One-Step Preparation and NMR Properties of 5-Amino-2-formylbenzenesulfonic Acid

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5-Amino-2-formylbenzenesulfonic acid has been prepared in one-step reaction by oxidation of 4,4′-diaminostilbene-2,2′-disulfonic acid using ferric salts. Large differences in ^{1}H spin-lattice NMR relaxation times are discussed and utilized for assessment of the ratio of the two possible conformers of the product.

4,4′-Diaminostilbene-2,2′-disulfonic acid (I) is a major intermediate used in the synthesis of fluorescent whitening agents (FWA's). The FWA's are widely used in textile, paper, and plastic manufacturing and in household detergents. The contamination of aquatic bodies by potentially harmful organic chemicals such as I is one of the great environmental problems. The FWA's and I are not easily degradable by the waste water treatment. Poiger et al. [1] and Stoll and Giger [2] have identified in rivers and in bank filtrates some aromatic sulfonate derivatives coming from the degradation of such compounds after drinking water treatment.

Among the different abiotic degradation processes, solar irradiation is one of the main factors responsible for pollutant degradation in aquatic environment. When the pollutant does not absorb the solar light, its transformation can be photoinduced by different absorbing species, present or added in the contaminated medium. Among these species Fe(III) aqua complexes are able to play an efficient role. The degradation of various organic and organometallic pollutants photoinduced by Fe(III) has been studied [3—5]. The degradation of a pollutant may proceed either through the formation of a complex between the pollutant and Fe(III), if the pollutant can act as a complexing agent [6—9], or through the formation of hydroxyl radicals after excitation of Fe(III) aqua complexes [10, 11].

In this work we describe a simple one-step transformation of I into its aldehyde derivative in the presence of Fe(III) aqua complexes. The products were identified using NMR spectrometries. The aldehyde III (see Scheme 1) was just mentioned (without any analyt-

ical data) in an old patent [12]. Large differences in proton T_1, relaxation times, discussed in detail, were utilized for the determination of the equilibrium conformer composition.

EXPERIMENTAL

All chemicals were used without further purification. 4,4′-Diaminostilbene-2,2′-disulfonic acid (95 %) was purchased from Acros organics. Fe(III) perchlorate nonahydrate $(Fe(ClO_4)_3 \cdot 9H_2O)$ (97 %) and silica gel were Fluka products. Sodium salt of 4-ethylbenzenesulfonic acid was a Tokyo Chemical Industry product extra pure grade. Sodium hydroxide (99 %) was a Merck product and the cationic Amberlite resin IRN-77 was a Prolabo product. KBr (99.5 %) purchased from Merck was used to make pellets for IR analysis. Methanol was HPLC grade from Erba and ethyl acetate was a Sigma-Aldrich product (99.8 %). All the deuterated solvents for NMR analysis were purchased from SDS firm with grade higher than 99 %. All the solutions were prepared with deionized ultrapure water ($\rho = 18.2$ MΩ cm). pH Measurements were carried out with an Orion pH-meter to 0.01 unit. The ionic strength was not controlled.

All NMR experiments were performed on a Bruker Avance DSX spectrometer operating at 300.13 MHz for protons. T_1 measurements were performed using standard inversion-recovery pulse sequence [13]. The relaxation period was set to 20 s. The array of the eight variable relaxation intervals after initial 180° inversion pulse was adjusted according to actual relaxation times with the maximum of 60 s. The first scan was

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not accumulated allowing thus fast-inversion recovery data processing [14, 15]. The experimental intensities were fitted to the theoretical equation allowing an independent optimization of the three parameters: initial magnetization, equilibrium magnetization, and relaxation times. In all cases very good fit with correlation coefficient, better than 0.99, was obtained. The values of the determined relaxation times are shown in Table 1. For ^{13}C peaks assignment, Heteronuclear Single Quantum Coherence (HSQC) sequence was used to attribute the resonances.

5-Amino-2-formylbenzenesulfonic Acid (*III*)

A solution of *trans* form of *I* (25.2 mg; 40 μmol) in water (1700 cm^3) was mixed with a fresh aqueous solution (300 cm^3) of Fe(III) perchlorate nonahydrate (Fe(ClO$_4$)$_3 \cdot$ 9H$_2$O, 309.8 mg, 2 mmol dm^{-3}) and allowed to stand at room temperature in the dark. At the end of the redox reaction (few minutes), followed by HPLC analysis, an aqueous solution of NaOH (0.5 mol dm^{-3}) was added dropwise until the pH was around 9.5. The solution was filtered to eliminate the iron hydroxide precipitate and the solvent was evaporated under vacuum at 30 °C. The aldehyde product was separated from the crude mixture through a silica gel column (Silica gel 60), using AcOEt—EtOH—H$_2$O ($\varphi_r = 70:18:12$) as eluent. The purification of the product was achieved by passing through an Amberlite column (H$^+$/Na$^+$). The final product was dried by lyophilization giving a white powder (4.6 mg).

