detector 200°, collector 190°, helium at 40 psi, and flow rate of 200 ml/min) yielded a small unidentified peak (2% of eluate) at 15 sec and a peak at 6 min which was **2**. Repeated injections and collections yielded sufficient material for characterization (although only about 50% of injected material was accounted for): $n^{25}\mathrm{D}$ 1.4641; ir (neat) no absorption at 6.0 (no enol C═C), no absorption at 2.95 (no -OH), 9.18 μ; nmr ($CDCl_3$) δ 4.02 (double doublet, 1, A of ABX pattern, J_{AB} = 7-8 Hz, cis J_{AX} = 4 Hz, $-OCH_AH_BCH_X<$), 3.78 (d, 1, B of ABX pattern, J_{AB} = 7-8 Hz, trans J_{BX} = 0), 3.32 (s, 3, $-OCH_3$), 1.2-2.6 (m, 9, cyclohexane ring CH_2 and CH).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.6; H, 9.92; O, 22.5. Found: C, 67.4; H, 9.76; O, 22.7.

The conversion of **1** into **2** was also observed on a 10-ft Reoplex 400 on Chromosorb W column (injector 200°, column 170°, detector 250°). Distillate from an unsuccessful simple distillation of crude reduction product in which vapor temperature reached 150-300° was combined with additional crude reduction product and separated on a spinning band column, yielding pure samples of **2**, bp 40° (0.3 mm), and impure **1**, bp 78-86° (0.3 mm), and polymer.

Lowering the column temperature of the Carbowax 30M column below 100° resulted in **1** not being converted into **2**.

3-Hydroxymethylcyclohexanone (3).—Hydrolysis of 0.68 g (0.0048 mol) of **1** with 25% H_2SO_4 yielded 0.47 g (0.0037 mol) of **3** (77% yield): $n^{25}\mathrm{D}$ 1.4806; nmr ($CDCl_3$) showed absence of both vinyl hydrogen and $-OCH_3$, δ 3.6 ("filled in" d, 2, J = 4 Hz, $-CH_2OH$), 2.7-0.9 (m, 10, ring and -OH hydrogens); ir (neat) 2.88 (-OH), 5.84 μ (C═O).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.44; O, 25.0. Found: C, 65.2; H, 9.62; O, 24.8.

3 was converted to its 2,4-dinitrophenylhydrazone,[13] mp 120-122° (inserted at 26°), 119-120° (inserted at 70°) (other derivatives[14]).

Anal. Calcd for $C_{13}H_{16}N_4O_5$: C, 50.6; H, 5.23; N, 18.18; O, 26.0. Found: C, 50.5; H, 5.53; N, 17.96; O, 26.1.

Sample of **3** made from acid hydrolysis of **2** had the same ir and nmr spectra and yielded 2,4-dinitrophenylhydrazone which gave no mixture melting point depression.

Registry No.—**1**, 34407-89-1; **2**, 34407-90-4; **3**, 32916-58-8; **3** DNP, 34407-91-5.

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[13] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1965, p 254.

[14] G. Stork and J. Ficine, *J. Amer. Chem. Soc.*, **83**, 4678 (1961).

The Alkaline Hydrolysis of Aryl α-Disulfones[1]

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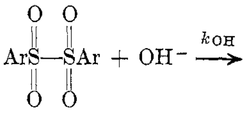
In alkaline solution aryl α-disulfones **1** undergo rapid hydrolysis to $ArSO_3^-$ and $ArSO_2^-$ (eq 1). Several years ago Allen and Conway[2] reported some kinetic data on this reaction in ethanol whose accuracy was later called into serious question by Kice and Kasperek.[3] The latter authors measured the rate of hydrolysis, k_h, of several **1** in various $Et_3N-Et_3NH^+$ buffers in 60% glyme at constant ionic strength. They found that under such conditions k_h was given by eq 2, where the first term is due to eq 1 and the second to general base catalysis of the hydrolysis of **1** by Et_3N. Their results showed that k_{OH} was apparently much more dependent on aryl group substituents (ρ = +3.7) than reported by Allen and Conway[2] (ρ = +0.3). However, the lack of values of K_w and $K_a^{Et_3NH^+}$ for 60% glyme prevented Kice and Kasperek from determining the absolute magnitude of k_{OH} for any of their α-disulfones under their reaction conditions.



1

$$\mathrm{ArS(O_2)\!-\!S(O_2)Ar} + OH^- \xrightarrow{k_{OH}}$$

$$ArSO_2^- + ArSO_3H \xrightarrow[\text{fast}]{OH^-} ArSO_2^- + ArSO_3^- \quad (1)$$

$$k_h = k_{OH}\left[\frac{K_w}{K_a^{Et_3NH^+}}\right]\frac{(Et_3N)}{(Et_3NH^+)} + k_{Et_3N}(Et_3N) \quad (2)$$

