Transition State Enthalpies of Transfer in the Reaction of Nucleophiles with *n*-Hexyl Tosylate

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Abstract: Rates of nucleophilic displacement of tosylate from *n*-hexyl tosylate by azide, chloride, bromide, iodide, and thiocyanate ions have been measured in methanol and dimethyl sulfoxide at three temperatures. The activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ have been calculated. Transition state enthalpies of transfer, $\Delta\Delta H^{t}$, for the reactions have been obtained from the appropriate enthalpies of transfer of reactants, $\Delta\Delta H_{s}$, and difference in the enthalpies of activation of the reaction, $\Delta\Delta H^{\ddagger}$, in the two solvents. The results show that the lower activation enthalpies, $\Delta H^{\ddagger}$, and faster rates in dimethyl sulfoxide are due mainly to desolvation of the reactant anion in the case of N_3^-, Cl^-, and Br^-, and stronger solvation of the transition state in the case of I^-. The transition states of N_3^- and SCN^- appear to be slightly more solvated by methanol, while that of Br^- is slightly more solvated by dimethyl sulfoxide.

Various explanations have been advanced for the observed rate enhancements of SN2 reactions in dipolar aprotic solvents.[1-6] Such explanations are for the most part similar in that each is based upon differences in solvation of ionic and neutral species in protic and dipolar aprotic solvents.

When a given reaction is transferred from a polar protic to a dipolar aprotic solvent an increase in rate and decrease in free energy of activation can most often be attributed to differences in solvation enthalpies and not to entropy differences.[7,8] The result is that direct analysis of solvent effects is possible by calculating the enthalpies of transfer for the reactants and transition state,[9,10] the latter being obtained from the relation

$$\Delta\Delta H^{t} = \Delta\Delta H_{s} + \Delta\Delta H^{\ddagger}$$

where $\Delta\Delta H^{\ddagger}$ is the difference in the activation enthalpies of the reaction in the two solvents, $\Delta\Delta H_{s}$ is the enthalpy of transfer of the reactants from one solvent to the other, and $\Delta\Delta H^{t}$ is the enthalpy of transfer of the transition state.

The separation of solvent effects into ground state and transition state contributions in SN2 and SNAr reactions involving charged nucleophiles[11] has revealed that the increased rates and smaller activation enthalpies in the dipolar aprotic solvent are due to the increased solvation of the transition states in that solvent. Furthermore, the value of $\Delta\Delta H^{t}$ for every reaction studied was highly exothermal. Consequently, all the transition states are solvated more in DMF, which contributes to the lower activation enthalpies even in those cases where desolvation of the nucleophile also occurs.

Results from the reactions of large polarizable reactant anions are similar to those results involving neutral nucleophiles. The reactions of pyridine[11,12] and of trimethylamine[13] with substituted benzyl chlorides are faster in the dipolar aprotic solvent, DMF, than in the polar protic solvent, methanol, mainly because the transition states are more strongly solvated in DMF.

While studies of this type have been limited to large polarizable reactant anions, it is often accepted that the smaller activation enthalpies of small "hard" anions (OH^-, Cl^-, and F^-) in SN2 reactions are due almost entirely to desolvation of the reactant anions in the dipolar aprotic solvent. Transition state contributions have received little or no attention in the cases of these small nucleophiles. In the present study we were interested in determining to what extent, if any, the transition state solvation contributes to the lower activation enthalpies. The rates of displacement of tosylate (*p*-toluenesulfonate) from *n*-hexyl tosylate by N_3^-, Cl^-, Br^-, I^-, and SCN^- were measured in methanol and in dimethyl sulfoxide. The rates were measured in both solvents at 20, 30, and 40° for each nucleophile with the exception of I^- in dimethyl sulfoxide where the rates were measured at 30, 40, and 50°.

It has been reported that alkyl tosylates and alkyl halides undergo solvolysis in dimethyl sulfoxide[14,15] and in methanol.[16] We have found the solvolysis of *n*-hexyl tosylate to be sufficiently slow that no serious complications result, in the measurement of the rates of reaction with anions. This is further supported by other reports in the literature[7,14] concerning studies on alkyl tosylates under similar conditions.

