[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Formation of Olefins by the Reaction of Sodium Hydroxide with α-Halo Sulfones[1]

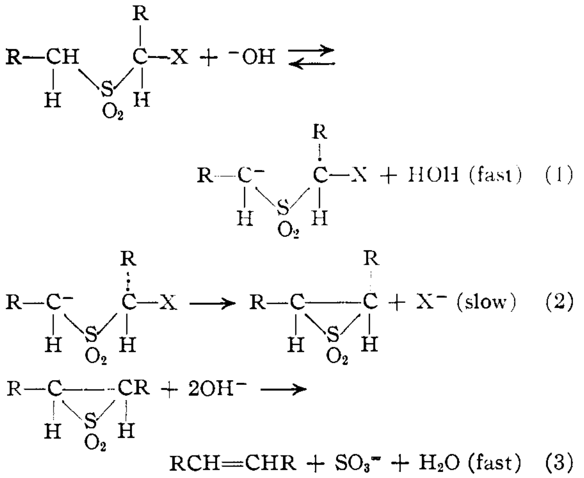
BY F. G. BORDWELL AND GLENN D. COOPER

The reaction in which an α-halo sulfone is converted by the action of hydroxide ion to an olefin, sulfite ion, and halide ion has been extended to four additional sulfones. A kinetic investigation in dilute solution for three of these α-halo sulfones revealed that the rate of release of halide ion is first order in sulfone and first order in hydroxide ion. These kinetics are consistent with a mechanism involving the formation and cleavage of an intermediate three-membered ring sulfone. Comparison of the rate of the reaction of chloromethyl methyl sulfone with the known rate of deuterium exchange of dimethyl sulfone allowed a decision as to the rate determining step in the reaction sequence. The suggestion of a similar mode of action for the decomposition of chloromethanesulfonanilide by hydroxide ion is supported by the observation that the rate of release of chloride ion in this reaction is essentially independent of the concentration of hydroxide ion.

Several years ago Ramberg and Bäckland[2] described a remarkable reaction in which α-bromoethyl ethyl sulfone was readily converted by 2 *N* aqueous potassium hydroxide to *cis*-2-butene (85%), potassium bromide and potassium sulfite. Similarly α-bromopropyl ethyl sulfone yielded *cis*-2-pentene, and bis-(α-chloroethyl) sulfone gave potassium 2-butene-2-sulfonate.

$$CH_3CH_2SO_2CHBrCH_3 + 3KOH = CH_3CH{=}CHCH_3 + KBr + K_2SO_3 + 2H_2O$$

The facile release of halide ion in this reaction is of particular interest, since it is well established that α-halo sulfones are very inert in intermolecular displacement reactions initiated by nucleophilic reagents.[3] The most reasonable representation of the reaction appeared to be one in which the halogen was displaced in an intramolecular process, such as



Steps (1) and (2) of this formulation gain credence by the recent evidence for cyclopropanone intermediates in a somewhat analogous reaction of α-halo ketones with bases, the Faworskii rearrangement.[4]

Ramberg and Bäckland[2] measured the rate of release of bromide ion from α-bromoethyl ethyl sulfone in the presence of a large excess of 1 or 2 *N* aqueous potassium hydroxide at 25°. Under these conditions the ratio of hydroxide ion to sulfone was too large to allow a decision as to the order with respect to hydroxide ion from a single run. However, comparison of the half-lives in 1 and 2 *N* potassium hydroxide indicated that the rate was dependent on a power of the hydroxide ion concentration greater than one and less than two. A second order dependence of the rate of halide release on hydroxide ion concentration would require a different mechanism from that given above, or would demand that steps (1), (2) and (3) be simultaneous. In order to check on this point and to obtain other information, the kinetics of the reaction with four additional α-halo sulfones has now been investigated.

