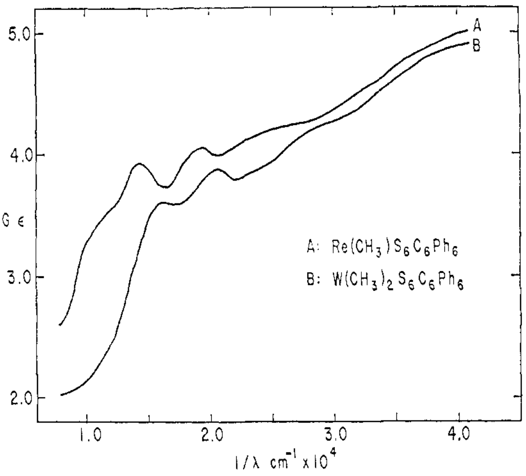

Figure 1. Absorption spectra of complexes **8** and **10** in CH_2Cl_2.

of W(IV) and Re(V). Their coordination geometry could be trigonal prismatic, but we predict them to be octahedral or distorted octahedral since the prismatic coordination appears to be energetically favored only in the delocalized trisdithienes and not in trisdithiolates. We finally point out that the electronic structure of anions $MS_6C_6R_6^{z-}$ (z = 1, 2) may depend on the nature of R as well as M. The unpaired electrons in the anions of first- and second-row transition metal derivatives occupy MO's with appreciable metal character.[5,7] If these ions are trigonal prismatic this would suggest that the 5e′ orbital rather than 2a′$_2$ is occupied in these cases.

[7] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 4, 55 (1965).

G. N. Schrauzer, H. N. Rabinowitz
Department of Chemistry, University of California at San Diego
La Jolla, California 92037
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The Mechanism of Formation of Sulfenes by Dehydrohalogenation of Alkanesulfonyl Chlorides

Sir:

It has been concluded from product analysis studies that sulfenes are produced as unstable intermediates by the action of base on alkanesulfonyl halides possessing at least one α-hydrogen atom.[1] We now report the results of a kinetic investigation which corroborates this hypothesis and permits a relatively detailed description of the mechanism of the formation of sulfenes in this reaction.

We have found that the rate of the reaction of methanesulfonyl chloride with triethylamine and aniline at −25° in 1,2-dimethoxyethane can be measured by isolation of the sulfonanilide, or, more efficiently, by titration of the chloride ion produced, the rate constants obtained either way being the same within experimental error.

$$CH_3SO_2Cl + Et_3N + PhNH_2 \longrightarrow CH_3SO_2NHPh + Et_3NH^+Cl^- \quad (1)$$

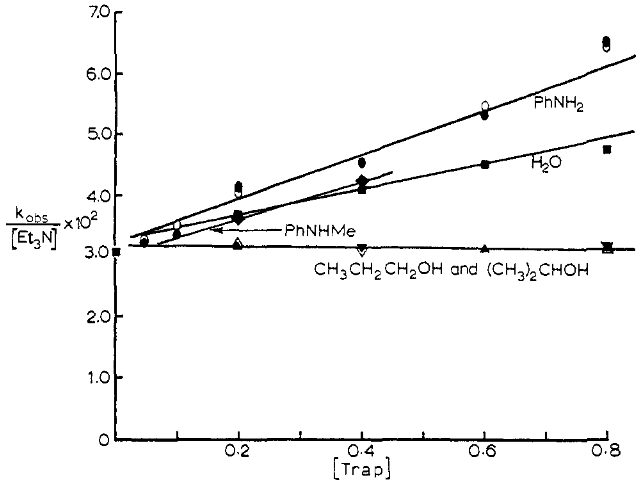

Figure 1. Plot of the pseudo-first-order rate constant divided by the triethylamine concentration *vs.* the concentration (*M*) of the "sulfene trapping agent" for the reaction of methanesulfonyl chloride (initial concentration 2.0 × 10^{-3} *M*) in 1,2-dimethoxyethane at −25.0 ± 0.2°. "Trapping agents" are indicated above except for 2-propanol and 1-propanol which are given by the triangles (△) and inverted triangles (▽), respectively. Closed ellipses, triangles, etc., refer to runs in which [Et_3N] = 4.0 × 10^{-2} *M;* open ellipses, etc., [Et_3N] = 2.0 × 10^{-2} *M.*

