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ON THE ACTIVATION ENERGY FOR THE HYDROLYSIS OF BIS-(2-CHLOROETHYLETHYL) SULFIDE. II

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ABSTRACT

Dilute solutions of mustard, bis-(2-chloroethylethyl) sulfide, hydrolyze to form the chlorohydrin and HCl: the chlorohydrin subsequently hydrolyzes to form the thiodiglycol and another mole of HCl. The kinetics of these reactions constitute consecutive, first-order reactions which past investigators approximated as a single, first-order reaction. In an earlier paper, a non-linear least-squares program was used to refit these data to consecutive, first-order kinetics in order to refine the activation parameters for mustard hydrolysis. It was shown, however, that the early work did not conform to consecutive, first-order reactions, suggesting that dissolution of mustard interfered with the hydrolysis. Only the data of Bartlett and Swain were clearly hydrolysis of mustard: however, rate data were only run at 25°C.

This paper reports kinetics of mustard hydrolysis measured in 0.025 mole fraction ethanol–water between 20 and 40°C. Over this temperature range, the enthalpies of activation for mustard and the chlorohydrin are 18.5 and 18.6 kcal mol^{-1}, respectively. These results are similar to enthalpies of activation for other 2-chloroethylalkyl sulfides, but smaller than those reported for mustard hydrolysis in the past.

INTRODUCTION

Mustard, bis-(2-chloroethylethyl) sulfide, hydrolyzes to produce mustard chlorohydrin and HCl, after which the mustard chlorohydrin loses another chloride to form thiodiglycol and HCl. The mechanism of the hydrolysis involves the formation of ethylenesulfonium ions [1] as shown in Scheme 1. Since $k_w \gg k_{-1}$ and $k_w \ll k_{-2}$, each step appears as a first-order reaction with rate coefficients k_1 and k_2, respectively.

Previous investigators measured the rate of mustard hydrolysis by monitoring changes in pH or conductance with time, and the overall process was approximated as a single reaction step, with k determined from the initial part of the reaction [2–5]. Bartlett and Swain [6] attempted a direct measure-

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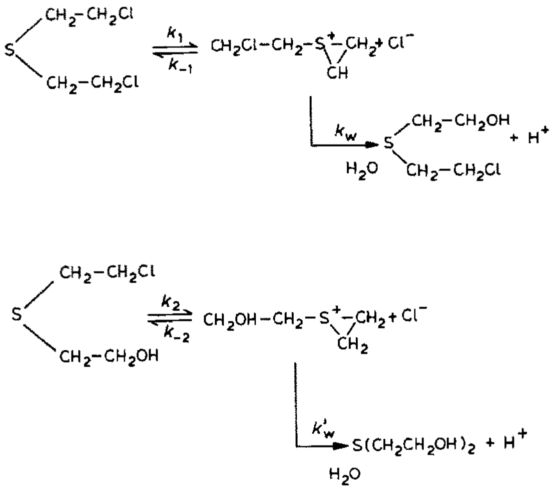

(1)

(2)

Scheme 1

ment of k_1 by first measuring the hydrolysis of mustard chlorohydrin to obtain k_2, and then using the value of k_2 with a graphical technique [7] to obtain k_1. They claimed that k_1 could be determined within 1% of the actual k_1 value with their graphical method. Bartlett and Swain did their measurements at one temperature, 25 °C, so that the activation parameters quoted for mustard hydrolysis [2–5] are based on the rate coefficients assuming a single reaction.

The advent of high-speed, digital computers eases the problem of treating complex kinetic schemes. We have modified a non-linear, least-squares program [8] to fit consecutive, first-order reactions and examined the literature for the original data on which the rate coefficients were calculated in order to obtain values of k_1 free of any approximation [9]. However, all of the published data on which activation parameters were based failed to conform to consecutive first-order kinetics.

In this article we report on calculations made with new measurements of mustard hydrolysis at eight temperatures, from 10 to 45 °C, in order to obtain reliable activation parameters for the hydrolysis of mustard at ambient conditions.

EXPERIMENTAL

All kinetic runs were conducted on the multiple computer-controlled pH stat at SRI, International [10].

Mustard was supplied by the U.S. Army Chemical Research, Development and Engineering Center (CRDEC), and used as received. The purity, as determined by gas chromatography, was 99.5%. Millipore water was degassed with nitrogen purge before use. Absolute ethanol was used as obtained from the U.S. Industrial Chemical Corporation.