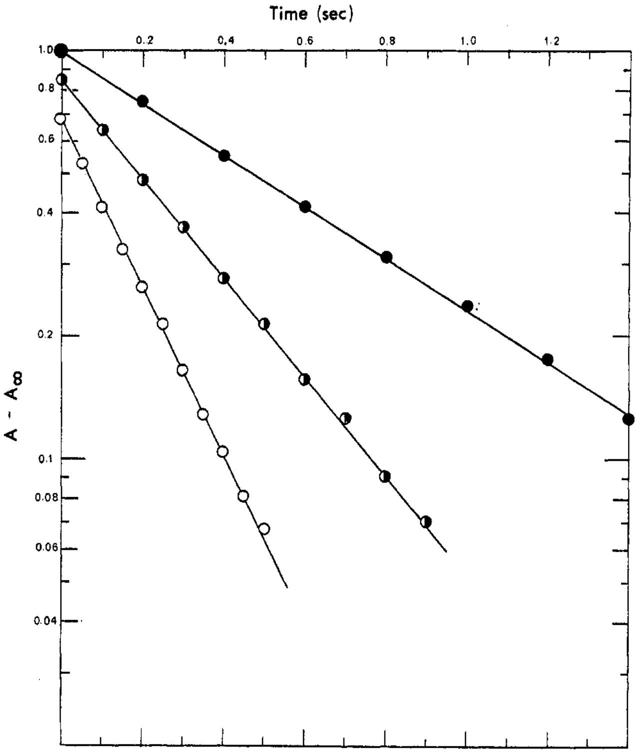


Figure 1.—Plot of log ($A - A_\infty$) *vs.* time for the alkaline hydrolysis aryl α-disulfones at 25°: ●, $PhSO_2SO_2Ph$, 3.7 × 10^{-5} *M*, $[OH]^-$, 0.02 *M*, 60% dioxane as solvent; ◐, $PhSO_2SO_2Ph$, 2.6 × 10^{-5} *M*, $[OH^-]$, 0.01 *M*, ethanol as solvent; ○, *p*-chlorophenyl α-disulfone, 1.6 × 10^{-5} *M*, $[OH^-]$, 0.01 *M*, 60% dioxane as solvent.

In the present work, by using a stopped-flow spectrophotometer to follow the very rapid disappearance of **1**, we have been able to measure k_{OH} at 25° for several aryl α-disulfones directly in solutions 0.01 or 0.02 *M* in NaOH in either 60% dioxane (v/v) or ethanol as solvent. Figure 1 shows plots of the data for representative runs. One can see that under the conditions used, where hydroxide ion is present in huge stoichiometric excess over **1**, excellent first-order kinetics are obtained. Table I summarizes the kinetic data for the various runs. In it k_1 is the experimental first-order rate constant for a run as obtained from the slope of a plot such as shown in Figure 1. Hence $k_{OH} = k_1/(OH^-)$.

Several aspects of the results merit discussion. First,

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[1] This research was supported by the National Science Foundation, Grant GP-25799.

[2] P. Allen, Jr., and P. J. Conway, *Can. J. Chem.*, **47**, 873 (1969).

[3] J. L. Kice and G. J. Kasperek, *J. Amer. Chem. Soc.*, **92**, 3393 (1970).

TABLE I
RATES OF ALKALINE HYDROLYSIS OF ARYL α-DISULFONES[a]

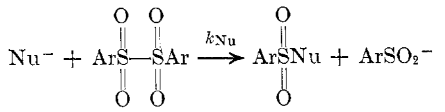
Solvent	$ArSO_2SO_2Ar$, Ar	Registry no.	$[ArSO_2SO_2Ar]_0$, M	$[OH^-]$, M	k_1, sec^{-1}	$k_{OH} = k_1/[OH^-]$, $M^{-1}\ sec^{-1}$
60% Dioxane	p-$CH_3C_6H_4$	10409-07-1	2.0×10^{-5}	0.010	0.17	17
	C_6H_5	10409-06-0	3.7×10^{-5}	0.010	0.75	75
				0.020	1.47	74
	p-ClC_6H_4	22040-25-1	1.6×10^{-5}	0.010	4.7	470
Ethanol[b]	p-$CH_3C_6H_4$		2.1×10^{-5}	0.010	0.76	76
	C_6H_5		2.6×10^{-5}	0.010	2.8	280

[a] All runs at 25.0°. [b] Actual solvent composition is 94% ethanol–4% dioxane–2% water; see Experimental Section.

it is obvious from the results in both 60% dioxane and ethanol that, contrary to the claim of Allen and Conway,[2] k_{OH} is very strongly dependent on the nature of the substituents in the aromatic rings of **1**. For the data in 60% dioxane a plot of log k_{OH} *vs.* σ is an excellent straight line with a slope, ρ, of $+3.6$, or essentially the same as that found by Kice and Kasperek[3] in 60% glyme. Clearly then the alkaline hydrolysis of aryl α-disulfones, in common with a number of other nucleophilic substitution reaction of **1**,[3,4] shows a large positive ρ value.