Results and Discussion

The order of nucleophilicity in methanol according to the rate data (Table I) is $N_3^- > I^- > SCN^- > Br^- > Cl^-$. The observed order of nucleophilicity in DMSO

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Table I. Rates[a] of Displacement on Hexyl Tosylate by Nucleophiles

Nu^-	Solvent	k^{40}	k^{30}	k^{20}
Cl^-	DMSO	50.4 ± 0.4	16.7 ± 0.1	5.06 ± 0.04
	MeOH	0.0852 ± 0.0004	0.0226 ± 0.0003	0.00550 ± 0.00007
N_3^-	DMSO	135 ± 0.7	48.3 ± 0.2	16.1 ± 0.1
	MeOH	1.66 ± 0.01	0.514 ± 0.002	0.152 ± 0.001
Br^-	DMSO	17.8 ± 0.1	5.69 ± 0.04	1.75 ± 0.01
	MeOH	0.250 ± 0.002	0.0721 ± 0.0007	0.0191 ± 0.0002
SCN^-	DMSO	1.11 ± 0.01	0.365 ± 0.003	0.115 ± 0.002
	MeOH	0.481 ± 0.005	0.165 ± 0.002	0.0512 ± 0.0005
I^-	DMSO	5.50 ± 0.07	1.75 ± 0.02	16.0 ± 0.1 (50°)
	MeOH	0.956 ± 0.007	0.275 ± 0.001	0.0767 ± 0.0006

[a] $k_2 \times 10^4$ l. mol^{-1} sec^{-1}. Error limits are standard deviations (see text).

is in good agreement with results reported for propyl[14,17] and methyl tosylate.[17] The order of nucleophilicity in methanol coincides with the results reported[7] for methyl tosylate in methanol.

Enthalpies and Entropies of Activation. Activation parameters are presented in Table II. The following observations may be made: (1) the enthalpies of activation decrease on transfer from MeOH to DMSO for all the anions except SCN^-; (2) the change in activation enthalpies, $\Delta\Delta H^{\ddagger}$, is larger than the change in activation entropies, $\Delta\Delta S^{\ddagger}$, for all anions (with the exception of SCN^-); (3) the entropies in both solvents decrease (become more negative) in the order $Cl^- > Br^- \sim I^- > N_3^- \gg SCN^-$. The first observation seems to be characteristic of most reactions that show a rate increase on transfer from protic to dipolar aprotic solvents. The free energy gap between reactants and activated complex ($\Delta G^{\ddagger}$) is smaller in DMSO than in MeOH for all the anions. This is reflected in $\Delta H^{\ddagger}$ values for all anions studied with the exception of SCN^-. Similar results were reported[7] in the reaction of SCN^- with methyl tosylate in DMF and MeOH, where the rates, E_a, and $\Delta S^{\ddagger}$ are similar to those in the present study in that (a) thiocyanate reacts faster in the dipolar aprotic solvents and (b) the energies of activation (or $\Delta H^{\ddagger}$) are smaller in methanol (Table III).

Table II. Activation Parameters for Nucleophile–Hexyl Tosylate Reactions

Nu^-	Solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal mol^{-1}
Cl^-	MeOH	24.3 ± 0.2	−4.2	25.5
	DMSO	20.2 ± 0.1	−4.4	21.6
N_3^-	MeOH	21.2 ± 0.1	−8.2	23.5
	DMSO	18.6 ± 0.1	−7.8	21.0
Br^-	MeOH	22.9 ± 0.2	−6.4	24.9
	DMSO	20.5 ± 0.1	−5.6	22.0
SCN^-	MeOH	19.8 ± 0.2	−15.8	24.2
	DMSO	20.0 ± 0.2	−12.4	23.7
I^-	MeOH	22.4 ± 0.1	−6.0	23.9
	DMSO	20.9 ± 0.2	−5.8	22.8

Table III. The Reaction of Thiocyanate with Tosylates

Reaction	Solvent	$10^5\ k_2$, l./(mol sec)	E_a, kcal	$\Delta S^{\ddagger}$, eu
$CH_3OTs + KSCN^7$	MeOH	14.3	18.0	−15.1
	DMF	78.0	19.3	−9.8
$C_6H_{13}OTs + KSCN$	MeOH	0.916	20.4	−15.8
	DMSO	2.07	20.6	−12.4

The second observation is in good agreement with previous reports.[18-22] According to Parker,[8] a decrease in enthalpy of activation, rather than an increase in entropy of activation, is the major factor increasing rates of reaction between anions and polar molecules, between anions and cations, and between two anions, on transfer from protic to dipolar aprotic solvents. In the present work, the entropies of activation in DMSO and in methanol (Table II) for the halide reactions are grouped together at −4.2 to −6.0 eu, and the values for azide are somewhat more negative (about −8.0 eu). The thiocyanate reactions have $\Delta S^{\ddagger}$ values which are considerably more negative (−15.8 and −12.4 eu) in MeOH and in DMSO, respectively.

