different possible routes are explicitly analyzed, a detail picture can be achieved.

TABLE 3: pK_a at 298.15 K[a]

	NH_3[b]		DNSA[c]	
[salt]/mol dm^{-3}	$LiClO_4$	$NaClO_4$	$LiClO_4$	$NaClO_4$
0.3	9.30	9.30	6.92	7.02
1.0	9.46	9.48	6.67	7.01
1.5	9.55	9.59	6.69	6.92
2.0	9.67	9.71	6.74	6.87
2.5	9.80	9.83	6.85	6.66
3.0	9.94	9.96	7.00	6.45

[a] The error was estimated to be ±0.02 pK_a units. [b] Taken from ref 11. [c] Measured spectrophotometrically in a previous work, ref 2.

However, additional information is required to solve eqs 4−6. In our experience, it is not always possible to gather these data from experimental results.

Salt Effects Analysis

Proton-Transfer Reaction between DNSA and H_2O. Since this reaction goes through intermediate **II**, we can apply the steady-state hypothesis to the concentration of the DNSA species where the intramolecular hydrogen bond is broken (LH′). The following expression can be derived:[10]

$$k_{21} = \frac{k_1 k_2}{k_{-1} + k_2} \tag{10}$$

where k_1 and k_{-1} are the rate constants for breaking and forming the intramolecular hydrogen bond, respectively, and k_2 the rate constant for tansferring the proton to water. As pK_a < 0, k_2 should be proportional to ΔpK_a. In Table 3 the pK_a values of DNSA and NH_3 are given. For DNSA there is a minimum when $LiClO_4$ is used as supporting electrolyte, and a clear decrease is found for $NaClO_4$. Accordingly, the clear decrease observed with $LiClO_4$ and the decrease with $NaClO_4$ cannot be related to ΔpK_a. Thus, we conclude that the salt effects observed on k_{21} should be associated with the salt effects on the first step in the mechanism and thus the salt effects on k_1 and k_{-1}. For both salts a decrease in k_1 and/or an increase in k_{-1} explains the negative salt effects observed. Therefore, on increasing the amount of added salt, the DNSA monoprotonated species is stabilized with respect to the species without an intramolecular bond. This can be understood on the basis of the structure-making effect of both cations on the water structure that would slow the formation of intermediate **II**, in favor of the original DNSA species, LH.

Proton Transfer between DNSA and Ammonia. The mechanistic analysis has shown that this proton-transfer reaction may occur through intermediate **II** or **III**, but not through a concerted reaction path. If intermediate **III** is realized in solution and applying the steady-state hypothesis to the intermediate, the following expression is obtained for the rate:

$$k_{23} = \frac{k_1 k_3}{k_{-1} + k_3} \tag{11}$$

where k_1 and k_{-1} represent the forward and back rate constants from **I** to intermediate **III**. If **II** were the intermediate realized in solution, then the expected expression for the rate would be

$$k_{23} = \frac{k_1 k_3}{k_{-1} + k_3[NH_3]} \tag{12}$$

k_1 and k_{-1} would certainly have here the same meaning as in eq 10, and k_3 would be the diffusion-controlled rate constant between LH′ and NH_3. Notice that if **II** were the intermediate, a dependence of k_{23} on [NH_3] should be observed. However, although this ammonia concentration has been varied in the range from (2.5−30) × 10^{-3} mol dm^{-3}, that is, 1 order of magnitude, no deviation from eqs 2 and 3 has been observed, and as far as we know, no such deviation has been observed in previous studies.[11,13a,15] This would be consistent with the proposed intermediate **III**.

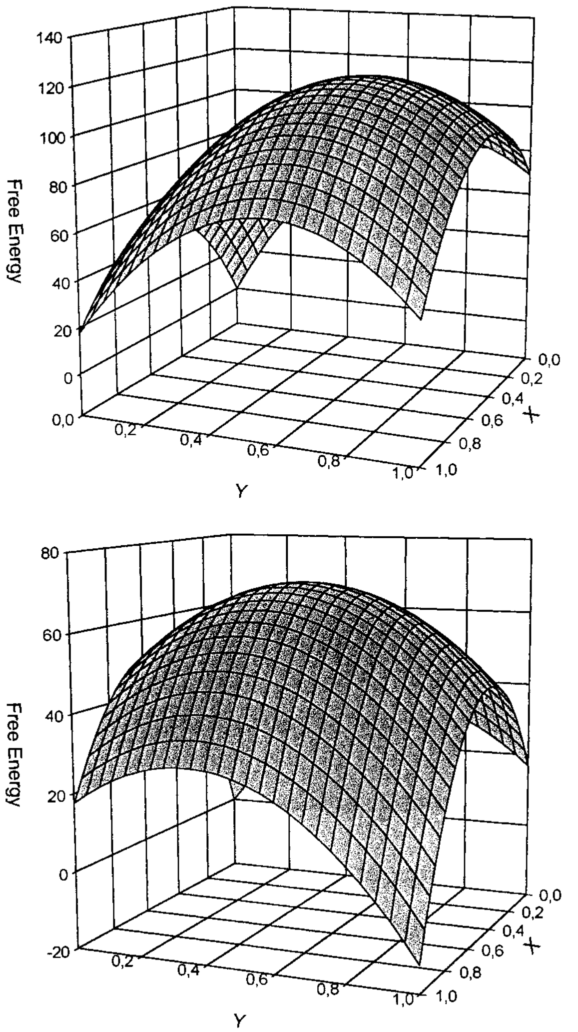


Figure 3. Free energy surfaces in Guthrie's model for the proton-transfer reactions 2−1 and 2−3: (a, top) reaction between DNSA and water; (b, bottom) reaction between DNSA and ammonia.

