

**Quantum Yield Measurements.** The reaction vessel consisted of a  $1 \times 4$  cm Pyrex cell fused to a glass pipe containing a gas-tight stopcock. The solution to be irradiated (4 cc) was placed in the cell and the apparatus evacuated. The reaction was allowed to proceed to 2–3% conversion and then ethane (marker) was introduced, using a gas-tight microsyringe, *via* a rubber septum which sealed the glass tube above the stopcock. The yield of carbon dioxide was determined by gas chromatography. Ferrioxalate actinometry was used as the reference for quantum yield measurements. A  $1 \times 0.5$  cm window in the reaction cell was irradiated

using a medium-pressure mercury vapor lamp and isolating the desired light with a Corning 7-37 glass filter, which was transparent to light in the region 3180–3860 Å (maximum transmission at 3600 Å). There was a dark reaction under these conditions but this only accounted for approximately 2% of the total reaction.

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## Solvation Enthalpies and Rates of Nucleophilic Displacement of Alkali Halides in Dimethyl Sulfoxide

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**Abstract:** Enthalpies of solution have been measured for LiCl, LiBr, LiI, KBr, and KI in DMSO. From these, the values in water, and lattice energies, enthalpies of solvation in both solvents have been calculated. Contrary to a number of suggestions, the solvation of halide ions in DMSO is  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ , the same as in water. The rates of displacement on *n*-propyl tosylate by halides in aqueous DMSO are in the order  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ , while in DMSO the opposite order is observed. The reversed nucleophilic order is attributed to the smaller difference in halide solvation in DMSO than in water. This would rationalize the observed rates if one assumes the order of nucleophilicities of the unsolvated ions toward *n*-propyl tosylate to be  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ .

In recent years a number of authors<sup>2–5</sup> have observed and reported that dipolar aprotic solvents such as DMSO accelerate the rates of certain nucleophilic displacement reactions. Miller and Parker<sup>3</sup> have also shown that, in going from protic to dipolar aprotic solvent, the reaction rates of small nucleophiles are increased to a greater extent than are the rates of larger ones. It has been suggested that in dipolar aprotic solvents anions are poorly solvated.<sup>2,6</sup> This idea has been used<sup>2,3</sup> to explain the rate enhancement under the supposition that an unsolvated nucleophile should be more reactive than a solvated one from which solvent molecules must be removed before reaction can occur.

Arnett and McKelvey<sup>7</sup> have indicated, through estimated single ion enthalpies of transfer from water to DMSO, that water is a better solvating medium for small anions than for large ones, and that the degree of solvation of the halide ions by water lies in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . The enthalpies of transfer (water to DMSO) are in the order  $\text{I}^-$  (exothermic)  $< \text{zero} < \text{Br}^- < \text{Cl}^-$ , suggesting that  $\text{I}^-$  actually undergoes a solvation increase in the transfer.

(1) Author to whom inquiries should be directed. Support of this work by the Robert A. Welch Foundation (Grant E-136) is gratefully acknowledged.

(2) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(3) J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961).

(4) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *ibid.*, **83**, 5835 (1961).

(5) D. Martin, A. Weise, and H. J. Niclas, *Angew. Chem. Intern. Ed. Engl.*, **6**, 318 (1967).

(6) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1796 (1961).

(7) E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966).

The idea that large, polarizable anions should be most solvated in DMSO has led to the alternative suggestion<sup>2,4</sup> that the increased rate of nucleophilic displacement may be due to preferential solvation of the  $\text{SN}_2$  transition state, which would lower the energy of the transition state, and the activation energy. Our present study casts some doubt on this viewpoint. While we believe that this idea and Arnett's assignment of equal enthalpies of transfer for  $(\text{C}_6\text{H}_5)_4\text{As}^+$  and  $(\text{C}_6\text{H}_5)_4\text{B}^-$  ions as a basis for single ion enthalpies both seem quite reasonable, we find no compelling evidence that large anions are, in fact, more strongly solvated than small anions in dipolar aprotic solvents. Measurements of solvation enthalpies in DMSO presented below suggest that the opposite is correct. Alternative explanations for a wide variety of rate, equilibrium, and thermodynamic observations can be based solely on the viewpoint that small anions are more strongly solvated in protic solvents than are large anions, and both the degree of solvation and the difference are diminished in dipolar aprotic solvents.