Entropies of activation have been discussed mainly from the twin aspects of molecular structure[23,24] and reaction mechanism.[25] The effect that structural change in a nonreacting part of a molecule has upon the entropy and enthalpy of activation for that molecule has been considered.[24]

The observed order of activation entropies (Table II) may result, in part, from structural differences in reactant anions rather than upon a change in reaction mechanism. Clearly, if a pair of molecules are to react upon collision, they must be so oriented that bond-breaking and bond-making can occur. The less probable the transition state (the more constrained or rigid it is compared to the reactant state), the more negative does $\Delta S^{\ddagger}$ become; the more probable the transition state (the less constrained or rigid), the more positive does $\Delta S^{\ddagger}$ become. Chloride ion which is symmetrical in shape and charge distribution has little or no orientation requirement of its own for bond-making. The same situation applies to iodide and bromide ions. Azide ion, however, has only two possible orientations for bond-making and thiocyanate has only one. The spatial requirements for bond-making as the transition states are approached become increasingly important, therefore, in the order $Cl^- \sim Br^- \sim I^- < N_3^- < SCN^-$,

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and the activation entropies become more negative in the same order.[26]

Transition State Enthalpies of Transfer. Transition state enthalpies of transfer, $\Delta\Delta H^{t}$, derived from enthalpies of solution (Table IV) and enthalpies of transfer (Table V) are presented in Table VI. In the case of the first three reactions, *i.e.*, N_3^-, Cl^-, and Br^-, the decrease in the value of $\Delta\Delta H^{\ddagger}$ in dimethyl sulfoxide is due almost entirely to desolvation of the nucleophiles in dimethyl sulfoxide and not to greater solvation of the transition states. However, in the case of iodide both the transition state and the nucleophile are more highly solvated in dimethyl sulfoxide, *i.e.*, both $\Delta\Delta H_s$ and $\Delta\Delta H^{t}$ have negative values. The larger factor here is increased solvation of the transition state.

Table IV. Enthalpies of Solution of Reactants in Methanol and Dimethyl Sulfoxide at 25°

Compd	$\Delta H_s(MeOH)^a$	$\Delta H_s(DMSO)^a$
n-$C_6H_{13}OTs$	2.6 ± 0.1	2.1 ± 0.1
Bu_4NCl^b	−0.8 ± 0.1	3.7 ± 0.1
NaN_3	−1.9 ± 0.2	−1.7 ± 0.1
Bu_4NBr^b	5.0 ± 0.2	5.1 ± 0.1
NaSCN	−4.7 ± 0.1	−7.1 ± 0.1
Bu_4NI^b	10.4 ± 0.2	7.2 ± 0.1

[a] kcal/mol. [b] Values from R. Fuchs, J. L. Bear, and R. F. Rodewald, *J. Amer. Chem. Soc.*, **91**, 5797 (1969).

Table V. Enthalpies of Transfer of Ions and of *n*-Hexyl Tosylate from Methanol to Dimethyl Sulfoxide at 25° [a]

Species	$\Delta\Delta H_s$, kcal/mol
n-$C_6H_{13}OTs$	−0.4
$Cl^{-\ b}$	6.6
N_3^-	3.6
$Br^{-\ b}$	2.3
SCN^-	1.0
$I^{-\ b}$	−1.1

[a] Based on the assumption that $\Delta\Delta H_s(Bu_4N^+) = \Delta\Delta H_s(Bu_4B^-)$. [b] Footnote *b*, Table IV.

