The Hydrolysis of Sulfamoyl Chlorides. I. Hydrolysis of Dimethylsulfamoyl Chloride. Heat Capacity of Activation, the Secondary γ-Deuterium Isotope Effect, and Solvent Isotope Effect

E. C. F. Ko[1] and R. E. Robertson*

Contribution from the Department of Chemistry, the University of Calgary, Calgary 44, Alberta, Canada. *Received April 12, 1971*

Abstract: The hydrolysis of dimethylsulfamoyl chloride in water is characterized by a large negative value of the apparent heat capacity of activation ($\Delta C_p^{\ddagger} = -76$ cal deg^{-1} mol^{-1}). The corresponding term in D_2O is -71 cal deg^{-1} mol^{-1} and in the presence of a 5% mol fraction of acetonitrile, -44 cal deg^{-1} mol^{-1}. These values point to a degree of solvent reorganization similar to that found in the hydrolysis of tertiary halides where an SN1 mechanism is accepted. That steric hindrance to the approach of the weak nucleophile water, rather than some unusual resonance release of electrons by the dimethyl group, favors the SN1 mechanism is supported by showing that the corresponding hexadeuterio isomer gives an *inverse* secondary γ-deuterium isotope effect of 0.95.

In general, values of the temperature coefficient of the enthalpy of activation ($\Delta C_p^{\ddagger}$) for the hydrolysis of a series of alkyl halides and related compounds fall into two regions, either close to -50 cal deg^{-1} mol^{-1}, or close to -80 cal deg^{-1}mol^{-1}. The former value is characteristic of those reacting by the SN2 mechanism, the latter are normally found for solutes reacting by an SN1 mechanism. The difference has been explained in terms of differences in the degree of charge development achieved in the activation process with resulting differences in solvent reorganization.[2] Of course, differences in $\Delta C_p^{\ddagger}$ can arise from a number of causes other than the effect of temperature on solvent reorganization in the activation process; *e.g.*, differences in initial state interaction,[3] specific substituent interaction,[4] mixed kinetics.[5,6] Such effects normally result in a less negative value of $\Delta C_p^{\ddagger}$ but not necessarily so.[7] Thus, in a recent detailed study of the hydrolysis of a series of para substituted benzenesulfonyl chlorides Rossall and Robertson[4] found $\Delta C_p^{\ddagger}$ for *p*-methylbenzenesulfonyl chloride was -72 cal deg^{-1} mol^{-1}, a value which suggested that solvent reorganization corresponded to an SN1 mechanism, while other evidence strongly supported the conclusion that for this compound as for the hydrolysis of most sulfonyl chlorides, the SN2 mechanism was operative. Since there are at least two examples in the literature[8,9] where solvolytic displacement of Cl$^-$ from a sulfonyl group was supposed to occur by an SN1 mechanism it became a matter of some interest to find what the value of $\Delta C_p^{\ddagger}$ could be expected for the hydrolysis of a suitable sulfonyl chloride by this mechanism.

Vizgert and Savchuk[8] claimed that 2,4,6-trimethylbenzenesulfonyl chloride reacted by such a mechanism but unfortunately this compound proves too insoluble for our purpose. Hall had suggested that the dimethylsulfamoyl chloride (I) reacted by an SN1 mechanism[9] and although more recently Rogne[10] presented evidence which raised doubts about such a conclusion, at least in the presence of azide ion, he also reported that the kinetic solvent isotope effect was 1.33, a value significantly lower than those found for the substituted benzenesulfonyl chlorides[4] and at least consistent with little or no nucleophilic interaction at the transition state.[11] In spite of the azide results, it seemed possible that I reacted by an SN1 mechanism and hence careful study of the temperature dependence of the rate of hydrolysis of I was made in H_2O, in D_2O, and in a mixture of water–acetonitrile, in which the organo addend was supposed to have broken down a greater part of the water structure.[12] The results of this investigation and the relation of these results to the Sneen–Larsen proposal[13] are discussed here.

Results and Discussion

Rate determinations and other procedures were the same as described previously.[4] Characterization of the reactants is given in the Experimental Section.

