The Dissociative Route in the Alkaline Hydrolysis of Aryl 4-Hydroxy-β-styrenesulfonates

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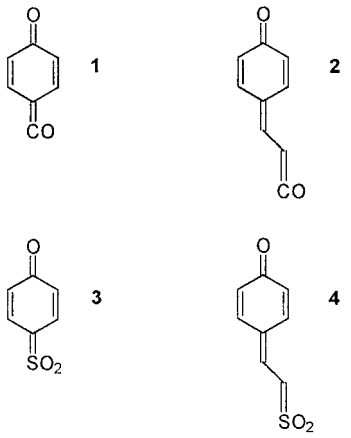
Reactivity comparisons, activation parameters, and the substituent effect in the leaving group indicate that the hydrolysis of title esters in moderately to strongly alkaline aqueous solution follows a dissociative pathway with the probable participation of an extended sulfoquinone (thioquinone dioxide) intermediate. The interposition of a vinylene group between the internal nucleophile and the reaction site favors the elimination−addition process. Present results further suggest the high tendency of suitably substituted sulfonyl derivatives to hydrolyze through dissociative mechanism.

Our continuing interest in the dissociative (E1cB) mechanism in acyl transfer reactions involving suitable carboxylate[1,2] and sulfonate[3] esters prompted us to extend our investigations aiming at enlarging the knowledge on this mechanism and defining more closely the circumstances under which it can be observed.

We have previously shown[1] that the alkaline hydrolysis of 4-hydroxybenzoate esters of acidic phenols does not occur through the usual $B_{Ac}2$ route but proceeds instead via a E1cB mechanism with the participation of the *p*-oxoketene intermediate **1**. More recently,[2] we have reported that also the alkaline hydrolysis of aryl 4-hydroxycinnamates having powerful leaving groups occurs through the E1cB mechanism via the "extended" *p*-oxoketene intermediate **2**. Our results indicated that the interposition of a vinylene group between the internal nucleophilic site (the 4-hydroxy group) and the carbonyl carbon atom is beneficial to the dissociative hydrolytic process. Thorough comparison between the reactions of 2′,4′-dinitrophenyl esters of 4-hydroxycinnamic and 4-hydroxybenzoic acid led to the suggestion that such rate enhancement could be due mostly to an increased stability of **2** with respect to **1** which, in turn, can be ascribed to a more extended delocalization of π electrons in the former.



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We have also found that, in alternative to the usual associative, intermolecular $S_N2(S)$ route of sulfonyl transfer reactions,[4] the E1cB mechanism carries the reaction flux in the alkaline hydrolysis of aryl *o*- and *p*-hydroxyarenesulfonates.[3] In particular, the hydrolysis of 2′,4′-dinitrophenyl 4-hydroxybenzenesulfonate follows a dissociative pathway involving the sulfoquinone intermediate **3**.

In this paper we report the results of a study on the alkaline hydrolysis of some aryl esters of 4-hydroxy-β-styrenesulfonic acid. This work was undertaken hoping to ascertain the participation of the "extended" sulfoquinone intermediate **4** in the reaction pathway: such a finding may provide valuable contribution to both a better understanding of acyl transfer reactions and a direct comparison of the relative tendencies of suitably substituted carbonyl and sulfonyl derivatives to hydrolyze through dissociative mechanisms.

Results and Discussion

The hydrolysis of 2,4-dinitrophenyl 4′-hydroxy-β-styrenesulfonate (**5**) and, for the sake of comparison, that of 2,4-dinitrophenyl β-styrenesulfonate were carried out under pseudo-first-order conditions in water at 60 °C and ionic strength held constant with added potassium chloride. The progress of the reaction was monitored by following the increase of the absorption at 400 nm due to liberation of 2,4-dinitrophenol. Since the ionization of the hydroxy group of **5** in alkaline solutions causes a large bathochromic shift in the UV−vis spectrum (the maximum absorbance region of the conjugate base of **5** extends well beyond 400 nm), the kinetic runs of this ester at pH's higher than 8.5 were followed monitoring the disappearance of the substrate at 315 nm. Control experiments (UV−vis spectra) at different pH values