Table VI. Enthalpies of Transfer[a] from Methanol to Dimethyl Sulfoxide at 25°

Reaction	$\Delta\Delta H_s{}^b$	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta H^{t}$
$Cl^- + n$-$C_6H_{13}OTs$	+6.2 ± 0.3	−4.1 ± 0.3	+2.1 ± 0.3
$N_3^- + n$-$C_6H_{13}OTs$	+3.2 ± 0.4	−2.6 ± 0.2	+0.6 ± 0.4
$Br^- \pm n$-$C_6H_{13}OTs$	+1.9 ± 0.3	−2.4 ± 0.2	−0.5 ± 0.3
$SCN^- + n$-$C_6H_{13}OTs$	+0.6 ± 0.4	+0.2 ± 0.4	+0.8 ± 0.5
$I^- + n$-$C_6H_{13}OTs$	−1.5 ± 0.3	−1.5 ± 0.3	−3.0 ± 0.4

[a] kcal/mol. [b] $\Delta\Delta H_s(Nu^-) + \Delta\Delta H_s(n\text{-}C_6H_{13}OTs)$.

The values of $\Delta\Delta H^{t}$ in the reactions of N_3^-, Br^-, and SCN^- are small. It appears that all have transition states that tend to be similarly solvated in methanol and in DMSO. The larger uncertainties in $\Delta\Delta H^{t}$ for N_3^- and SCN^- are due mainly to the procedure used in calculating the corresponding enthalpies of transfer, $\Delta\Delta H_s$. Nevertheless, according to the calculated values, it appears that both N_3^- and SCN^- have transition states that are only slightly more solvated by methanol than by dimethyl sulfoxide while the transition state involving Br^- is slightly more solvated in dimethyl sulfoxide.

Up to the present, enthalpies of transfer of transition states have been reported for reactions involving large neutral nucleophiles, *i.e.*, the Menshutkin reaction[12,13] and large polarizable anions, *i.e.*, SCN^-.[11] In most cases solvation of the transition state was shown to be the major factor for the increases in rates of reaction in the dipolar aprotic solvent. The results from the present study indicate, however, an entire range of behavior may be observed. The major rate accelerating factor in DMSO (in terms of enthalpy) is nucleophile desolvation (N_3^-, Cl^-, Br^-), increased transition state solvation (I^-), or a nonenthalpy (entropy) term (SCN^-). It should be noted that the thiocyanate case is uncertain because the error limits in $\Delta\Delta H_s$, $\Delta\Delta H^{\ddagger}$, and $\Delta\Delta H^{t}$ are nearly as large as the values themselves.

Experimental Section

Materials. Hexyl tosylate was prepared by the method of Tipson[27] from practical grade hexyl alcohol and *p*-toluenesulfonyl chloride. Dimethyl sulfoxide was Baker Aanlyzed reagent grade listed as containing less than 0.05% water. Methyl alcohol was Fisher Certified reagent and was dried with 3A molecular sieve. Tetrabutylammonium salts were commercially available from Eastman Organic Chemicals. These salts were vacuum dried and had melting points in good agreement with literature values. A high grade of sodium azide (mp 300° dec) was available from Matheson Coleman and Bell. Potassium thiocyanate was Baker Analyzed reagent.

Rate Measurements. The general procedure was that previously reported.[28] We have examined the question of whether the nucleophile titer is affected by other species present, and have found that the titrations are not affected by hexyl tosylate, solvent, or tosylate ion.[29,30]

Rate Equation. The rate of reaction for each individual run was calculated from the second-order rate equation

$$kt = \frac{1}{(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

Method of Least Squares. Standard deviations of the rate constants were determined from a plot of the quantity $1/(a - b) \ln b(a - x)/a(b - x)$ *vs.* time which was found to be a straight line. Slopes were determined from values of $\ln b(a - x)/a(b - x)$ (given equal weight on the y axis) against time on the x axis in the least-squares calculations.

Single Ion Enthalpies of Transfer. The single ion enthalpies of transfer, $\Delta\Delta H_s$, from methanol to dimethyl sulfoxide, for Cl^-, Br^-, and I^- have been reported elsewhere.[31] The same experimental procedures were used in the present study to calculate enthalpies of transfer for N_3^- and SCN^- with the extrathermodynamic assumption $\Delta\Delta H_s[(C_4H_9)_4N^+] = \Delta\Delta H_s[{}^-B(C_4H_9)_4]$.

Errors. The rate constants are the result of two or more runs. The standard deviation of each set of rate constants at a given temperature was obtained by a least-squares treatment of the data employing a STATPAC X-7 computer system. The standard deviations are listed in Table I.