TLC: $R_f \approx 0.5$ (silica gel sheet, eluent AcOEt—EtOH—H$_2$O ($\varphi_r = 70:18:12$); IR spectrum (KBr): $\tilde{\nu}(\nu(C{=}O)) = 1700$ cm^{-1}; ^{1}H NMR spectrum (D$_2$O), δ: 7.35 (1H, dd ($J_{ba} = 8.5$ Hz, $J_{bc} = 2.3$ Hz), H$_b$), 7.65 (1 H, d ($J_{ab} = 2.3$ Hz, H$_a$), 8.25 (1H, d ($J_{cb} = 8.5$ Hz) H$_c$), 10.7 (1H, s, H$_d$); HSQC NMR spectrum (D$_2$O), δ: 116 (C$_a$), 120 (C$_b$), 131 (C$_c$), 176 (C$_d$); ES/MS spectrum (negative detection, m/z ($I_r/\%$): 124 (21), 200 (100), 329 (24), 546 (26), 427 (39).

RESULTS AND DISCUSSION

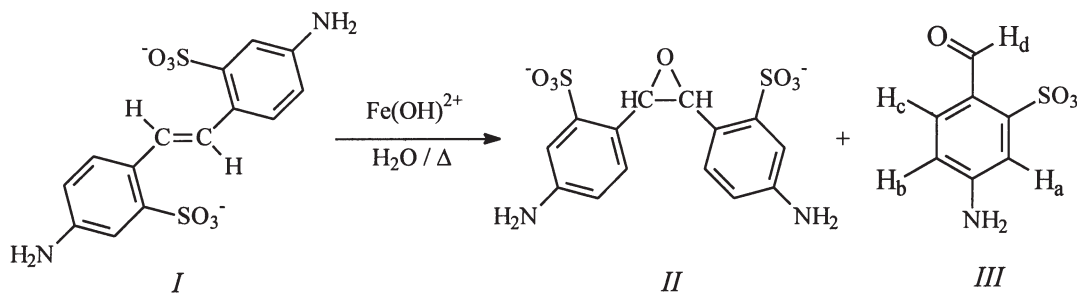The reaction between Fe(OH)$^{2+}$ and *I*, in the dark at room temperature, leads to the fast formation of two products: epoxide derivative *II* and 5-amino-2-formylbenzenesulfonic acid (*III*) (Scheme 1) [16]. Epoxidation and an oxidative cleavage of the double bond were established to be responsible for the formation of these products.

The ratio of these two products is correlated to the initial concentration of iron species, in particular to the concentration of [Fe(H$_2$O)$_5$(OH)]$^{2+}$ species, *e.g.* as Fe(OH)$^{2+}$. At low concentrations of Fe(OH)$^{2+}$ (*I* is in excess), a mixture of *II* and *III* is obtained in which the epoxide is the major component. The ratio aldehyde/epoxide increases with the concentration of Fe(OH)$^{2+}$ (at constant *I* concentration, 3.4×10^{-3} mol dm^{-3}). At a very large excess of Fe(OH)$^{2+}$ species (around 10^{-2} mol dm^{-3}), 5-amino-2-formylbenzenesulfonic acid *III* is the only observed reaction product. Although the oxidation of the double bond has been known for decades, the only reference related to oxidation of the *I* double bond in the literature [12] is a patent reporting on the reaction of *I* with KMnO$_4$, leading to the formation of aldehyde *III*. Despite the relatively low yield (≈ 20 %, without optimization of reaction conditions), the very easy one-step synthesis of 5-amino-2-formylbenzenesulfonic acid may make this reaction valuable for synthetic purposes.
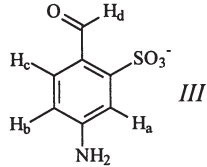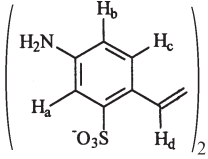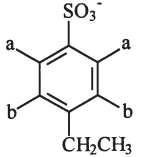
^{1}H NMR spectra of aldehyde *III* measured under standard setting of proton NMR acquisition parameters (relaxation delay 4 s, acquisition time 2 s) showed a substantial distortion of the integral intensities. The possible explanation was significant differences of the relaxation times T_1 of individual protons. To confirm this hypothesis, the relaxation measurements were performed at 25 °C and 60 °C in D$_2$O and DMSO solutions. To assess the role of SO$_3^-$ group in the observed effect, two other sulfonic acids were investigated: the starting molecule *I* and 4-ethylbenzenesulfonic acid *IV*.