First-order rates with a precision of 0.5% or better were fitted to a three-parameter equation[14] (1). A

$$\log k = A_1 + \frac{A_2}{T} + A_3 \log T \qquad (1)$$

parallel study was done in D_2O and in the acetonitrile–water mixture. The calculated empirical constants A_1, A_2, and A_3 for each series together with the number of rate constants in the temperature range for such a calculation are reported in Table I. The pseudothermodynamic activation parameters calculated from eq 1 according to the method outlined previously[2a] are given in Table II. From the empirical constants in

---

[1] Postdoctoral Fellow, 1970.

[2] (a) R. E. Robertson, *Progr. Phys. Org. Chem.*, **4**, 213 (1967); (b) E. A. Moelwyn-Hughes, R. E. Robertson, and S. E. Sugamori, *J. Chem. Soc.*, 1965 (1965).

[3] R. E. Robertson and P. M. Laughton, *Can. J. Chem.*, **43**, 154 (1965).

[4] B. Rossall and R. E. Robertson, *ibid.*, **49**, 1441 (1971).

[5] L. J. Bruebaker, L. Treindl, and R. E. Robertson, *J. Amer. Chem. Soc.*, **90**, 4611 (1968).

[6] A. Queen, *Can. J. Chem.*, **45**, 1619 (1967).

[7] J. M. V. Scott and R. E. Robertson, *ibid.*, in press.

[8] R. V. Vizgert and E. V. Savchuk, *Zh. Obshch. Khim.*, **26**, 2268 (1956).

[9] H. K. Hall, *J. Amer. Chem. Soc.*, **78**, 1450 (1956).

[10] O. Rogne, *J. Chem. Soc. B*, 663 (1969).

[11] P. M. Laughton and R. E. Robertson, "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter VII.

[12] R. E. Robertson and S. E. Sugamori, in press.

[13] R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362 (1969).

[14] Wold (S. Wold, *Acta Chem. Scand.*, **24**, 2321 (1970)) has published an alternative treatment which is claimed to have certain advantages over this treatment. The value of $\Delta C_p^{\ddagger}$ so derived is not likely to be significantly different from that given here.

Table I. Empirical Constants for the Three-Parameter Equation (1) for the Hydrolysis of Dimethylsulfamoyl Chloride

Solvent	A_1	$-A_2$	$-A_3$	$N_{T_1}{}^{T_2\,b}$
H_2O	119.4790	8870.663	37.23724	$33_1{}^{24}$
D_2O	113.1678	8691.576	34.97399	$36_4{}^{33}$
H_2O–MeCN[a]	71.65205	6515.594	21.19692	$24_1{}^{40}$

[a] 0.95 mol fraction of water. [b] N is the number of rate determinations. T_1 and T_2 define the lower and upper limits of the experimental temperature range.

Table II. Pseudothermodynamic Activation Parameters for the Hydrolysis of Dimethylsulfamoyl Chloride at 15°

Solvent	$\Delta H^{\ddagger}$, cal mol^{-1}	$-\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	$-\Delta C_p{}^{\ddagger}$, cal deg^{-1} mol^{-1}
H_2O	18,694 ± 12	6.84 ± 0.04	76 ± 1
D_2O	19,171 ± 35	5.75 ± 0.12	71 ± 4
H_2O–MeCN[a]	17,103 ± 9	13.28 ± 0.02	44 ± 1

[a] 0.95 mol fraction of water.

Table III. Secondary Deuterium Isotope Effect for the Hydrolysis of Dimethylsulfamoyl Chloride and Its d_6 Analog in H_2O

Temp, °C	10^4k_H, sec^{-1} [a]	10^4k_D, sec^{-1} [b]	k_H/k_D
0.791	2.120	2.241	0.946
5.002	3.715	3.920	0.948
10.029	7.036	7.369	0.955
15.108	12.93	13.48	0.959
20.105	22.78	23.70	0.961
25.142	39.13	40.97	0.955

[a] Calculated from the empirical constants, Table I. [b] Experimental.