(1) (a) Cevasco, G.; Guanti, G.; Hopkins A. R.; Thea, S.; Williams, A. *J. Org. Chem.* **1985**, *50*, 479. (b) Thea, S.; Cevasco, G.; Guanti, G.; Kashefi-Naini, N.; Williams, A. *ibid.* **1985**, *50*, 1867.
(2) Cevasco, G.; Thea, S. *J. Org. Chem.* **1994**, *59*, 6274.
(3) (a) Thea, S.; Guanti, G.; Hopkins, A. R.; Williams, A. *J. Am. Chem. Soc.* **1982**, *104*, 1128. (b) Thea, S.; Cevasco, G.; Guanti, G.; Hopkins, A. R.; Kashefi-Naini, N.; Williams, A. *J. Org. Chem.* **1985**, *50*, 2158. (c) Thea, S.; Cevasco, G.; Guanti, G. *Gazz. Chim. Ital.* **1987**, *117*, 705. (d) Cevasco, G.; Thea, S. *J. Org. Chem.* **1996**, *61*, 6814.
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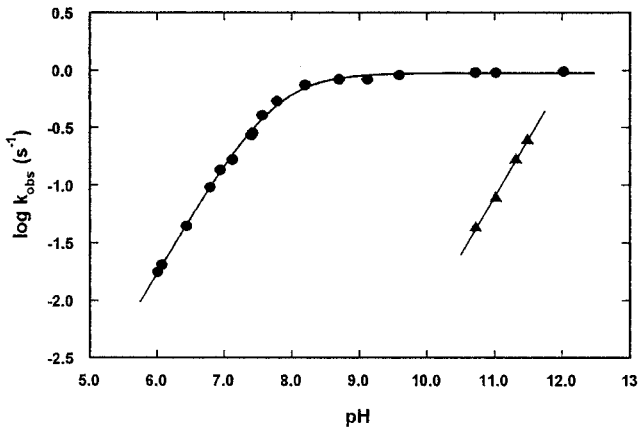

Figure 1. pH-rate profiles for the hydrolysis of 2,4-dinitrophenyl 4′-hydroxy-β-styrenesulfonate (●) and 2,4-dinitrophenyl β-styrenesulfonate (▲) in aqueous buffers at 60 °C and ionic strength 0.1 M (KCl). Lines are calculated from eqs 1 and 2 from parameters in the tables.

(readjusting the pH, if required, to reprotonate the hydroxy group of the liberated acid) indicated that 100% liberation of 2,4-dinitrophenol occurred.

The rates of hydrolysis of the esters were pH dependent and were found to obey eqs 1 and 2 for 4′-hydroxy-β-styrenesulfonate and β-styrenesulfonate, respectively.

$$k_{obs} = k_a/(1 + a_H/K_a) \quad (1)$$

$$k_{obs} = k_{OH}K_w/a_H \quad (2)$$

In eq 1 k_a is the pseudo-first-order rate constant in the plateau region of the pH−rate profile, depicted in Figure 1 (where circles and triangles represent experimental data for **5** and 2,4-dinitrophenyl β-styrenesulfonate, respectively), K_a is the ionization constant of the hydroxyl group of the ester, and a_H is the proton activity. The high reactivity of **5** did not allow the spectrophotometric determination of its pK_a. A reliable value, however, was obtained from primary kinetic data, together with the rate constant, by iterative nonlinear curve-fitting performed with the Fig.P program.[5] The values of k_a and K_a for **5** are reported in Table 1 and Table 2 respectively, together with parameters and conditions relevant to the hydrolyses of other aryl 4′-hydroxy-β-styrenesulfonates (see below). In eq 2 K_w is the ionic product of water (pK_w = 13.017 at 60 °C),[6] and k_{OH} is the second-order rate constant related to the $S_N2(S)$ attack of hydroxide ion on the aryl β-styrenesulfonates. The alkaline hydrolyses of the aryl β-styrenesulfonates investigated here obey eq 2, and the parameters are recorded in Table 3.

