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REVERSIBLE AND IRREVERSIBLE E1cB MECHANISMS OF SULFENE FORMATION FROM ARYL ARYLMETHANESULFONATES

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In connection with our previous study[1] of the mechanism of formation of sulfenes from alkanesulfonyl halides, we have looked at the reaction of aryl arylmethanesulfonates (1), in the hope of finding for comparison an example of sulfene formation by an E1cB mechanism. We wish to report experiments which indicate that these esters may react by either "reversible" or "irreversible" E1cB processes[2], depending on the leaving group $\bar{O}Ar^2$. While this paper was being written, a preliminary report by Williams *et al.*[3] appeared, describing closely related and in some ways complementary experiments leading to similar conclusions.

Reaction of 1a with triethylamine (Et_3N) in 1,2-dimethoxyethane (DME) containing D_2O merely

$$\underset{\underline{1}}{Ar^1CH_2SO_2OAr^2} + Et_3N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\underline{2}}{Ar^1\bar{C}HSO_2OAr^2} + Et_3\overset{+}{N}H$$

$$\underset{\underline{2}}{Ar\,\bar{C}HSO_2OAr^2} \xrightarrow{k_2} \underset{\underline{3}}{Ar^1CH{=}SO_2} + \underset{\underline{4}}{\bar{O}Ar^2}$$

$$ArCH{=}SO_2 + H_2O + Et_3N \xrightarrow{k_3} Ar^1CH_2SO_3^- + Et_3\overset{+}{N}H$$

	Ar^1	Ar^2
a)	phenyl	phenyl
b)	phenyl	*p*-nitrophenyl
c)	*p*-nitrophenyl	*p*-nitrophenyl
d)	*p*-chlorophenyl	*p*-nitrophenyl
e)	*m*-chlorophenyl	*p*-nitrophenyl
f)	*m*-nitrophenyl	*p*-nitrophenyl
g)	phenyl	2,4-dinitrophenyl
h)	*p*-nitrophenyl	2,4-dinitrophenyl
i)	*p*-chlorophenyl	2,4-dinitrophenyl
j)	*m*-chlorophenyl	2,4-dinitrophenyl
k)	*m*-nitrophenyl	2,4-dinitrophenyl
l)	*p*-cyanophenyl	2,4-dinitrophenyl
m)	*p*-tolyl	2,4-dinitrophenyl
n)	phenyl	2-chloro-4-nitrophenyl

gave the exchanged ester ($PhCD_2SO_2OPh$), but *1b* gave[4] $PhCD_2SO_3^-$ as well as $PhCD_2SO_2O$-C_6H_4-*p*-NO_2. With *1g* or *1n*, however, the recovered ester after partial reaction was unexchanged and the product *monodeuteriated* ($PhCHDSO_3^-$). With *N*-(2-methyl-1-propenyl)pyrrolidine, *1b*[4] and *1h* gave the characteristic sulfene-enamine cycloadducts. Under these conditions *1b*, *1g*, *1h* and *1n* evidently react with Et_3N to form the sulfene (*2*)[5,6].

We have measured spectrometrically the rates of formation of *4* from *1* and Et_3N (or pyridine) in 20% H_2O-DME (*i.e.* 20 volumes of H_2O made up to 100 volumes with DME). Reaction of *1c* with Et_3N showed specific base promotion, and a Hammett plot for the reaction of the *p*-nitrophenyl esters (*1b* to *1f*) with Et_3N (at "pH" 9.40[7], $\mu = 0.05$) gave $\rho^- = 0.54$ ($r = 0.992$). These data taken with the deuterium exchange found with *1b* strongly suggest the reversible ElcB mechanism for the *p*-nitro-esters.

The 2,4-dinitro-esters, however, behave differently: (a) with pyridine the series *1g* to *1ℓ* gave[8] $\rho^- = 2.38$ ($r = 0.9995$), (b) with Et_3N *1g*, *1h* and *1m* gave $\rho^- = 2.7 \pm 0.2$, and (c) reaction of *1m* with Et_3N showed only general base promotion. These data together with the formation of monodeuteriated product are consistent with *either* an E2 process (evidently "ElcB-like" or "paenecarbanion") *or* an irreversible ElcB mechanism, for the 2,4-dinitro-esters.

