to form a species **2** with a structure similar to that of SF_4.[15] The "dangling" oxygen then rotates over the two hydrogens (**3**), and separation to the products H_2O and SO_2 occurs. A similar mechanism can be realized for the mercaptan reaction.

The ratio of cross sections for the production of chemiluminescence from the CH_3SH and H_2S reactions with ozone has been measured over more than four orders of magnitude in pressure, and the results are shown in Table I.[16] At high pressures (multiple-collision conditions), the intensity of the light produced by the mercaptan reaction is almost two orders of magnitude greater than that produced by H_2S. As the pressure decreases, the intensities approach a ratio of 1. In the single-collision regime, the intensity from the H_2S reaction is greater than that for the CH_3SH reaction by a factor of 2. This shows a change in the dominant mechanism for producing the luminescence that is strongly pressure dependent. In the single-collision regime the reaction of H_2S with ozone is more efficient at producing light. As the pressure increases into the multiple-collision regime, a chain mechanism becomes the dominant means for producing luminescence. The chain mechanism is more efficient in the case of the mercaptan than in the case of the sulfide.

We are pursuing further studies of these reactions and those of other sulfur containing compounds in order to provide further information about the dynamics of these reactions and the spectroscopy of SO_2.

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Registry No. O_3, 10028-15-6; H_2S, 7783-06-4; CH_3SH, 74-93-1; SO_2, 7446-09-5.

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[15] King, E. L. "Chemistry"; Painter Hopkins: Sausalito, CA, 1979 p 430–431.

[16] An estimate of the cross section for the production of chemiluminescence in reaction 2 is 1×10^{-5} Å^2.

Elimination-Addition Mechanisms of Sulfonyl Group Transfer: Evidence for a Sulfoquinone Intermediate in the Hydrolysis of 2,4-Dinitrophenyl 3,5-Dimethyl-4-hydroxybenzenesulfonate[1]

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We report here the first definitive evidence for the participation of a dissociative (EA)[2] mechanism in the basic hydrolysis of a 4-hydroxybenzenesulfonic acid ester, namely, 2,4-dinitrophenyl 3,5-dimethyl-4-hydroxybenzenesulfonate (**1**).[3]

Reaction rates were measured by following spectrophotometrically the formation of the phenolate ion, which was released quantitatively in every case. Pseudo-first-order rate constants were found to depend on pH according to eq 1, and the sigmoidal log

$$k_{obsd} = k'/(1 + a_H/K_a) \qquad (1)$$

k_{obsd} vs. pH profile is shown in Figure 1. In the pH range 9–13.5, the k_{obsd} values are essentially constant and equal to k' (3.18×10^{-3} s^{-1}) and the inflection corresponds to pK_a = 7.4, identical in value (within the experimental error) with the apparent pK_a determined spectrophotometrically under identical conditions.

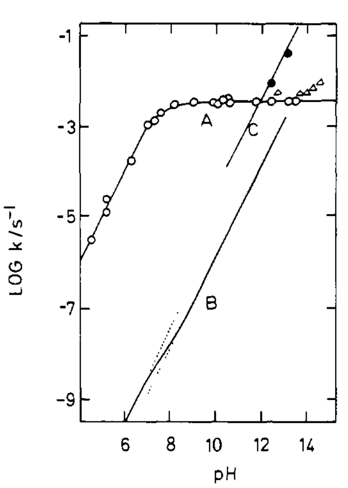
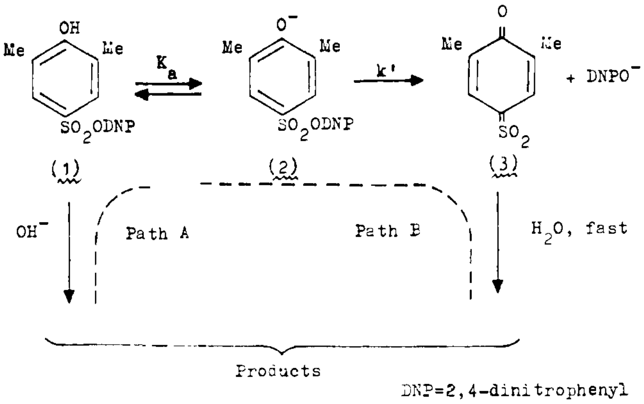


Figure 1. Dependence on pH of the hydrolysis of 2,4-dinitrophenyl 3,5-dimethyl-4-hydroxybenzenesulfonate (20% dioxane/water (v/v), 25 °C, ionic strength made up to 0.2 M (○) or 1 M (△). (A) Theoretical, from data in the text and eq 1; (B) calculated reactivity of the ester hydrolyzing through a normal BAc2 mechanism (see text); dotted lines are to accentuate the inflexion at the pK; (C) 2,4-dinitrophenyl benzenesulfonate. The kinetic results are extrapolated to zero buffer concentration.