Table IV. Solvent Isotope Effect for the Hydrolysis of Dimethylsulfamoyl Chloride in H_2O and in D_2O

Temp, °C	$10^4k_{H_2O}$, sec^{-1}	$10^4k_{D_2O}$, sec^{-1}	k_{H_2O}/k_{D_2O}
5	3.713	2.718	1.366
15	12.75	9.598	1.328
25	38.55	29.90	1.289

Table I, rate constants were evaluated at any desired temperatures. Typical values are presented in Tables III and IV, respectively. Table III also includes the secondary deuterium isotope ratio, k_H/k_D, while in Table IV we give the solvent isotope ratio, k_{H_2O}/k_{D_2O} found by repeating the rate study in D_2O. Rogne[10] has reported the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, as being 16.6 kcal mol^{-1} and -22.0 cal mol^{-1} deg^{-1}, respectively, and k_{H_2O}/k_{D_2O} being 1.33 at 25° for the hydrolysis of I. A least-mean-square fit of his data to eq 1 when $A_3 = 0$ gives $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ equal to 15.80 ± 0.9 kcal and -10.5 ± 3.1 cal mol^{-1} deg^{-1} at 25°. The discrepancy between his results and those shown in Table II is probably due to the larger error (±3%) in his rate data. A similar explanation will account for the even more negative value of $\Delta S^{\ddagger}$ reported by Hall.[9]

Before it is possible to make use of the pseudothermodynamic terms derived from kinetic data it is necessary to estimate the relative differences of interaction with water of the compounds of interest in the initial states. Here this interaction applies particularly to the relative stability of the hydrogen-bonded water structure adjacent to the sulfonyl oxygens. The solvent structure about the weakly polar methyl groups tends to be proportional to volume[15–18] and important in determining $\Delta C_p{}^{\ddagger}$ only if extensive solvent reorganization occurs about these groups in the activation process (see, *e.g.*, ref 4 and 19). To estimate whether the differences in interaction between the sulfonyl oxygens and water were likely to be responsible for the more negative value of $\Delta C_p{}^{\ddagger}$ found for the hydrolysis of I compared to other sulfonyl chlorides, we applied the test developed by Kartha, *et al.*[20] The results are summarized in Table V and show that hydrogen bonding under favorable conditions is far smaller than that found for the sulfonic esters and under similar conditions does not vary significantly between methanesulfonyl chloride and *p*-methylbenzenesulfonyl chloride, which give evidence of reacting by an SN2 mechanism, in spite of having quite different $\Delta C_p{}^{\ddagger}$ values,[4,19] and I which Hall believes reacts by an SN1 mechanism.

Table V. The Wave-Number Shift for Hydrogen Bonding between Sulfonyl Oxygens and *p*-Chlorophenol in CCl_4 at20°

Compound	Concn, $M \times 10^2$	Δv, cm^{-1} [a]
p-ClC_6H_4OH	2.55	0
CH_3SO_2Cl	5.76	60.0[b]
p-$CH_3C_6H_4SO_2Cl$	5.12	64.0
$(CH_3)_2NSO_2Cl$	5.67	62.0
$(CH_3CH_2)_2NSO_2Cl$	5.95	65.0

[a] Δv is the displacement of the maximum of the complex band from that of free *p*-chlorophenol. [b] 58.5 at 25° (see ref 20).

The ion-pair mechanism introduced by Winstein and coworkers[21,22] and more recently extended by Sneen and Larsen[13] gives explicit formalism to what was implicit in the SN1–SN2 designations. This statement in no way detracts from the desirability of recognizing the potential kinetic complexity inherent in solvolytic mechanism nor diminishes the value of the formal treatment. Thus, while the solvent-separated ion pair may be viewed as a logical necessity interposed between the activated intermediate and the classical solvent-separated ions, the possible presence of such a species provides an intermediate pathway to products with intermediate requirements in solvent reorganization. We may expect to find evidence of such differences in the temperature coefficient of the enthalpy of activation for hydrolysis if the differences in the activation enthalpy are favorable.

Though we are unaware of any explicit statement, it would appear that interaction between the moieties of the intimate ion pair was assumed to be purely electro-

---

(15) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(16) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

(17) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

(18) E. M. Arnett, W. B. Kouer, and W. Carter, *J. Amer. Chem. Soc.*, **91**, 4028 (1969).