The rate of release of chloride ion from chloromethyl methyl sulfone (I), α-chlorobenzyl methyl sulfone (II) and chloromethyl benzyl sulfone (III) in the reaction with dilute sodium hydroxide in 40% dioxane solution at 50° was measured. The reaction was followed by titration of the chloride ion produced. Second order rate constants were calculated from the formula[2]

$$k_{\text{bi}} = \frac{2.303}{t(b - \phi a)} \log \frac{a(b - \phi x)}{b(a - x)}$$

and third order constants from

$$k_{\text{ter}} = \frac{1}{t(b - \phi a)^2}\left[2.303 \log \frac{a(b - \phi x)}{b(a - x)} - \frac{\phi(b - \phi a)}{b} \times \frac{x}{b - \phi x}\right]$$

where *a* is the initial concentration of sulfone, *b* is the initial concentration of hydroxide ion, *x* is the chloride ion produced, and ϕ is the experimentally determined ratio of hydroxide ion consumed to chloride ion produced. The reaction with α-chlorobenzyl methyl sulfone (II) and chloromethyl benzyl sulfone (III) exhibits good second order kinetics. With chloromethyl methyl sulfone (I) the reaction is too slow to follow conveniently under these conditions, but in water at 75° the reaction is second order (Fig. 1). Table I gives typical data for three runs with chloromethyl benzyl sulfone (III) with different values of *a* and *b*, and compares the calculated bimolecular and termolecular rate constants.

The second order rate constants for I, II, III and α-chlorobenzyl benzyl sulfone (IV) are summarized in Table II. The rate with IV is too rapid to allow accurate measurements under these conditions.

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[1] This investigation was supported by the Office of Naval Research under Contract No. N7onr-45007.

[2] L. Ramberg and B. Bäckland, *Arkiv. Kemi Mineral. Geol.*, **13A**, No. 27 (1940).

[3] This deactivation is probably due to a steric effect of the $-SO_2-$ group; see F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5184 (1951).

[4] R. B. Loftfield, *ibid.*, **72**, 632 (1950); Abstracts of the Boston Meeting of the American Chemical Society, April, 1951, p. 48M.

TABLE I

KINETICS OF THE REACTION OF CHLOROMETHYL BENZYL SULFONE WITH SODIUM HYDROXIDE IN 40% DIOXANE AT 50°

Time, sec.	% reacted	k_{bi} (l. mole^{-1} sec.$^{-1}$)	k_{ter} (l. mole^{-2} sec.$^{-2}$)
Run 1: $a = 0.0376$, $b = 0.3382$, $\phi = 2.85$			
52	22.1	0.0150	0.0456
141	38.3	.0109	.0345
259	56.9	.0108	.0357
443	75.8	.0112	.0372
730	89.4	.0112	.0420
1091	96.5	.0119	.0506
$SO_3^=$ = 97.4% of theoretical			
k_{50} (determined graphically) = 0.0110 l. mole^{-1} sec.$^{-1}$			
Run 2: $a = 0.0409$, $b = 0.1628$, $\phi = 2.88$			
75	10.75	0.0096	0.0600
134	18.4	.0100	.0655
206	26.2	.0100	.0687
355	38.9	.0100	.0730
504	47.9	.0100	.0788
622	54.3	.0101	.0839
1111	69.7	.0097	.0891
1783	80.4	.0094	.1050
2472	86.8	.0092	.1140
3210	90.8	.0091	.1200
$SO_3^=$ = 97.2% of theoretical			
k_{50} (determined graphically) = 0.0100 l. mole^{-1} sec.$^{-1}$			
Run 3: $a = 0.0463$, $b = 0.0807$, $\phi = 2.94$, $NaNO_3 = 0.10$			
86	10.6	0.0099	0.129
186	19.1	.0088	.121
317	29.8	.0090	.137
503	41.5	.0090	.148
809	55.2	.0089	.172
1061	63.2	.0089	.192
1441	72.0	.0088	.226
1969	80.1	.0086	.280
2702	87.0	.0085	.366
3480	91.9	.0085	.400
5570	96.6	.0092	.525
$SO_3^=$ = 95.0% of theoretical			
k_{50} (determined graphically) = 0.0089 l. mole^{-1} sec.$^{-1}$			

TABLE II

SECOND ORDER RATE CONSTANTS FOR THE REACTION OF α-HALO SULFONES WITH DILUTE SODIUM HYDROXIDE IN 40% DIOXANE SOLUTION AT 50°