The data for this and some related experiments are summarized in Figure 1; analogous results were obtained with phenylmethanesulfonyl chloride and pyridine at 25°. With propyl or isopropyl alcohol as the "sulfene trap" the reaction was found to be strictly second order: first order in both sulfonyl chloride and tertiary amine and *zero* order in the alcohol. As is evident from Figure 1, with the other "sulfene trapping agents" there is a linear dependence of k_{obsd}, the pseudo-first-order rate constant, on the concentration of the "sulfene trap," and each of these straight lines extrapolates to the same intercept within experimental uncertainty. These observations are in accord with eq 2,[2]

$$\text{rate} = k_2[RSO_2Cl][\text{base}] + k_3[RSO_2Cl][\text{base}][\text{trap}] \quad (2)$$

in which [base] and [trap] refer to the concentrations of, respectively, the tertiary amine and the "sulfene trapping agent," *i.e.*, aniline, water, etc., as indicated in Figure 1.[3] The observation that at least part of the reaction is zero order in a stoichiometric component of the reaction *requires* the formulation of an intermediate which reacts with that component in a step having no detectable influence on the rate. Taken with previous work these results are reasonably interpreted only in terms of the intermediacy of a sulfene and constitute the first *kinetic* evidence for such a species.

Three mechanisms for the title reaction which are compatible with the above and previously known data warrant further discussion:[4] (a) direct one-step elim-

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[1] For leading references see G. Opitz, *Angew. Chem. Intern. Ed. Engl.*, 6, 107 (1967).

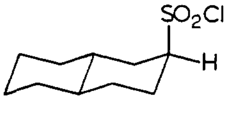
[2] Control experiments showed that reaction of the sulfonyl chloride with the "trapping agents" in the absence of the tertiary amine was negligible under the conditions of the kinetic measurements.

[3] The origin of the third-order component has not been fully investigated, but among the more plausible mechanistic possibilities are (a) hydrogen bonding of the leaving chloride ion in the transition state by the "sulfene trap" and (b) attack of the α hydrogen by a "sulfene trap"–tertiary amine hydrogen-bonded complex. That the third-order term also leads to sulfene formation is shown by the almost exclusive formation of CH_2DSO_2NHPh (after work-up) from the reaction of methanesulfonyl chloride, triethylamine, and aniline-d_2 under conditions in which the third-order term contributes about half of the product.

ination (E2 mechanism), (b) slow formation of the conjugate base of the sulfonyl halide[5] followed by rapid loss of $\mathrm{Cl^-}$ (E1cb mechanism), (c) substitution of chlorine by the tertiary amine in the slow step followed by rapid Hofmann-like elimination[6] of the elements of $\mathrm{Et_3N^+H}$ ("SN2 followed by E" mechanism).

The E1cb mechanism is excluded on the following grounds. The rates of formation of $\mathrm{Ph\bar{C}HSO_2Z}$ from a number of compounds of the type $\mathrm{PhCH_2SO_2Z}$, where Z = Ph, $\mathrm{OCH(CH_3)_2}$, $\mathrm{CF_3}$, and NMePh, with triethylamine in dimethoxyethane–$\mathrm{D_2O}$ were measured by following the rate of exchange of deuterium for hydrogen. These rates were found to vary over a range of less than 10^2, and even the fastest of these reactions was about 10^8 times slower than the reaction of $\mathrm{PhCH_2SO_2Cl}$ under the same conditions. Such a disproportionately large effect is only interpretable in terms of a different mechanism of reaction, *i.e.*, $\mathrm{Ph\bar{C}HSO_2Cl}$ formation cannot be involved in formation of $\mathrm{PhCH{=}SO_2}$ from $\mathrm{PhCH_2SO_2Cl}$.

To distinguish between the remaining two possibilities given above, namely the E2 and "SN2 followed by E" mechanisms, compounds **1** and **2** were synthesized



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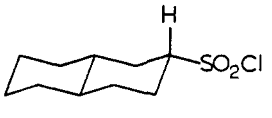

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in order to determine their relative ease of sulfene formation. From conformational considerations it can be predicted that direct E2 elimination of HCl from **1** to give the sulfene would be faster than the same reaction of **2**, owing to (a) lowering of the relatively greater nonbonding interaction energy[7] in **1** and perhaps also (b) the existence of greater nonbonding repulsions in the transition state from **2** between the attacking triethylamine and groups adjacent to the hydrogen being removed as compared with that from **1**. Such a prediction finds support in the faster rate of reaction of axial *vs.* equatorial epimers in (a) chromic acid oxidation of cyclohexanols[8a] and (b) formation of 1-*t*-butyl-4-methylenecyclohexane either by thermolysis of the corresponding axial and equatorial phenyl sulfoxides or elimination of HBr from the 4-*t*-butylcyclohexanemethyl bromides with potassium *t*-butoxide in *t*-butyl alcohol.[9] On the other hand, if the rate-determining step is a SN2 displacement on the sulfur of the $\mathrm{SO_2Cl}$ group, the reaction would be expected to be slower for **1** than for **2**. This may be argued by analogy with the rates of (a) hydrolysis of esters[8b] and (b) the reaction of the 4-*t*-butylcyclohexanemethyl *p*-nitrobenzenesulfonates with lithium bromide,[9] but is most clearly indicated by the simple solvolysis of **1** and **2** in the absence of added base (a reaction which does not proceed *via* the sulfene[10]), in which **2** reacts roughly 15 times faster than **1**. It was found that **1** forms the sulfene 71 times faster than **2** with triethylamine at −25° in dimethoxyethane, clearly excluding the "SN2 followed by E" mechanism and therefore leaving the direct E2 mechanism as the only route compatible with the available data. As confirmation of the intermediacy of the sulfene in the triethylamine-induced reactions of **1** and **2**, it was found that essentially the same mixture of 2-decalinsulfonate salts was obtained by treating either **1** or **2** with triethylamine in dimethoxyethane–water.