From the values of k_a and K_a for the ester **5** one can *calculate* the apparent second-order rate constant ($k_{app} = k_aK_a/K_w = 1.95 \times 10^5$ M^{-1} s^{-1}) related to the attack of hydroxide ion on neutral substrate, and it appears that this rate constant is more than 4 orders of magnitude *larger* than the second-order rate constant for the unambiguous $S_N2(S)$ hydrolysis of 2,4-dinitrophenyl β-styrenesulfonate (k_{OH} = 8.32 M^{-1} s^{-1}, Table 3). This very large difference cannot be accounted for by a simple substituent effect (OH vs H) thus pointing to the intervention of a different mechanism in the hydrolysis of the hydroxy ester i.e. the dissociative pathway depicted in Scheme 1 involving the participation of a putative "extended" sulfoquinone intermediate (**4**).

Other lines of evidence are also consistent with the E1cB route. In Table 4 are reported the activation parameters for the reactions of the two substrates: the $\Delta S^{\ddagger}$ values for the hydrolysis of **5** at various pH's are positive as expected for an unimolecular process, whereas the large, negative entropy of activation for the hydrolysis of 2,4-dinitrophenyl β-styrenesulfonate is consistent with an associative mechanism.[7]

Since leaving group sensitivities of linear free energy relationships are among the most dependable criteria of mechanism in this area, we have also studied the effect of leaving group variation on reactivity. We have therefore investigated the hydrolyses of other aryl 4′-hydroxy-β-styrenesulfonates, and the relevant kinetic data are reported in Table 1 together with those of the 2,4-dinitrophenyl ester. The pH−rate profiles (here not shown) for the hydrolysis of these other substrates were found to obey eq 3

$$k_{obs} = (k_a + k_b[OH^-])/(1 + a_H/K_a) \quad (3)$$

where k_b represents the second-order rate constant related to the bimolecular attack of hydroxide ion on the ionized ester and causes an upward curvature, at sufficiently high pH values, of the pH−rate profile. The k_b value for the 2,4-dinitrophenyl ester is experimentally inaccessible.

In Table 2 the pK_a values of the leaving substituted phenoxides (pK_{LG}) are reported. Because of the uncertainty about the pK_a value for pentachlorophenol, we are indeed aware of two different values reported in the literature i.e. 4.8[8] and 5.26,[9] we employ the value 4.79 ± 0.01 spectrophotometrically determined by us in water at 25 °C (this work).

Table 2 collects also the pK_a values of the substrates. These values were spectrophotometrically measured except those of 2,4-dinitrophenyl (which is a kinetic value, see above) and pentachlorophenyl esters. As for the latter, owing to its exceedingly low solubility particularly in the pH range where it is not fully ionized, we could obtain neither the spectrophotometric nor the kinetic pK_a. Nevertheless, we find that the following relationship holds between the pK_a and pK_{LG} values of the other substrates:

$$pK_a = (7.54 \pm 0.05) + (4.11 \pm 0.53) \times 10^{-2}pK_{LG} \quad (4)$$

Therefore, from a pK_{LG} of 4.79 a pK_a value of 7.74 can be estimated, with some confidence, for the pentachlorophenyl ester.