(19) R. E. Robertson, B. Rossall, and S. E. Sugamori, *Can. J. Chem.*, **47**, 4199 (1969).

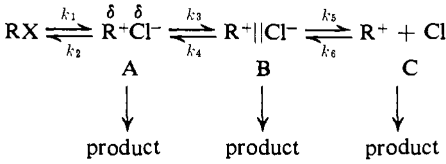
(20) V. Kartha, R. N. Jones, and R. E. Robertson, *Proc. Indian Acad. Sci.*, **58**, *A*, 216 (1963).

(21) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chem. Ind.* (*London*), 664 (1954).

(22) S. Winstein, B. Appel, R. Baker, and A. Diez, *Chem. Soc. Spec. Publ.*, No. **19**, 109 (1965).

static. While this assumption seems appropriate as a limiting condition, it is hardly a necessary condition. Hence, we regard the generalized intimate ion pair as used by Sneen and Larsen[13] in solvolytic mechanisms to be indistinguishable from a classical activated intermediate; for many examples reported[22] this intermediate probably tended toward the limiting condition.

In the Sneen–Larsen generalization the basis for mechanistic distinctions (hitherto designated by the terms SN1–SN2) will result still from characteristic differences in the path by which this activated intermediate goes to product. We recognize here a competition between nucleophilic interaction with the cationic moiety, R⁺, and solvent displacement of the quasianion from the intimate ion pair or from the solvent-separated ion pair. Under favorable conditions, such competition could lead to "mixed kinetics." If the kinetic scheme such as the following is valid for the hydrolysis of the sulfonyl chlorides, presumably nucleophilic



$$\mathrm{RX} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{A}}{\overset{\delta\quad\delta}{\mathrm{R^+Cl^-}}} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{\mathrm{B}}{\mathrm{R^+\|Cl^-}} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \underset{\mathrm{C}}{\mathrm{R^+ + Cl^-}}$$

product product product

interaction will occur at A for the benzenesulfonyl chlorides and at B or C or B and C for I. The differences in the accompanying solvent reorganization will be reflected in the corresponding values of $\Delta C_p^{\ddagger}$. It is this added reorganization, arising from the displacement of the anion from the intimate ion pair to give the solvent-separated ion pair, or an even greater degree of solvent reorganization in the case of the solvent-separated ions which we believe accounts for the more negative value of $\Delta C_p^{\ddagger}$ found for I ($\Delta C_p^{\ddagger} = -76$ cal deg^{-1} mol^{-1}) compared to the value of about -55 cal deg^{-1} mol^{-1} found for the sulfonyl chlorides where there is evidence of significant nucleophilic interaction. Queen has reported a value of $\Delta C_p^{\ddagger} = -83$ cal deg^{-1} mol^{-1} for hydrolysis of the related dimethylcarbamyl chloride[6] (II) and -86 cal deg^{-1} mol^{-1} for methyl thiochloroformate[23] (III). Both II and III are believed to hydrolyze by an SN1 mechanism.

An examination of Courtauld models for the initial state of I, II, and III reveals that in I the "backside" of S opposite Cl is closely restricted, the approach of a nucleophile being opposed by unshared electrons on the sulfur and N in one orientation or by the methyl groups in another. In II and III there is a similar crowding, leading to steric hindrance to the approach of a nucleophile. The fact that Rogne found a linear acceleration with azide ion and Hall an acceleration with the strong nucleophile, *m*-cresoxide ion, but no acceleration of rate for I with the weaker and bulkier pyrrolidine and piperidine or the solvated OH⁻, is consistent with the SN1 mechanism being favored in the presence of the still weaker base, water. The smaller kinetic solvent isotope effect ($k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}} = 1.33$) reported by Rogne and confirmed here (Table IV) is just about the same as found for *tert*-butyl chloride[10] and significantly lower than the corresponding values reported for other sulfonyl chlorides.[4] The importance of steric hindrance to nucleophilic interaction in I makes unnecessary Hall's suggestion that electron release is promoted by some kind of resonance involving the dimethylamino group (see also ref 10). The fact that the corresponding hexadeuterio isomer gives an inverse secondary γ-deuterium isotope effect ($k_{\mathrm{H}}/k_{\mathrm{D}} = 0.95$, Table III) shows that such a process is probably negligible. However, such an inverse effect could arise from strong solvation of the incipient cation.