α-Halo sulfone	k (l. mole^{-1} sec.$^{-1}$)
$CH_3SO_2CH_2Cl$ (I)	$\sim 3 \times 10^{-6}$
$C_6H_5CHClSO_2CH_3$ (II)	1.4×10^{-5}
$C_6H_5CH_2SO_2CH_2Cl$ (III)	8.9×10^{-3}
$C_6H_5CHClSO_2CH_2C_6H_5$ (IV)	$\sim 4 \times 10^{-2}$

From the above data it is clear that in dilute solution the rate of release of chloride ion during the reaction is first order in both hydroxide ion and sulfone. These results are consistent with the series of steps postulated (equations 1–3) with either step (1) or step (2) being rate determining. Comparison of the rate data for the reaction of I in aqueous solution with the rate of deuterium exchange of dimethyl sulfone[5] allows a decision between the latter two possibilities.

Hochberg and Bonhoeffer[5] measured the rate of deuterium exchange over a wide range of temperatures and found that for the ionization of dimethyl sulfone

$$CH_3SO_2CH_3 + O\overline{D} \longrightarrow CH_3SO_2\overline{C}H_2 + DOH$$

log k = 13.23 − 4035/T. From this $k_{75} \cong 43$ l. mole^{-1} min.$^{-1}$. Assuming that the chlorine atom would have only a small effect on the rate of proton removal from the unsubstituted carbon atom, and that the rate of ionization of the sulfone is about 50% greater in deuterium oxide than in water, as has been found to be the case for the ionization of nitroparaffins,[6] k_{75} for the reaction

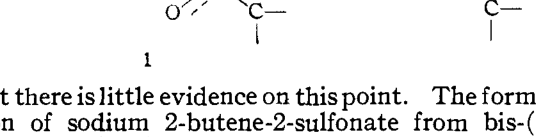
$$ClCH_2SO_2CH_3 + \overline{O}H \longrightarrow ClCH_2SO_2\overline{C}H_2 + HOH$$

should be about 14 l. mole^{-1} min.$^{-1}$. The rate constant for the elimination of chloride ion, measured in aqueous solution at 75° was found to be 9.47×10^{-4} l. mole^{-1} min.$^{-1}$ (Fig. 1). It is apparent that the ionization of the sulfone is not the rate-determining step in the reaction.

The differences in the rates for I, II, III and IV (Table I) can be rationalized with the aid of the suggested mechanism. The fivefold increase in rate observed when a phenyl group is substituted for a hydrogen of the carbon holding the chlorine in chloromethyl methyl sulfone (compare I and II) is probably largely due to an increase in the rate of step (2). This effect is comparable in direction to the effect of a phenyl group on intermolecular displacements, but is smaller in magnitude. On the other hand, the 3000-fold increase in rate observed in going from I to III must be due for the most part to a shift to the right of the equilibrium expressed in step (1) caused by the increase of acidity due to the phenyl substituent. These effects are combined in IV.

The stereochemistry of the reaction remains obscure. Whereas Ramberg and Bäckland[2] obtained *cis*-2-butene and *cis*-2-pentene (structure assigned on the basis of the physical properties of the dibromides), we obtained a 94% yield of pure *trans*-stilbene from IV. It seems probable that the stereochemical configuration will be decided in step (2). A *trans* configuration for the three-membered ring sulfone would appear more likely *a priori*, and this structure is evidently favored when the substituents are phenyl. With alkyl substituents it might be anticipated that preference for the *trans* structure would be less pronounced, and a mixture of *cis* and *trans* structures would not seem unreasonable, but the selective formation of *cis* products is surprising.

It seems likely that step (3) of the reaction may be an elimination reaction initiated by attack of hydroxide ion on the sulfone grouping



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but there is little evidence on this point. The formation of sodium 2-butene-2-sulfonate from bis-(α-chloroethyl) sulfone[2] can be formulated in an analo-

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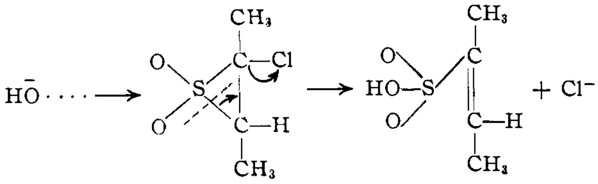
[5] V. Hochberg and K. F. Bonhoeffer, *Z. physik. Chem.*, **A184**, 419 (1939).