Now, from the k_a and K_a values it is possible to calculate the apparent second-order rate constants ($k_{app} = k_aK_a/K_w$) for aryl 4′-hydroxy-β-styrenesulfonates, and the logarithms of these rate constants (reported in Table 2) correlate very well with the corresponding pK_{LG} values,

(5) Program Fig.P from Biosoft, Cambridge, U.K., 1991.
(6) Albert, A.; Serjeant, E. P. *Ionization Constants of Acids and Bases*; Methuen & Co. Ltd.: London, 1962.
(7) Schaleger, L. L.; Long, F. A. *Adv. Phys. Org. Chem.* **1963**, *1*, 1. Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969. Douglas, K. T. *Prog. Bioorg. Chem.* **1976**, *4*, 194.
(8) Blackman, G. E.; Parke, M. H.; Garton, G. *Arch. Biochem. Biophys.* **1955**, *54*, 55.
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Table 1. Hydrolysis of Aryl 4-Hydroxy-β-styrenesulfonates in Water at 60 °C and μ = 0.1 (pK_w = 13.017)

leaving substituted phenoxide	λ, nm [a]	k_a, s^{-1}	k_b, M^{-1} s^{-1}	log k_{app}	N[b]	pH[c]
2,4-dinitro	400[d]	$(9.20 \pm 0.16) \times 10^{-1}$		5.286	17	6.01−12.02
pentachloro	370	$(1.05 \pm 0.02) \times 10^{-3}$	0.023 ± 0.001	3.706	7	8.95−12.02
2,5-dinitro	365	$(1.69 \pm 0.06) \times 10^{-4}$	0.233 ± 0.011	3.297	15	7.41−12.02
3,4-dinitro	360	$(1.44 \pm 0.08) \times 10^{-4}$	0.537 ± 0.038	2.567	10	7.41−12.02
2-chloro-4-nitro	400	$(4.03 \pm 0.13) \times 10^{-5}$	0.113 ± 0.004	2.269	16	7.22−12.02
4-nitro	400	$(1.38 \pm 0.08) \times 10^{-5}$	0.098 ± 0.004	−0.406	10	7.41−12.02

[a] Wavelength employed for the kinetics. [b] Number of data points, not including duplicates. [c] pH range employed. [d] For pH higher than 8.5, λ = 315 nm.

Table 2. Ionization Constants of Aryl 4-Hydroxy-β-styrenesulfonates (pK_a) in Water at 60 °C and μ = 0.1 and of Substituted Phenols (pK_{LG}) in Water at 25 °C

leaving substituted phenoxide	pK_a[a]	pK_{LG}[b]
2,4-dinitro	7.69 ± 0.02[c]	4.11
pentachloro	7.64[d]	4.79[e]
2,5-dinitro	7.76 ± 0.03	5.22
3,4-dinitro	7.78 ± 0.02	5.42
2-chloro-4-nitro	7.78 ± 0.03	5.45
4-nitro	7.82 ± 0.01	7.15

[a] Spectroscopically determined values (λ = 360 nm) unless otherwise stated. [b] Jencks, W. P.; Regestein, J. *Handbook of Biochemistry and Molecular Biology*, 3rd ed.; Fasman, G., Ed.; Chemical Rubber Co.: Cleveland, 1976. [c] Measured from the kinetics. [d] See text. [e] This work.

Table 3. Second-Order Rate Constants for the Hydrolysis of Aryl β-Styrenesulfonates in Water at 60 °C and μ = 0.1[a]

leaving substituted phenoxide	k_{OH}, M^{-1} s^{-1}	N[b]	pH[c]
2,4-dinitro	8.32 ± 0.19	5	10.72−11.49
3,4-dinitro	1.13 ± 0.01	4	10.72−11.72
3-nitro	0.12 ± 0.02	4	11.02−12.02

[a] Kinetic runs were followed at 400 nm. [b] Number of data points, not including duplicates. [c] pH range employed.

as shown in Figure 2, giving rise to the Brønsted-type correlation (eq 5).

$$\log k_{app} = (12.71 \pm 0.62) - (1.85 \pm 0.11)\, pK_{LG} \quad (5)$$

Also the values of k_b and k_{OH} (Tables 1 and 3, respectively) correlate with pK_{LG} according to eqs 6 and 7.