Scheme I



The observed dependence of rate on pH could be attributed either to an associative (AE)[2] mechanism in which nucleophilic attack of the hydroxide ion on the substrate **1** is inhibited as the latter undergoes ionization (path A in Scheme I) or to a dissociative (EA) mechanism where the limiting rate k' represents the unimolecular breakdown of the substrate conjugate base **2**.

We can calculate to a good approximation the nucleophilic reactivity of the hydroxide ion toward esters **1** and **2** as expressed by the second-order rate constants (k_{OH}^{calcd}) on the basis of the known reactivity of 2,4-dinitrophenyl benzenesulfonate[4] and the sensitivity of the reaction to substituents in the acid moiety (ρ 2.24).[5] The second-order rate constant $k_{OH} = k'K_a/K_w$ for the bimolecular reaction of ester **1** with the hydroxide ion, calculated from the experimental values of k' and K_a and the reported value[6] of K_w for the mixed solvent used, is some 5×10^5-fold larger than the k_{OH}^{calcd} value for the same ester. Such a very large reactivity ratio is considered as good evidence in favor of different mechanisms operating in the reactions under comparison,[7] and we conclude that only the dissociative mechanism is operating. It is most likely that the unsaturated intermediate involved in the EA route is the sulfoquinone species **3** (path B). If the mechanism

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[1] We are grateful to NATO (Grant RG 115.80) for partial financial support of this research.

[2] A. Williams and K. T. Douglas, *Chem. Rev.*, **75**, 627 (1975).

[3] This ester was prepared from the corresponding sulfonyl chloride[9] and had satisfactory analytical and spectroscopic data. Product analysis carried out by UV spectroscopy and HPLC indicate that a simple hydrolysis to phenol and sulfonic acid occurs.

[4] R. V. Vizgert, *Zh. Obshch. Khim.*, **28**, 1873 (1958).

[5] V. A. Palm and R. V. Vizgert, *Dolk. Akad. Nauk. SSSR*, **142**, 1091 (1962).

[6] H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, **61**, 2374 (1939).

[7] K. T. Douglas *Prog. Bioorg. Chem.*, **1976**, *4*, 193.

involved attack of the hydroxide ion on the neutral ester **1**, the reactivity for the anionic ester **2** would be expected to be only marginally less; the effect of changing the para substituent from –OH to $-O^-$ ($\sigma = -0.37$ and -0.52) would be to lower the reactivity by some 2-fold as calculated from the Hammett ρ value of 2.24.[5] The similarity in rate constants would lead to a narrow plateau region as illustrated in Figure 1 (Line B). Figure 1 indicates the presence of a hydroxide term which must represent bimolecular attack of hydroxide ion on the ionized ester; the rate constant comes close to the calculated value as does that for the alkaline hydrolysis of 2,4-dinitrophenyl benzenesulfonate.

A mechanism consisting of nucleophilic aromatic substitution is discarded by labeling studies which indicate that less than 0.2% of the reaction involves O–Ar bond cleavage; the 2,4-dinitrophenol from the reaction using ^{18}O-enriched water (5.796% enriched) had an $M + 2$ peak at 1.230% enrichment (natural has 1.224%), and O–Ar cleavage should yield $M + 2$ at 7.026% enrichment.

A low positive entropy of activation for k' for the 4-hydroxy ester is consistent with the proposed dissociative mechanism. The Arrhenius parameters at $[OH^-] = 0.01$ M, ionic strength 0.2 M, and 20% dioxane/water are $\Delta S^\ddagger = +0.71$ eu/mol and $\Delta H^\ddagger = 21.1$ kcal/mol at 25 °C.

Trapping experiments with ammonia using HPLC product analysis indicate that at pH 10.19 and 1 M ammonium buffer (fraction of base = 0.8) 7% of the product is the suulfonamide. This yield is only 3-fold larger than that expected from the molar ratio of water and ammonia. The poor selectivity indicates that the intermediate is very reactive toward nucleophiles as would be expected from an analogue of sulfur trioxide. Methyl glycinate, imidazole, 2-picoline, carbonate, and ammonia showed no S_NAr reaction; piperidine, morpholine, aniline, pyridine, benzylamine, and phenol gave some aromatic substitution.