[6] W. F. K. Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934); S. H. Maron and V. K. La Mer, THIS JOURNAL, **60**, 2588 (1938).

gous manner, expulsion of chloride ion rather than bisulfite ion being in line with the relative ease of cleavage of carbon–sulfur and carbon–chlorine bonds in other displacement processes.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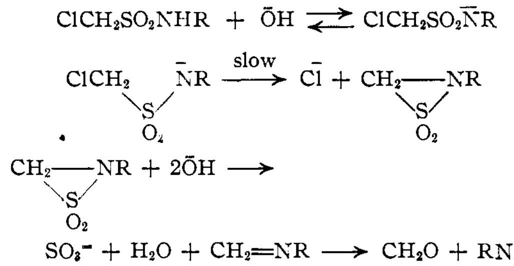
Although attempts to oxidize olefin sulfides (thiacyclopropanes) to sulfones have thus far been unsuccessful,[7] a few aryl substituted three-membered ring sulfones have been made by other methods.[8] These sulfones are unstable and decompose readily to sulfur dioxide and olefin, so the possibility of a thermal decomposition in step (3) must be considered. However, with bis-(α-chloroethyl) sulfone a thermal expulsion of sulfur dioxide in step (3) would give 2-chloro-2-butene; therefore the isolation of sodium 2-butene-2-sulfonate[2] is evidence for the participation of hydroxide ion.

Johnson and Douglass[9] have observed that whereas the chlorine atoms in chloromethanesulfonate ion, $ClCH_2SO_3^-$, and N,N-diethylchloromethanesulfonamide, $ClCH_2SO_2N(CH_2CH_3)_2$, are very inert toward displacement in alkaline solution,[3] chloromethanesulfonamide, $ClCH_2SO_2NH_2$, reacts rapidly in alkaline solutions to give chloride ion, sulfite ion and formaldehyde. Chloromethanesulfonanilide also readily releases its halogen.[9] These differences are most readily accounted for by assuming a mechanism for the latter two decompositions analogous to that presented above.



Since the sulfonamides are comparatively strong acids, it would be expected that in the presence of excess hydroxide ion, they should be virtually completely ionized. The rate of the reaction, assuming the above mechanism, should then be independent of the hydroxide ion concentration. It has been found that the rate of elimination of chloride ion from chloromethanesulfonanilide is indeed almost unaffected by the hydroxide ion concentration. Using solutions 0.05 molar in chloromethanesulfonanilide and 0.625, 1.25 and 2.50 molar in sodium hydroxide, the rate constants at 75° were 1.63, 1.63 and 1.96 $\times 10^{-3}$ min.$^{-1}$ (the 0.625 and 1.25 *M* sodium hydroxide solutions were brought up to 2.50 *M* by adding sodium nitrate). This observation alone does not rule out the possibility of direct displacement of Cl^- or $(SO_2NH_2)^-$ from $ClCH_2SO_2NH_2$, since the concentration of this species is inversely proportional to the hydroxide ion concentration. However, the failure of $ClCH_2SO_2N(CH_2CH_3)_2$ to undergo a comparable reaction and the inertness of $ClCH_2SO_2NH_2$ toward other nucleophilic reagents[4] seem comprehensible only on the basis of the intramolecular displacement mechanism.

Experimental[10]

Benzyl Chloromethyl Sulfone.—Seventeen and two-tenths grams (0.1 mole) of benzyl chloromethyl sulfide[11] was added dropwise with mechanical stirring over about one hour to a cold solution of 3 g. of anhydrous sodium acetate and 60 g. (0.03 mole) of 40% peracetic acid in acetic acid. Stirring was continued for 15 minutes after addition was completed. The sulfone was precipitated by the addition of 200 ml. of water and recrystallized from alcohol–water; yield 18.3 g. (90%), m.p. 103–104°; literature[11] m.p. 103°.