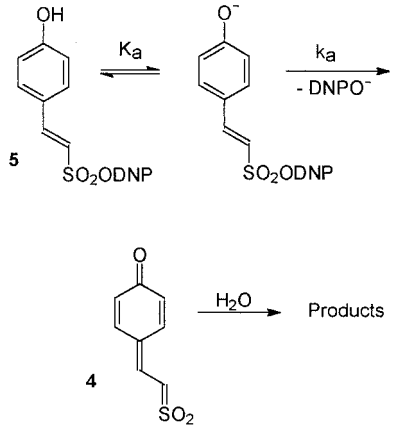
$$\log k_b = (2.20 \pm 0.70) - (0.61 \pm 0.13)\, pK_{LG} \quad (6)$$

$$\log k_{OH} = (3.30 \pm 0.18) - (0.59 \pm 0.03)\, pK_{LG} \quad (7)$$

The leaving group sensitivities of eqs 6 and 7 are almost identical, thus suggesting that the mechanisms which k_b and k_{OH} are related to are the same and, as above stated, k_{OH} is a $S_N2(S)$ process; furthermore, since these β_{LG} values are consistent with an associative pathway,[3c,10] the nature of k_b is unambiguously assessed.

On the contrary, a large negative value of β_{LG} (−1.85) in eq 5 is indicative of an advanced fission of the S−OAr bond in the transition state of the rate-determining step and is well within the range expected for a E1cB mechanism (−1.5 to −2.4).[3a−c,11] Moreover, the notable linearity of such Brønsted-type relationship suggests that within this range of substituents a single mechanism (i.e. the E1cB) holds.

Scheme 1



DNP = 2,4-dinitrophenyl

Table 4. Activation Parameters for the Hydrolysis of 2,4-Dinitrophenyl Esters in Water, μ = 0.1[a]

	pH	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$,[b] cal/mol K
4′-hydroxy-β-styrenesulfonate	10.72	21.5 ± 0.2	5.7 ± 0.8
4′-hydroxy-β-styrenesulfonate	9.59	21.1 ± 0.1	4.4 ± 0.5
4′-hydroxy-β-styrenesulfonate	6.79	25.9 ± 0.2	14.6 ± 0.7
β-styrenesulfonate	10.72	15.2 ± 0.3	−19.2 ± 0.9

[a] Temperature range: 18.5−60.0 °C. [b] Calculated at 25 °C.

In the hydrolyses of aryl 4-hydroxybenzoates,[1a] 2-[12] and 4-hydroxycinnamates[2] we have previously observed a break in the Brønsted-type plots occurring at about pK_{LG} 6.0−6.5 and for the less reactive esters the bimolecular associative mechanism was invoked to account for the markedly reduced β_{LG} values in this region. On the other hand, we have found that a similar change in mechanism could occur in the hydrolysis of aryl 3,5-dimethyl-4-hydroxybenzenesulfonates at pK_{LG} higher than ca. 10.6.[3c] Furthermore, in a very recent paper,[13] we have suggested that for the hydrolysis of aryl 4-hydroxybenzenesulfonates a changeover point could occur at pK_{LG} about 8.7.

Now, it is worthwhile estimating where the corresponding mechanistic break-point should occur for β-styrenesulfonates. The following equation

$$\rho^* = [\rho_0(X) - \rho_0]/\sigma(X)$$

(10) Maremae, V. M.; Palm, V. *Reakts. Sposobnost. Org. Soedin.* **1964**, *1*, 85. See also Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972; p 23.

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(13) Cevasco, G.; Thea, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2215.