Granted the above arguments in favor of an SN1 mechanism, it is simple to attribute the more negative $\Delta C_p^{\ddagger}$ values found for the hydrolysis of I to the need for a greater degree of solvent reorganization compared to the benzenesulfonyl chlorides but whether the rate-controlling step for I corresponds to the formation of B or C (above) is not determined. It is difficult for us to see how the rate-controlling step to C could be more energy demanding than that to B—hence rate controlling.

The possibility that the more negative value of $\Delta C_p^{\ddagger}$ might arise from some anomalous combination of rates as suggested by Albery and Robinson[24] was made less likely by showing that when 5% mf of acetonitrile was added to the solvent the apparent $\Delta C_p^{\ddagger}$ was -44 cal deg^{-1} mol^{-1} (Table III), a change most easily explained in terms of the breakdown of water structure in the initial state by the organo cosolvent, acetonitrile,[13] with a consequent reduction in the effect of temperature on that solvent structure which must be reorganized in the activation process.

A comparison of the pseudothermodynamic parameter for hydrolysis in D_2O and H_2O shows the difference, $\delta_{\mathrm{I}}\Delta C_p^{\ddagger}$,[25a,b] found here (5 ± 5 cal deg^{-1} mol^{-1}) is about the same as for the benzenesulfonyl chlorides.[4] The differences in $\delta_{\mathrm{I}}\Delta H^{\ddagger}$ (477 cal) and $\delta_{\mathrm{I}}\Delta S$ (1.09 cal deg^{-1} mol^{-1}) are somewhat larger than the corresponding values for the sulfonyl chlorides but smaller than the values reported for the hydrolysis of the tertiary halides.[25b] At this point we merely draw attention to these differences.

Experimental Section

Materials. Dimethylsulfamoyl chloride was a commercial sample and purified by distillation under reduced pressure using a spinning band column; bp 53° (5 mm) (lit. 66° (10 mm[26]). The dimethylsulfamoyl chloride-d_6 was prepared by the method of Binkley and Degering.[26] Dimethylamine-d_6 (Merk Sharpe and Dohme Canada Ltd.), 2 g, was added dropwise to a 1.5-fold excess of sulfuryl chloride (10 g) with cooling. The solution was gently refluxed (40–50°) overnight with stirring. After the excess of sulfuryl chloride was evaporated off at a water pump, the reaction mixture was extracted with ether, washed with water, dried over anhydrous magnesium sulfate, and subjected to vacuum distillation; bp 53–54 (5 mm); nmr showed no proton absorption. Homogeneity and similar absorption properties were shown to be the same as the undeuterated sample on a Bendix analytical gc using a 6 ft × 1/4 in. glass column packed with 5% (Silicon-Gum-Rubber SE-30-Methyl-General Electric) on Chromosorb W.

Solvent. The purification of light and heavy water was the same as previously reported.[4] The 0.95-mol fraction of water–acetonitrile solvent mixture was prepared by weighing 9.5 mol of water (171.19 g) and 0.5 mol of acetonitrile using spectrograde acetonitrile.

---

(23) A. Queen, T. A. Naur, M. N. Paddon-Row, and K. Preston, *Can. J. Chem.*, **48**, 522 (1970).

(24) W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, **65**, 980 (1969); for a criticism of this paper, see ref 7.

(25) (a) ($\Delta C_p^{\ddagger}{}_{\mathrm{D_2O}} - \Delta C_p^{\ddagger}{}_{\mathrm{H_2O}}$); (b) L. Treindl, R. E. Robertson, and S. E. Sugamori, *Can. J. Chem.*, 47, 3377 (1969).

(26) W. W. Binkley and E. F. Degering, *J. Amer. Chem. Soc.*, **61**, 3250 (1939).