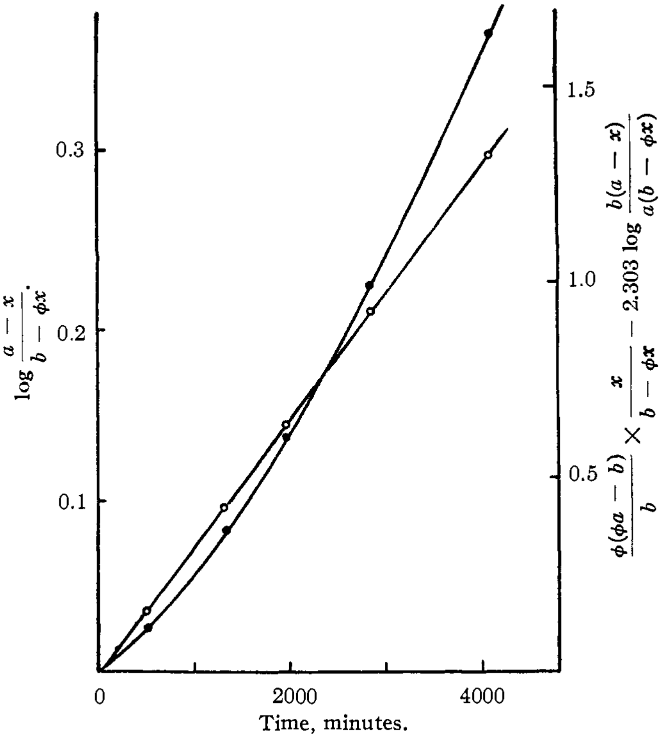


Fig. 1.—Reaction of methyl chloromethyl sulfone with aqueous sodium hydroxide at 75°: open circles, plotted as a second order reaction; shaded circles, plotted as a third order reaction (second order in hydroxide ion); $a = 0.1000$; $b = 0.0923$; $\phi = 2.50$; $k_{bi} = 9.47 \times 10^{-4}$ l. mole^{-1} min.$^{-1}$.

α-Chlorobenzyl Benzyl Sulfone.—Ten and seven-tenths grams (0.05 mole) of benzyl sulfide was chlorinated with 6.7 g. (0.05 mole) of sulfuryl chloride in pentane.[12] The chlorosulfide could not be distilled at 1 mm. pressure without decomposition, so the crude product was oxidized with monoperphthalic acid in ether according to the procedure of Böhme.[11] After several recrystallizations from benzene–petroleum ether, there was obtained 7.1 g. (51%) of a product melting at 116.2–117°; the melting point was not raised by further crystallization from a variety of solvents.

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[7] C. C. J. Culvenor, W. Davies and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

[8] L. v. Vargha and E. Kovács, *Ber.*, **75B**, 794 (1942); H. Staudinger and F. Pfenninger, *ibid.*, **49B**, 1941 (1916).

[9] T. B. Johnson and I. B. Douglass, This Journal, **63**, 1571 (1941).

[10] Microanalyses were by Miss Joyce Sorensen.

[11] H. Böhme, H. Fischer and R. Frank, *Ann.*, **563**, 54 (1949).

[12] Dr. Burnett M. Pitt, unpublished work from this Laboratory.

Böhme[11] reported m.p. 123° for α-chlorobenzyl benzyl sulfone.

Anal. Calcd. for $C_{14}H_{13}SO_2Cl$: C, 60.0; H, 4.67. Found: C, 60.0; H, 4.80.

α-Chlorobenzyl Methyl Sulfone.—Ten grams (0.058 mole) of α-chlorobenzyl methyl sulfide, prepared by chlorination of methyl benzyl sulfide with sulfuryl chloride,[12] was oxidized with monoperphthalic acid in ether. The product was recrystallized from ethanol–water; yield 6.5 g. (55%), m.p. 108–109°.

Anal. Calcd. for $C_8H_9SO_2Cl$: C, 46.9; H, 4.43. Found: C, 47.0; H, 4.70.