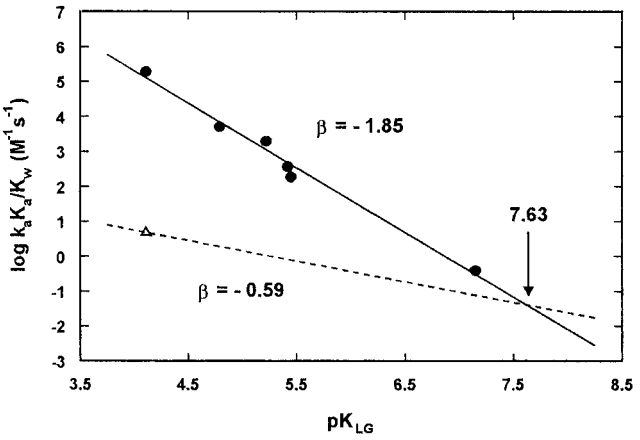

Figure 2. Brønsted plot for the hydrolysis of aryl 4′-hydroxy-β-styrenesulfonates. The solid line is calculated from eq 5. Identity, in increasing order of pK of the leaving substituted phenoxide is as in Table 1. The dashed line is calculated for the bimolecular attack of hydroxide ion on neutral aryl 4′-hydroxy-β-styrenesulfonates, and the arrow shows the calculated changeover point from E1cB to $S_N2(S)$ mechanism (see text).

had been previously proposed[4a] by other authors to relate the reaction constant $\rho_0(X)$ for the alkaline hydrolysis of X-substituted-phenyl esters of a series of substituted benzenesulfonic acids (with X, the substituent in the leaving phenoxide, invariable in the series) to ρ_0, the reaction constant for the alkaline hydrolysis of (unsubstituted) phenyl esters of substituted benzenesulfonic acids, and $\sigma(X)$, the Hammett constant of the X-substituent in the leaving phenoxide, through the constant ρ^*, which was calculated[4a] by cross-correlation from kinetic data relative to the alkaline hydrolysis of aryl esters of benzenesulfonic acids substituted in both rings. This way, employing the reported[4a] values $\rho_0 = 2.24$, $\rho^* = -0.61$ and $\sigma(X) = 0.91$ for the 2-nitro substituent (and the usual value of 0.78 for the 4-nitro one) we obtain, neglecting the temperature-dependence of ρ^*, the Hammett relationship $\log k/k_0 = 1.21\Sigma\sigma$ for the alkaline hydrolysis of 2,4-dinitrophenyl esters of benzenesulfonic acids. Taking into account the attenuation factor of 0.54 related to the vinylene group,[14] such Hammett correlation becomes $\log k/k_0 = 0.65\Sigma\sigma$, and it is now applicable to the $S_N2(S)$ hydrolysis of 2,4-dinitrophenyl esters of substituted β-styrenesulfonates. If we employ the rate constant k_{OH} of 2,4-dinitrophenyl β-styrenesulfonate (8.32 M^{-1} s^{-1}, Table 3) as k_0, using the σ_p substituent constant (-0.37) for the hydroxyl we finally obtain the *calculated* bimolecular rate constant for $S_N2(S)$ attack onto **5** (k_{calcd} = 4.8 M^{-1} s^{-1}). It is noteworthy to emphasize that the value of the measured, apparent second-order rate constant ($k_{app} = k_aK_a/K_w$) for this ester is about 40000-fold larger than the calculated value (k_{calcd}), and this is a further indication that the actual mechanism is different from the associative one. Now, if the dashed line with slope -0.59 (β_{LG} from eq 7) is drawn through the point indicated as Δ in Figure 2 ($\log k_{calcd}$), it will intersect the solid line at pK_{LG} 7.6, which therefore represents the break-point for mechanism.

It is interesting to note that this value is not so much different from that estimated for the alkaline hydrolysis of aryl 4-hydroxybenzenesulfonates (8.7) and that both are larger than those found for the carboxylate esters (6.0−6.5). These observations add further support to our previous indication[13] that aryl hydroxyarenesulfonates seem to be more prone to hydrolyze through dissociative pathways than the corresponding carboxylate esters.