For all compounds in both solvents an increase in temperature led to an increase in relaxation rates of all protons. This is a clear indication that all molecules are in the fast motion region of the T_1-NMR time scale. Relatively long relaxation times were observed for all protons of the two smaller molecules (*III* and *IV*) in aqueous solution. This points to their very

Scheme 1

Table 1. Proton Relaxation Times T_1/s

Compound	Proton	$T_1(\theta,\text{ water})$/s		$T_1(\theta,\text{ DMSO})$/s	
		25 °C	60 °C	25 °C	60 °C
III	a	11.4	31.5	1.6	2.2
	b	4.6	10.0	1.3	2.2
	c	4.2	10.0	1.8	2.7
	d	9.7	23.1	1.8	2.1
I	a	6.4	13.4	7.6	15.0
	b	1.6	3.1	1.7	2.2
	c	0.7	1.4	0.7	0.7
	d	0.9	2.0	0.9	1.1
IV	a	4.9	9.2	3.6	5.6
	b	3.7	7.6	2.7	4.2
	CH$_2$	2.3	5.0	1.6	2.8
	CH$_3$	3.5	6.8	2.7	4.1

fast tumbling rates in aqueous medium at 25 °C. The differences between relaxation rates of aromatic protons in *III* and *I* can account for the smaller tumbling rates and thus more efficient relaxation of the heavier *I* molecule.

In aqueous solution a significantly slower relaxation of proton "a" (Table 1) was observed for the three investigated compounds. This effect was relatively low for *IV* but very pronounced for compounds *I* and *III*. An extremely long relaxation time was observed in the aldehyde molecule at 60 °C. This observation indicates that there is no efficient intermolecular or intramolecular relaxation source for the "a" proton. Protons of the amino group are in a fast exchange and their dipolar interactions with the "a" proton are effectively decoupled. The sulfonic acid group effectively shields this proton from intermolecular interactions.
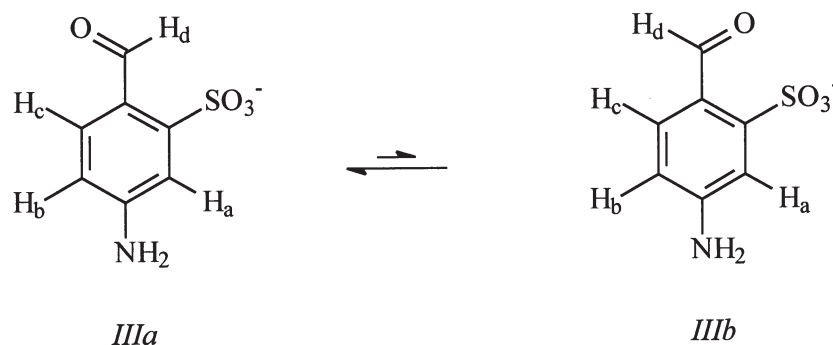
An interesting difference was observed between the relaxation behaviour of proton "d" in the aldehyde and *I*. While the aldehydic proton showed similar behaviour as the "a" proton, the olefinic proton in *I* was relaxing fast. The explanation is probably the different configuration of the carbons bearing proton "d". In *I* molecule, because of the steric hindrance, the aromatic rings are twisted with respect to the double bond. On the contrary, in *III*, the three atoms of the aldehyde group are in the plane of the aromatic ring with the aldehyde proton "d" probably pointing to the sulfonic acid group; in this configuration, aldehydic proton is effectively shielded from all dipolar interactions in a similar way as proton "a". The very long relaxation time of the aldehydic proton clearly indicates that there is no intermolecular relaxation with

proton "c", which would be observed if there were a significant contribution of the other planar conformer of the aldehyde group. On the other hand, relatively fast relaxation of the olefinic protons in *I* suggests that this proton is efficiently relaxed with "c" proton and that in this case the effect of sulfonic acid group is of minor importance.

The change of the solvent, from water to more viscous DMSO$_2$ brought a significant reduction of the relaxation times for both smaller molecules. This is obviously associated with the decrease in their tumbling rates. The relaxations of "a" and "d" protons in *III* became similar to the behaviour of other aromatic protons. This can be caused by the change of the molecule conformation (aldehydic proton being close to proton "c") and also by the presence of NH$_2$ protons (because of slower exchange), which might become the possible relaxation source for the "a" proton. Almost no effect was observed for the *I* molecule.

The ratio of the two possible planar conformers of *III*, represented below, can be estimated from the analysis of the relaxation rates ($R = 1/T_1$) of the aldehydic proton (Scheme 2).

The following assumptions were made: *i*) only planar configurations have significant population; *ii*) in the first conformation (*IIIa*), the relaxation rate of the aldehydic proton R_d is equal to the relaxation rate of proton "a", R_a; *iii*) in the *IIIb* conformation, R_d is equal to the relaxation rate of proton "c", R_c. Under these assumptions, the relaxation rate of the aldehydic proton is the weighted average of the two contributions, the weights being taken as the mole fractions of conformers *IIIa* and *IIIb*, x and $(1 - x)_2$, respectively

Scheme 2

$$R_d = xR_a + (1-x)R_c$$

from which the fraction of the first conformer can be expressed as

$$x = (R_c - R_{ald})/(R_c - R_a) =$$
$$= (1/T_{1c} - 1/T_{1ald})/(1/T_{1c} - 1/T_{1a})$$

Using the values given in Table 1, we obtained $x = 0.88$ at $25\,^\circ$C and $x = 0.83$ at $60\,^\circ$C.

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