For an ElcB process, assuming a steady-state carbanion concentration and also that the sulfene trapping (step 3) is relatively fast[1], one obtains

$$k_{obs} = \frac{k_1k_2[Et_3N]}{k_{-1}[Et_3\overset{+}{N}H] + k_2} \qquad (1) \qquad \text{or} \qquad \frac{[Et_3N]}{k_{obs}} = \frac{k_{-1}}{k_2k_1}[Et_3\overset{+}{N}H] + \frac{1}{k_1} \qquad (2)$$

If the reaction of *1g* is an irreversible ElcB process then $k_{obs}/[Et_3N]$ equals k_1, and should be predictable from a Hammett plot of k_1 for a series of esters (*1*) in which $k_2 \ll k_{-1}[Et_3NH^+]$, *i.e.* those which either do not yield the sulfene at all or which do so *via* the reversible ElcB mechanism. In the hope of approximating a Hammett plot for k_1 we have measured the rate constant (per hydrogen) for the reaction $PhCH_2SO_2OAr^2 + D_2O \xrightarrow{Et_3N} PhCD_2SO_2OAr^2$ in D_2O-DME (see Figure). Also shown in the Figure is the Hammett plot for the elimination with *1g*, *1n* and two other esters which give a *mono*exchanged product. The best straight lines for the two plots are parallel and *almost co-linear*[9], in excellent agreement with an irreversible ElcB mechanism for *1g*, *1n* and the two others.

A change from the reversible to the irreversible ElcB mechanism on changing from *1b* to *1n*

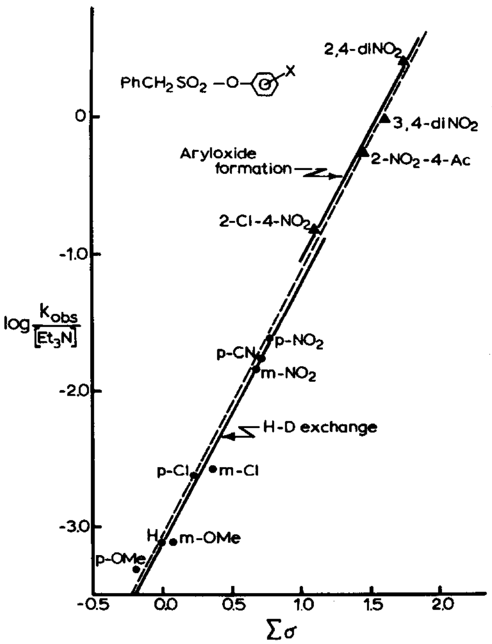

FIGURE. Hammett plot for (a) $(k_{obs})_{exch}/[Et_3N]$, the rate constant (per hydrogen) for the H-D exchange at the methylene group in aryl phenylmethanesulfonates (closed circles), and (b) $(k_{obs})_{ArO^-}/[Et_3N]$, the rate constant for formation of the aryloxide anion from aryl phenylmethanesulfonates (triangles) (both sets of reactions with Et_3N in 20% D_2O-DME at 20.0°). The solid lines are the least squares lines for each reaction, the broken line is that for all points; σ^n values were used for *meta* and *para* substituents, and for *ortho* substituents the $\sigma^0_{\underline{o}}$ values of Jones and Smith[10].

would mean that $k_{-1}[Et_3\overset{+}{N}H]$ changes from greater than k_2 to less than k_2. It seemed possible that with *1n* k_2 might be sufficiently small that an increase in $[Et_3NH^+]$ might make $k_{-1}[Et_3\overset{+}{N}H] > k_2$, *i.e.* give a change from the irreversible to the reversible (or at least to a mixed) process. This would show up experimentally as a decrease in $k_{obs}/[Et_3N]$ with increase in $[Et_3\overset{+}{N}H]$, whereas if *1n* reacts *via* an E2 process, $k_{obs}/[Et_3N]$ should be independent of $[Et_3NH^+]$. We observed the following. (a) A change in $[Et_3NH^+]$ from 0.02 to 0.1 M (μ = 0.1) *decreased* $k_{obs}/[Et_3N]$ by about 25%, and a plot of $[Et_3N]/k_{obs}$ *vs* $[Et_3NH^+]$ gave a straight line, as predicted by eq. (2), from which we obtained $k_1 = 0.28\ M^{-1}s^{-1}$ and $k_{-1}/k_2 = 5.5$. (b) When *1n* was treated with Et_3N in D_2O-DME (i) in the absence of added Et_3NH^+ the unreacted ester recovered after ~80% reaction was undeuteriated, but (ii) in the presence of 0.07 M $Et_3\overset{+}{N}HCl^-$ (enough to give a lowering of $k_{obs}/[Et_3N]$ of about 20%) the recovered ester was partly deuteriated at the methylene group (the ratio of CH_2:CHD:CD_2 products was 60:35:4). These results are readily accounted for on the basis of an ElcB mechanism but not by an E2 process.

We should point out, however, that there is a possibility that the exchange reactions proceed primarily by reversal of the sulfene (*3*) formation, rather than reversal from the carbanion (*2*). Trapping of the sulfene by the phenoxide is, of course, the method by which these esters are prepared in the first place (though under different conditions) and this possibility should not, in our view, be disregarded or dismissed without evidence. We found, however, that on increasing the concentration of 4n, there was no increase in deuterium exchange comparable to that found with $Et_3NH^+Cl^-$, as would be required if there were a substantial proportion of sulfene reversal; we estimate that a small number of the sulfenes (~5% of the total) probably do undergo this reversal.

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