Note in Figure 2 that k_3 is expected to be diffusion controlled, and as one reactant is uncharged (NH_3), the salt effects on this elementary rate constant should be dominated by the viscosity dependence on the salt:

$$k_{\text{dif}} \propto 1/\eta \tag{13}$$

Since η increases on increasing the concentration of $LiClO_4$ or $NaClO_4$, if this were the only salt-dependent rate constant in (11) and (12), a decrease would be expected. In eq 12 as stated above k_1 and k_{-1} are the same elementary rate constants as in (10), and we have assumed that they are responsible for the negative salt effect observed on k_{21}. Thus, a consistent picture for the whole experimental data cannot be achieved this way.

This again suggests that this proton-transfer reaction occurs through intermediate **III**. From the pK_a values for ammonia in Table 3, it can be seen that, on increasing the salt concentration and according to the previous estimate of ΔG for species **III**, a

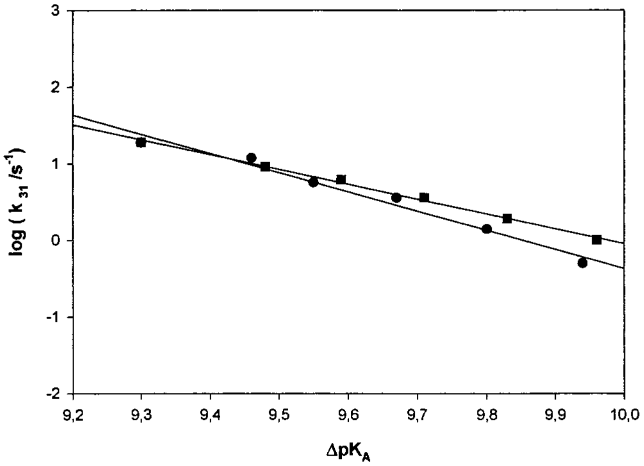


Figure 4. Plot of $\log(k_{31}/s^{-1})$ versus ΔpK_a: ●, $LiClO_4$; ■, $NaClO_4$.

stabilization of this intermediate is expected with both salts. As the forward process is not diffusion controlled, this stabilization of the intermediate would cause an increase in the rate constant k_1 in eq 11, while k_{-1}, for the same reason as k_3, should also decrease. Thus, the observed increment of k_{23} would be justified.

Proton Transfer between Ammonia and Water. Finally, the salt effects on k_{13} and k_{31} will be discussed. These rate constants are the direct proton transfer from water to ammonia and the backward reaction. (It corresponds to a one-step process, in Guthrie's model.) The first one is diffusion-controlled, as $\Delta pK_a \approx 9.2$ is larger than zero,[5] and no intramolecular hydrogen bond impedes the proton-transfer reaction. As expected for a diffusion-controlled reaction, there is a decrease of the rate constant on increasing the salt concentration. This decrease is larger for $LiClO_4$ than for $NaClO_4$, in good agreement with the larger viscosity decrement observed for the former salt.[27]

$\log(k_{31})$ should be dependent on the pK_a of ammonia with a negative slope.[5] This plot is shown in Figure 4, where the results for both salts are shown. Note that the slopes are rather different from unity. The reason for this is the salt effect on k_{13}, as discussed above, since in the correlation proposed by Eigen[5] the diffusion-controlled process should not vary on changing ΔpK_a. This is certainly also the case here, but the viscosity dependence of k_{13} introduces an apparent dependence on ΔpK_a and a deviation of the theoretical slope from unity. This suggests the possible use of the slope as a parameter to characterize salt effects on proton-transfer reactions proceeding in one step. A negative deviation, slopes less than -1, suggests a negative salt effect on the diffusion-controlled process, while positive deviations would be characteristic of a positive one. Notice that the use of these plots for analyzing salt effects is based on the slope in the region of $\Delta pK_a > 0$. No deviation in the typical appearance is expected, however.

Concluding Remarks

In this work the mechanism and salt effects on the title system have been analyzed. Three possible mechanisms ought to be considered in the reaction involving the monoprotonated DNSA with water and ammonia as proton acceptors: (a) a two-step mechanism where the intramolecular hydrogen bond is first broken, to achieve a more acidic species, which then transfers the proton to the final acceptor; (b) a two-step mechanism where the proton is first transferred and then the intramolecular hydrogen bond (no longer intramolecular hydrogen bond, in fact) is broken, or (c) a concerted pathway as a combination of both extreme situations.

With the aid of a theoretical model based on idealized free energy surfaces, it is possible to distinguish between these possibilities and to determine the most plausible one. We find for the present system that the basic character of the final proton acceptor may change the mechanism from a two-step mechanism where the intramolecular hydrogen bond is first broken and then the proton is transferred (the case with water) to a mechanism where the proton is first transferred and in a second very fast step the intermolecular hydrogen bond is broken. For this mechanism to be preferred, a strong base is required as proton acceptor to lower the free energy of intermediate **III**. According to our calculations, ammonia has enough basic character to favor this pathway. According to the present results, no concerted pathways are expected, and this should be ascribed to large reorganization energies for the steps along the dimensionless coordinates x and y.[24] It is also well-known that, when water is the solvent, charge-localized species are stabilized compared to charge-delocalized ones, as would be the intermediate in a concerted mechanism.[28]

The salt effects further support our conclusions concerning the reaction mechanism, since the opposite salt effects on k_{21} and k_{23} can be easily understood based on this change in the mechanism.

Finally, the salt effects on the proton-transfer reactions between water and ammonium ions have been studied. The deviations in the slopes of the plot of $\log(k)$ versus ΔpK_a have been employed as a useful criterion to assess the salt effects observed.

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