Moreover, as far as 2,4-dinitrophenyl esters are involved, such indication is sustained by the values of the ratio (R, Table 5) between the apparent second-order rate constant (k_aK_a/K_w) for attack of hydroxide ion on neutral *p*-hydroxy esters, this term being related to the dissociative pathway, and the bimolecular rate constant for the attack of hydroxide ion onto the esters lacking the hydroxy group. As shown in Table 5, the kinetic advantage of the dissociative mechanism over the associative one for the hydrolysis of 2,4-dinitrophenyl sulfonates is indeed 10 to 20 times larger than that for the hydrolysis of the corresponding carboxylates.

We are now in a position to make a comparison between the dissociative hydrolysis of 2,4-dinitrophenyl 4′-hydroxybenzenesulfonate and 4′-hydroxy-β-styrenesulfonate and to evaluate the effect of the interposition of a vinylene group between the SO_2 and OH interacting groups. The k_a value for the hydrolysis of **5** (0.92 s^{-1}, Table 1) is ca. 150-fold larger than that of the corresponding 4′-hydroxybenzenesulfonate ($k_a = 6.06 \times 10^{-3}$ s^{-1} in water at 60 °C).[3d] It is generally thought that the driving forces for the E1cB mechanism are the nucleofugality of the leaving group, the internal nucleophilicity of the substrate, and the "relative" stability of the putative intermediate; in the present case the leaving groups are the same, and therefore the difference in reactivity has to be ascribed to the other two factors. The internal nucleophilicity represents the ability of the conjugate base of the substrate to expel the leaving group, and it is related to the pK_a of the substrate itself. We have previously reported[3d] that the k_a term for the dissociative hydrolysis of 2,4-dinitrophenyl esters of substituted 4-hydroxybenzenesulfonic acids obeys the Brønsted relationship $\log k_a = 0.74 \times pK_a - 6.61$ when the phenolic hydroxy group does not suffer severe steric constraints. From this correlation, employing the data pertinent to 2,4-dinitrophenyl 4′-hydroxybenzenesulfonate ($k_a = 6.06 \times 10^{-3}$ s^{-1} and pK_a = 6.66)[3d] and the pK_a value of **5** (7.69, Table 2), we can estimate the k_a value expected for the (hypothetical) 2,4-dinitrophenyl 4′-hydroxy-X-benzenesulfonate which has exactly the same pK_a of ester **5**. The resulting value (0.12 s^{-1}) accounts for only ca. 13% of the experimental ratio, thus suggesting that the increase in reactivity on going from 2,4-dinitrophenyl 4′-hydroxybenzenesulfonate to **5** should be ascribed mainly to an increased stability of the intermediate **4** with respect to **3**. As we have previously suggested in the case of the corresponding carboxylic acid esters,[2] such increased stability could be the result of a more extended delocalization of π electrons due to the presence of an additional vinylene group.

Experimental Section

General. Starting reagents and solvents were purified and/or distilled before use. Buffer materials were of analytical reagent grade. Water was double distilled and preboiled to free it from dissolved carbon dioxide. The ^1H NMR spectra were recorded with a Varian Gemini 200 spectrometer (200 MHz) with TMS as internal standard and acetone-d_6 or $CDCl_3$ as solvent.

(14) Williams, A. *Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: Amsterdam, 1984; p 127.

Table 5. Second-Order Rate Constants for the Attack of Hydroxide Ion on 2,4-Dinitrophenyl Esters[a]

	X = CO		X = SO_2	
	k (M^{-1} s^{-1})	ref	k (M^{-1} s^{-1})	ref
p-HO-C_6H_4-X-ODNP	1.09×10^3	1b	1.38×10^4	3d
C_6H_5-X-ODNP	18.9	1a	27.6	3c
R	**58**		**500**	
p-HO-C_6H_4-CH=CH-X-ODNP	1.06×10^4	2	1.95×10^5	this work
C_6H_5-CH=CH-X-ODNP	10.6	2	8.3	this work
R	**1000**		**23500**	

[a] Each couple of kinetic data giving rise to each *R* value (*R* is the ratio between the rate constants, see text) was determined under the same experimental conditions.