A typical kinetic run proceeded as follows. First, 4 ml of neat mustard (5.08×10^{-3} g, 3.19×10^{-5} mol) was added to 4 ml of absolute ethanol. Then, 2 ml of the mustard–ethanol solution was transferred to a 250-ml reaction flask containing 17.25 ml of absolute ethanol and 230.7 ml of degassed millipore water, which was adjusted to pH 7. The resulting solution contained 0.025 mole fraction ethanol. The hydrolysis was monitored by following the production of HCl from 10 to 45°C at 5°C intervals. The temperature was maintained within 0.01°C using a circulating coolant. The head-space in the reaction flask was purged with nitrogen for each run. To verify our experimental procedures and data analyses, we measured the rates at identical conditions to that of Bartlett and Swain [6]: consistent k_1 values were obtained.

RESULTS AND DISCUSSION

The mechanism depicted in equations (1) and (2) can be represented as

$$\mathrm{M} \overset{k_1}{\rightarrow} \mathrm{CH} \overset{k_2}{\rightarrow} \mathrm{TG} \tag{3}$$

$$[\mathrm{H}^+]_t = [\mathrm{M}]_0\left[2 - \left(\frac{k_1 - 2k_2}{k_1 - k_2}\right)\mathrm{e}^{-k_1 t} - \left(\frac{k_1}{k_1 - k_2}\right)\mathrm{e}^{-k_2 t}\right] \tag{4}$$

where $[\mathrm{M}]_0$ is the initial concentration of mustard, and it is assumed that only mustard is present initially.

Equation (4) was fitted with the non-linear, least-squares program with: $[\mathrm{H}^+]$ as the dependent variable; time, t, as the dependent variable; k_1, k_2 and [M] as the parameters to be fitted. De Tar [11] and, more recently, Swain et al. [12], elaborated on the need to treat the experimental value at infinite time as a parameter to be fitted. Bentley and Carter [13] discussed the difficulties encountered when measuring solvolyses of *t*-butyl halides in water, such as the apparent induction period caused by dissolved carbon dioxide or the failure of the substrate to dissolve completely. Mismatched experimental and "best-fit" infinity values reflect such errors. These concerns are magnified with mustard, since the rate of solvation is slower than common alkyl halides and the kinetics are not simple, first-order.

In addition to precautions urged by Bentley [13] in making solvolysis measurements, we imposed another requirement on the values of k_1, k_2 and $[\mathrm{M}]_0$ computed from fitting hydrogen ion production to equation (4), namely that k_2 must agree with predicted values of k_2 based on those measured directly from CH at 10 and 25°C by McManus et al. [14, personal

TABLE 1

Hydrolysis of mustard in 0.025 x_2 EtOH at 40.0°C [a]

Time (s)	$[H^+]$ ($\times 10^6$ M)		
	Experimental	Calculated [b]	Calculated [c]
19	25	25	25
37	49	48	48
56	71	71	71
74	90	89	89
93	104	105	105
112	118	119	119
130	127	129	138
149	133	138	138
167	144	145	145
186	149	150	150
204	156	154	154
223	159	158	158
241	161	160	160
260	160	163	162
	163	–	–
k_1 ($\times 10^3$/s)		15.4±1.3	15.2±0.4
k_2 ($\times 10^3$/s)		20.1±5.3	21.1 (fixed)
$[H^+]_\infty$ ($\times 10^6$ M)		169±1.8	169±1.4

[a] Mustard concentration, 8.8×10^{-5} M.

[b] Calculated values of $[H^+]$ letting k_1, k_2, and $[M]_0$ vary: errors are sample standard deviation computed by program.

[c] Calculated with k_2 fixed.

communications]. The hydrolysis data were refitted to equation (4) with the k_2 value fixed to McManus' result: if the results were unchanged, it was felt that we were indeed monitoring mustard hydrolysis free from unwanted dissolution or reaction paths leading to the formation of sulfonium salts [15].

The majority of the runs failed to meet all the checks imposed on the data, however, successful runs were made at 20 and 40°C. Table 1 lists results of one run at 40°C.

Table 2 lists the enthalpies of activation and entropies of activation for mustard, the chlorohydrin and 2-chloroethylethyl sulfide [16]. The entropy

TABLE 2

Activation parameters for 2-chloroethylalkyl sulfide hydrolysis in 0.025 x_2 EtOH

Compound	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal mol^{-1} K^{-1})	Ref.
$S(CH_2CH_2Cl)_2$	18.5	−9.3 [a]	This work
$HOCH_2CH_2SCH_2CH_2Cl$	18.6	−7.1	This work
$CH_3CH_2SCH_2CH_2Cl$	20.2	+1.0	[16]

[a] Symmetry-corrected.

of activation is symmetry-corrected in order to compare with the other 2-chloroethylalkyl sulfides. Published values of $\Delta H^{\neq}$ for mustard ranged from 20–24 kcal mol^{-1} [1].

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