Further definition of the nature of the transition state is provided by the following. (a) A reasonable correlation with σ^- was obtained for the rates of reaction of $\mathrm{XC_6H_4CH_2SO_2Cl}$ with pyridine in dimethoxyethane and aniline, $\rho^- = 2.35$. (b) Deuterium isotope effects ($k_\mathrm{H}/k_\mathrm{D}$, obtained by determining product ratios) for the reaction of $\mathrm{PhCHDSO_2Cl}$ with base in the presence of water are: pyridine 2.0,[11] triethylamine 2.6,[11] and sodium hydroxide 4.0. (c) A rate difference of $\sim 2 \times 10^5$ was found between triethylamine and pyridine with methanesulfonyl chloride. These data are entirely consistent with the E2 mechanism and suggest a transition state in which the transfer of the proton from carbon to base is nearing completion and a partial negative charge has developed on the carbon as well as on the chlorine.

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(4) The data summarized here also permit the exclusion of the considerable number of less likely mechanisms that come to light in a systematic search for alternatives to the ones given here. These will be discussed in the full paper.

(5) Rapid and reversible formation of the conjugate base followed by slow loss of $\mathrm{Cl^-}$ is precluded by deuterium labeling experiments,[1] in which exchange of one and only one hydrogen of a methyl or methylene group was observed.

(6) If the elimination were the slow step the reaction would have to be *second* order in $\mathrm{Et_3N}$.

(7) Comparison of the nmr spectra of cyclohexanesulfonyl chloride and **1** and **2** shows that cyclohexanesulfonyl chloride exists almost entirely in the equatorial form. There seems to be no reported determination of the conformational energy of the $\mathrm{SO_2Cl}$ group, but that of the $\mathrm{SO_2Ph}$ group has been estimated to be 2.5 kcal/mole by E. L. Eliel, E. W. Della, and M. Rogic, *J. Org. Chem.*, 30, 855 (1965).

(8) For a summary see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965: (a) pp 81–84; (b) pp 72–78.

(9) J. F. King and M. J. Coppen, unpublished results.

(10) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 87, 5684 (1965).

(11) Determined by Mr. B. G. Peterson.

(12) Holder of a Province of Ontario Graduate Fellowship, 1966–1969.

J. F. King, T. W. S. Lee[12]
Department of Chemistry, University of Western Ontario
London, Ontario, Canada

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Reaction of Oxepin–Benzene Oxide with Nucleophiles

Sir:

The metabolic products of aromatic compounds are often observed to be the corresponding 1,2-dihydroxy-1,2-dihydrobenzene or derivatives thereof.[1] Other metabolic products containing oxygen and nitrogen functions on the saturated carbon atoms of a 1,3-cyclohexadiene have been reported.[5] Chorismic acid, the

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(1) For example, in mammalian systems chlorobenzene is metabolized to 4-chloro-*trans*-1,2-dihydroxy-1,2-dihydrobenzene,[2] naphthalene to *trans*-1,2-dihydroxy-1,2-dihydronaphthalene,[3] and phenanthrene to 1,2-hydroxy-1,2-dihydrophenanthrene.[4]

(2) J. N. Smith, B. Spencer, and R. T. Williams, *Biochem. J.*, 47, 284 (1950).

(3) J. Holtzman, J. R. Gillette, and G. W. A. Milne, *J. Amer. Chem. Soc.*, 89, 6341 (1967), and references cited therein.

(4) E. Boyland and G. Wolf, *Biochem. J.*, 42, XXXII (1948).

(5) They include *trans*-3-hydroxy-2,3-dihydroanthranilic acid,[6] *trans*-2,3-dihydroxy-2,3-dihydrobenzoic acid,[7] isochorismic acid,[8] and the antibiotic gliotoxin.[9]

(6) J. R. D. McCormick, *et al.*, *J. Amer. Chem. Soc.*, 84, 3711 (1962).