Synthesis. General Procedure for the Synthesis of Esters. (a) Aryl β-styrenesulfonates. β-Styrenesulfonyl chloride, prepared by the reaction of styrene with sulfuryl chloride in DMFA,[15] was treated with equimolar amounts of the appropriate substituted phenol and triethylamine in anhydrous methylene chloride at room temperature giving, after usual workup of the reaction, the ester. **(b) Aryl 4′-hydroxy-β-styrenesulfonates.** 4-Acetoxy-β-styrenesulfonyl chloride was prepared from 4-acetoxystyrene (Aldrich) following the above procedure. The chloride was then treated with equimolar amounts of the appropriate substituted phenol and triethylamine in anhydrous methylene chloride for several hours at room temperature. After usual workup of the reaction, the resulting ester was deacetylated by refluxing it for 10 min under nitrogen in a solution of dry hydrochloric acid in absolute ethanol. Finally the solvent was removed affording the required product in satisfactory yield. The structures of the final products were confirmed by ^{1}H NMR spectroscopy, and the vinylic coupling constants (J = 15−16 Hz) clearly indicated formation of *trans*-esters in all cases. The esters recrystallized to constant mp from toluene were as follows; mp is given together with analytical data. **Aryl β-styrenesulfonates.** Aryl = **2,4-dinitrophenyl**: mp 131−2 °C. Anal. Calcd for $C_{14}H_{10}N_2O_7S$: C, 48.0; H, 2.9; N, 8.0. Found: C, 47.6; H, 3.0; N, 7.8. **3,4-Dinitrophenyl**: mp 98−9 °C. Anal. Calcd for $C_{14}H_{10}N_2O_7S$: C, 48.0; H, 2.9; N, 8.0. Found: C, 48.3; H, 3.1; N, 7.9. **4-Nitrophenyl**: mp 108−9 °C. Anal. Calcd for $C_{14}H_{11}NO_5S$: C, 55.1; H, 3.6; N, 4.6. Found: C, 55.6; H, 3.6; N, 4.4. **Aryl 4-Hydroxy-β-styrenesulfonates.** Aryl = **2,4-Dinitrophenyl**: mp 169−170 °C. Anal. Calcd for $C_{14}H_{10}N_2O_8S$: C, 45.9; H, 2.8; N, 7.7. Found: C, 46.0; H, 3.0; N, 7.5. **Pentachlorophenyl**: mp 189−190 °C. Anal. Calcd for $C_{14}H_7O_4Cl_5$: C, 37.5; H, 1.6. Found: C, 37.1; H, 2.0. **2,5-Dinitrophenyl**: mp 140−1 °C. Anal. Calcd for $C_{14}H_{10}N_2O_8S$: C, 45.9; H, 2.8; N, 7.7. Found: C, 46.5; H, 3.1; N, 7.8. **3,4-Dinitrophenyl**: mp 75−6 °C. Anal. Calcd for $C_{14}H_{10}N_2O_8S$: C, 45.9; H, 2.8; N, 7.7. Found: C, 45.3; H, 3.1; N, 7.2. **2-Chloro-4-nitrophenyl**: mp 134−5 °C. Anal. Calcd for $C_{14}H_{10}NClO_6S$: C, 47.3; H, 2.8; N, 3.9. Found: C, 47.4; H, 2.9; N, 3.9. **4-Nitrophenyl**: mp 165−6 °C. Anal. Calcd for $C_{14}H_{11}NO_6S$: C, 52.3; H, 3.5; N, 4.4. Found: C, 52.6; H, 3.6; N, 4.4.

Methods. Kinetic and other methods including the determination of pK_a of the substrates were described in a previous paper.[2]

Ionization Constant of Pentachlorophenol. The spectrophotometric determination of the pK_a was carried out in water at 25 °C and 320 nm in propionate buffers (ionic strength 0.1 M).

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