Although the hypothesis that sulfoquinones can be formed by the action of bases on substituted 4-hydroxybenzenesulfonyl chloride was advanced in the first decade of this century,[8] subsequent work was not able to confirm it.[9] As far as we are aware, this is the first definitive evidence for the existence of a sulfoquinone in a reaction pathway.

Registry No. 1, 80540-65-4; **3**, 80540-66-5.

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[8] T. Zincke and R. Brune, *Chem. Ber.*, **41**, 902 (1908).

[9] W. L. Hall, *J. Org. Chem.*, **31**, 2672 (1966).

Why Do Rate–Equilibrium Relationships Break Down?

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One of the fundamental concepts of physical organic chemistry is the idea of the rate–equilibrium relationship.[1,2] This relationship, expressed by eq 1 suggests that perturbations on equilibria

$$\Delta(\Delta G^\ddagger) = \alpha\Delta(\Delta G^\circ) \qquad (1)$$

will only be partially reflected in the reaction rates, i.e., α will take on values between 0 and 1. This idea has taken on added scope with the development of Marcus theory[3a,b] which attempts to relate the free energy of activation for a given reaction to the "intrinsic" barrier, $\Delta G_0^\ddagger$ ($\Delta G^\ddagger$ when $\Delta G^\circ = 0$), and the free energy change, ΔG°, of the reaction. On the basis of Marcus theory, α is given by eq 2.[3c] Yet it is apparent, despite the

$$\alpha = 1/2 + \Delta G^\circ/8\Delta G_0^\ddagger \qquad (2)$$

conceptual advance associated with these ideas and their successful application to a wide range of reaction types, electron transfer,[3] proton transfer,[4] and methyl transfers[5] that breakdowns exist. A particularly controversial example is the deprotonation reaction of nitroalkanes which has been the subject of intense study, since for this system α values outside the range 0–1 were observed.[6,7]

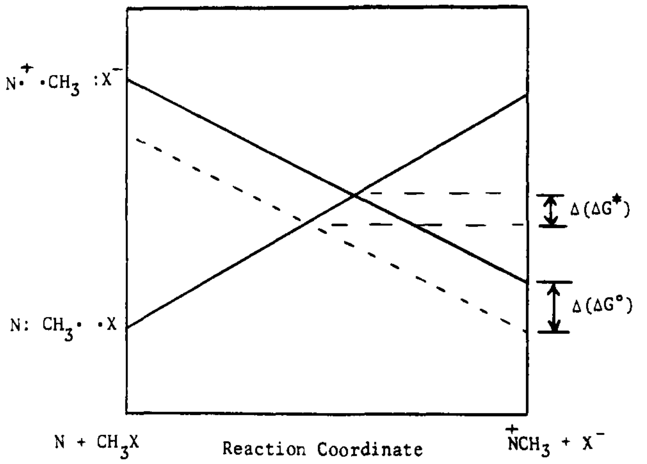

Figure 1. Energy plot of reactant ($N\!:CH_3\cdot\,\cdot X$) and product ($N\cdot^+\,\cdot CH_3\;:X^-$) configurations as a function of reaction coordinate. Effect of a perturbation [$\Delta(\Delta G^\circ)$] on product stability is only partially reflected in the transition state [$\Delta(\Delta G^\ddagger)$].

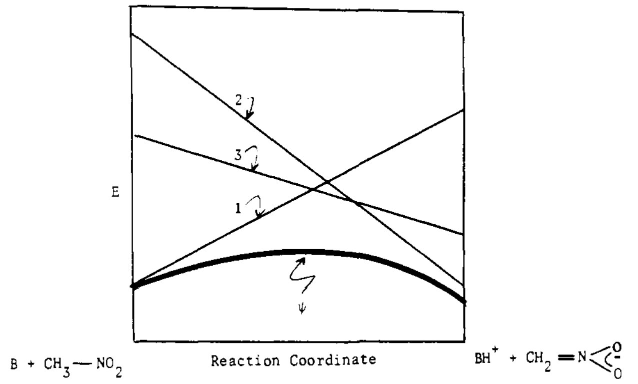

Figure 2. Energy plot of the reactant (**1**), product (**2**), and intermediate (**3**) configurations (see text) for the deprotonation reaction of CH_3NO_2 by a base (B).

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[7] For various explanations of the anomalous α values, see: (a) Agmon, N. *J. Am. Chem. Soc.* **1980**, *102*, 2164. (b) More O'Ferrall, R. A. In "Proton Transfer Reactions"; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975. (c) Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224. (c) Kresge, A. J. *Ibid.* **1970**, *92*, 3210; *Can. J. Chem.* **1974**, *52*, 1897. (e) Reference 6. (f) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69.

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