The errors reported for $\Delta\Delta H^{\ddagger}$ are the result of the individual errors in the corresponding values of $\Delta H^{\ddagger}$ obtained by drawing straight lines through the respective plots and calculating maximum and minimum values of the slope from the equation

$$\Delta H^{\ddagger} = \frac{RT'T}{T' - T} \ln \frac{k'T}{kT'}$$

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(26) A referee has suggested that the more negative $\Delta S^{\ddagger}$ values for N_3^- and SCN^- may result from greater association of NaN_3 and NaSCN than the tetrabutylammonium halides

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using standard deviations in rate constants and the accuracy of ±0.01° in temperature measurements. Deviations in the values of $\Delta\Delta H^{\ddagger}$ represent the estimated error. The error, here, was determined by a complete treatment of all primary errors.

Activation entropies, $\Delta S^{\ddagger}$, were determined from $k = (eKT/h) \exp(-E_a/RT) \exp(\Delta S^{\ddagger}/R)$, and at a given temperature, the free energy of activation, $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

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Enthalpies of Formation of Nortricyclene, Norbornene, Norbornadiene, and Quadricyclane

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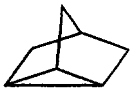
Abstract: Heats of formation of the following gaseous substances at 25° were determined by combustion calorimetry: nortricyclene (**1**), +14.82 ± 0.54 kcal mol^{-1}; norbornene (**2**), +15.12 ± 0.42 kcal mol^{-1}; norbornadiene (**3**), +50.59 ± 0.26 kcal mol^{-1}; and quadricyclane (**4**), +60.54 ± 0.26 kcal mol^{-1}. Discrepancies between these and literature values are discussed.

Because of their manifold and fascinating reactions, nortricyclene (**1**), norbornene (**2**), norbornadiene (**3**), and quadricyclane (**4**) have been the subject of numerous chemical investigations in the past two decades. The reactivity displayed by these compounds suggests that they are highly strained, and estimates of their strain energies and heats of formation obtained in various ways have been published. In this paper we present a brief study of the heats of formation, obtained by combustion calorimetry, of these compounds.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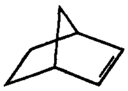
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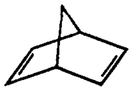
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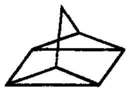
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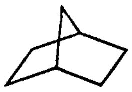
Results

Compounds **1–4**, purified by distillation and preparative gas chromatography, were subjected to combustion in a rotating bomb calorimeter, and the enthalpies of combustion and of formation were calculated by standard procedures. Vapor pressures were measured over a range of temperatures and from these data the enthalpies of vaporization were calculated. With the aid of these values, the enthalpies of formation for the materials in their condensed phases were corrected to the vapor state at 25°. The details of the experiments are given in Tables I–V and are summarized in Table VII, along with those of previous investigators.

Comparison with the Results of Previous Investigators. Norbornane. The enthalpies of formation of the various bicyclic hydrocarbons, which are the subject of this report, have been studied by Turner and his colleagues.[2] Their experimental approach consisted of the determination of the enthalpies of hydrogenation (or hydrogenolysis) of the hydrocarbons in acetic acid solution. By combination of these data with a value for the enthalpy of formation of norbornane (**5**), enthalpies of formation of the other hydrocarbons could readily be deduced.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Turner and coworkers took −8.4 kcal mol^{-1} as the enthalpy of formation of gaseous norbornane. This value was obtained by combining an experimental enthalpy of combustion for solid norbornane[3] with an estimated enthalpy of vaporization. Recently, however, Boyd and his coworkers[4] directly determined the enthalpy of vaporization, obtaining a value of 9.59 kcal mol^{-1}. Our independent determination (Table V) agrees well with this value, 9.40 kcal mol^{-1}. This causes the enthalpy of formation of gaseous bicycloheptane to become −12.4 kcal, and leads to a downward revision of the values deduced by Turner and his coworkers. These revised values are also listed in Table VII.

The earlier workers calculated strain energies of the various hydrocarbons by comparing their values of the enthalpies of formation with hypothetical "strainless" values calculated by the method of Franklin.[5] Recently, however, Schleyer, Williams, and Blanchard[6] showed that this type of calculation is not appropriate for bicyclic hydrocarbons, and that the "single conformation increment" method of Benson and Buss[7,8]

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