Second, comparison of the k_{OH} values for the p-tolyl and phenyl α-disulfones in ethanol in Table I with those reported by Allen and Conway[2] shows that in each case the true values are much larger than the ones they reported. Where Allen and Conway[2] list k_{OH} for phenyl α-disulfone in ethanol as 7.1 M^{-1} sec^{-1}, we find the actual value to be about 40 times larger than this, or 280 M^{-1} sec^{-1}. Similarly, the actual k_{OH} for the p-tolyl α-disulfone in ethanol, 76 M^{-1} sec^{-1}, is over ten times larger than their reported value of 6.5 M^{-1} sec^{-1}. The fact that the data in Table I are for 25° while theirs were obtained at 23° could hardly be responsible for any significant part of these differences, since the activation energy for the alkaline hydrolysis is almost certainly not very large. Thus the present results appear to confirm what Kice and Kasperek[3] had strongly suspected, namely, that the kinetic data of Allen and Conway[2] are almost certainly in error. Although one cannot be absolutely sure, we suspect that the explanation given in footnote 14 of ref 3 probably accounts for their low rates and apparent lack of dependence of rate on substituent.

The third point worth noting is what the k_{OH} values in Table I for 60% dioxane indicate regarding the reactivity of hydroxide ion as compared with the reactivity of various other nucleophiles toward **1** in this same solvent. From previous work[4] values of k_{Nu} are available for the reaction of a wide variety of nucleophiles with aryl α-disulfones in 60% dioxane at 21.3° (eq 3).



$$Nu^- + ArS(O_2)\text{—}S(O_2)Ar \xrightarrow{k_{Nu}} ArS(O_2)Nu + ArSO_2^- \qquad (3)$$

Using this data[4] and that in Table I one calculates that OH^- is about 3×10^4 more reactive than acetate ion toward **1**. This compares with values for (k_{Nu}/k_{OAc}) of 330 for N_3^-, 59 for F^-, and 10 for NO_2^-.[4] From the various data one can also calculate that OH^- is only about five times more reactive toward **1** as a nucleophile than is a simple n-alkylamine like n-butylamine.

Kice and Kasperek[3] had previously attempted to make estimates of k_{OH} in 60% glyme by using their measured values of $k_{OH}(K_w/K_a^{Et_3NH^+})$ and what were thought to be reasonable estimates of K_w and $K_a^{Et_3NH^+}$. The values of k_{OH} actually found in 60% dioxane in the present work are uniformly smaller by about a factor of ten than their earlier estimates, indicating that their assumed values of K_w and $K_a^{Et_3NH^+}$ for 60% glyme were apparently considerably poorer ones than they had thought.

Rogne[5] has recently obtained data on the reactivity of a series of nucleophiles toward aryl sulfonyl chlorides (eq 4) in aqueous solution. He noted that a plot of log

$$Nu^- + ArSO_2Cl \xrightarrow{k_4} ArSO_2Nu + Cl^- \qquad (4)$$

k_4 *vs.* log k_{Nu} for eq 3 for those nucleophiles for which data were available for both systems was linear with a slope of about 0.7. Based on this and Rogne's measured value of k_4 for OH^-, one would calculate a value of k_{OH} for $PhSO_2SO_2Ph$ in 60% dioxane of about 50, which is reasonably close to the measured value of 75, particularly when one recalls that the actual value of k_{OH} at 21.3° would be somewhat lower than the values in Table I, which are for 25°.

Experimental Section

Preparation and Purification of Materials.—The preparation and purification of the α-disulfones and the method of purifying the dioxane used have already been described.[4] Absolute ethanol was subjected to careful fractional distillation before use.

Procedure for Kinetic Runs.—For the runs in 60% dioxane the sodium hydroxide solutions were prepared by taking either 1 or 2 ml of standard 1.000 N NaOH and diluting it to 50 ml with sufficient dioxane and water so that the final solution contained 60% dioxane (v/v). A stock solution of the α-disulfone in anhydrous dioxane was prepared by dissolving a carefully weighed amount of the disulfone in 25 ml of dioxane. Two milliliters of this stock solution were then pipetted into a 50-ml volumetric flask and made up to volume with sufficient dioxane and water so that the final solution contained 60% dioxane. This solution and the solution of NaOH in 60% dioxane were placed in the two separate reservoir syringes of a Durrum–Gibson stopped-flow spectrophotometer which was thermostatted at 25°, and the disappearance of **1** was followed by monitoring the change in optical density with time at an appropriate wavelength in the ultraviolet. The wavelengths used were 244 mμ for the phenyl compound, 258 mμ for the p-tolyl, and 263 mμ for the p-chlorophenyl α-disulfone.

For the runs in ethanol the sodium hydroxide solution was prepared by taking 1.00 ml of 1.000 N NaOH, adding 2 ml of anhydrous dioxane, and diluting to 50 ml with absolute ethanol. The solution of the α-disulfone was prepared by making a stock solution of **1** in anhydrous dioxane, pipetting 2.0 ml of this solution into a volumetric flask, adding some ethanol, then 1.0 ml of water, and finally diluting to 50 ml with ethanol. The procedure for following the kinetics was then the same as for the runs in 60% dioxane.

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(4) J. L. Kice, G. J. Kasperek, and D. Patterson, *ibid.*, **91**, 5516 (1969).

(5) O. Rogne, *J. Chem. Soc. B*, 1056 (1970).