Kinetic Experiments.—The procedure in all cases was essentially as follows:

The sulfone was weighed into an erlenmeyer flask and immersed in a constant temperature bath at 50 ± 0.05°. A solution of sodium hydroxide in 40% dioxane by volume was brought to 50° and standardized at that temperature. An appropriate amount of the solution was then transferred by means of a pipet to the flask containing the sulfone, and the flask was swirled vigorously to dissolve the sulfone. As soon as the sulfone was completely dissolved, a 10-ml. sample was transferred by means of a fast-flowing pipet to a flask containing 1.5 ml. of 6 *N* nitric acid. A few drops of 10% hydrogen peroxide were added to oxidize the sulfite to sulfate, and the solution titrated for chloride ion by the Volhard procedure. Samples were titrated in this fashion at suitable intervals.

In most cases the reaction was fast enough to proceed essentially to completion within a reasonable time. When the reaction was complete, a 10-ml. sample was analyzed for chloride, another 10-ml. sample was titrated with standard acid, and another 10-ml. sample was treated with bromine water to oxidize the sulfite, and the sulfate was determined gravimetrically as barium sulfate.

Taking the time of the first sample as $t = 0$, the starting concentrations of the reactants were calculated as follows: $a = C_{\text{sulfone}}$ = sulfone originally present − chloride produced at $t = 0$; $b = C_{OH^-}$ = original concentration of hydroxide ion − ϕ (chloride produced at $t = 0$), where ϕ is the experimentally determined ratio of hydroxide consumed to chloride produced at completion of the reaction. In the absence of side reactions, the value of ϕ should be 3; values obtained ranged from 2.83 to 2.94, depending on the nature of the sulfone and the concentration of the reactants. The rate constants were calculated as previously described.

The yields of olefin were not determined in the kinetic experiments. In a separate experiment 5 g. (0.025 mole) of benzyl chloromethyl sulfone was refluxed for 30 minutes with 50 ml. of 2 *N* sodium hydroxide. The styrene was removed by steam distillation, dried and redistilled; yield 1.98 g. (79%). Three grams of phenylchloromethyl methyl sulfone similarly treated yielded 0.99 g. (65%) of styrene.

Chlorobenzyl benzyl sulfone is not sufficiently soluble in 40% dioxane to allow the rate to be measured by the technique previously used. One hundred milliliters of 0.1846 *N* sodium hyroxide (warmed to 50°) was added to a flask containing 1.3991 g. (0.004988 mole) of chlorobenzyl benzyl sulfone immersed in a constant temperature bath at 50°. The sulfone dissolved very slowly and flat plates of *trans*-stilbene began to deposit almost immediately. After 425 seconds a 10-ml. sample was withdrawn and analyzed; 83% of the theoretical amount of chloride was present; assuming $\phi = 3$, $k_{\text{bi}} > 0.04$ liter mole^{-1} sec.$^{-1}$. After 15 minutes 100 ml. of water was added, and the mixture was filtered, yielding 0.76 g. (94%) of *trans*-stilbene, m.p. 122–123°; the melting point of a mixture with an authentic sample of *trans*-stilbene was undepressed.

Reaction of Chloromethanesulfonanilide with Aqueous Sodium Hydroxide at 75°.—The reaction was followed in a manner comparable to that described above except that no hydrogen peroxide was used.

Time, min.	% reacted	$10^3 k$ (min.$^{-1}$)
Initial concentration of chloromethanesulfonanilide, 0.0500 *M*; sodium hydroxide, 2.50 *M*		
60	11.2	1.99
150	26.3	2.02
240	35.4	1.82
	Average	1.96
Initial concentration of chloromethanesulfonanilide, 0.0500 *M*; sodium hydroxide, 1.25 *M*; sodium nitrate, 1.25 *M*		
60	9.5	1.68
150	22.1	1.65
240	32.2	1.62
280	35.7	1.58
	Average	1.63
Initial concentration of chloromethanesulfonanilide, 0.0500 *M*; sodium hydroxide, 0.625 *M*; sodium nitrate, 1.875 *M*		
60	9.7	1.69
150	21.7	1.65
240	31.9	1.60
330	40.8	1.59
	Average	1.63

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