It has been demonstrated<sup>8</sup> that picric acid is stronger than HBr in DMSO while the reverse holds true in water. This is in agreement with the idea<sup>2,4</sup> that large anions are poorly solvated in water but are more solvated in dipolar aprotic solvents than are small ones. In water the bromide ion may be stabilized through solvation, leading to strong dissociation of the acid, while in DMSO there may be less dissociation due to less anion solvation. The picrate ion may be less solvated in water than is bromide but more solvated in DMSO, and

(8) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *ibid.*, **90**, 23 (1968).

**Table I.** Enthalpies of Solution and Solvation of Some Alkali Halides in DMSO and H<sub>2</sub>O at 25°<sup>a</sup>

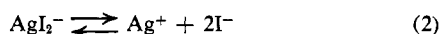
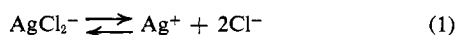
Halide	$\Delta H_{\text{soln}}(\text{DMSO})^b$	$\Delta H_{\text{soln}}(\text{H}_2\text{O})^c$	Lattice energy <sup>d</sup>	$\Delta H_{\text{solv}}(\text{DMSO})$	$\Delta H_{\text{solv}}(\text{H}_2\text{O})$
LiCl	-10.9 ± 0.3	-8.85	203.4	-214.3 ± 0.3	-212.2
LiBr	-17.1 ± 0.1	-11.67	191.3	-208.4 ± 0.1	-203.0
LiI	-24.2 ± 0.3	-15.13	177.0	-201.2 ± 0.3	-192.1
KBr	-2.7 ± 0.1	4.75	162.1	-164.8 ± 0.1	-157.4
KI	-6.5 ± 0.1	4.86	151.1	-157.6 ± 0.1	-146.2

<sup>a</sup> Values of  $\Delta H_{\text{soln}}$  and  $\Delta H_{\text{solv}}$  in kcal/mol are the average of from six to ten separate runs ± the average deviation. <sup>b</sup> Concentrations range from  $1 \times 10^{-3}$  to  $3 \times 10^{-3} M$ ; results are independent of concentration in this range. <sup>c</sup> Values from National Standards Reference Data System NRSDS-NBS 2. <sup>d</sup> C. M. Kachhava and S. C. Saxena, *Indian J. Phys.* **38**, 388 (1964).

picric acid would therefore appear to be the stronger acid in that medium. However, it is possible that picric acid is intrinsically a stronger acid (that is, has a lower free energy of heterolytic dissociation in the dilute gaseous state; this depends mainly on the ability of the anion to disperse negative charge<sup>9</sup>) than is hydrogen bromide. Bromide ion solvation in water would contribute to the greater dissociation of HBr compared to picric acid, for which little anion solvation would occur. From this viewpoint picric acid is more ionized in DMSO than in water because of the greater basicity toward protons of DMSO.<sup>10</sup> HBr is less dissociated in DMSO than in water because the greater interaction with H<sup>+</sup> in DMSO is exceeded by the loss in Br<sup>-</sup> solvation.

Kolthoff<sup>8</sup> has also studied the dissociation constants of a series of uncharged acids in DMSO, acetonitrile, and water. With the exception of picric acid, all of the acids investigated are more dissociated in water than in DMSO. Since DMSO is a stronger base toward protons than is water, solvation of the conjugate bases (other than picrate) by water must occur to a greater extent than solvation by DMSO.

Parker<sup>11</sup> has recently examined instability constants in protic and aprotic solvents and concluded that the ions AgX<sub>2</sub><sup>-</sup> are more stable in dipolar aprotic than in protic solvents because AgX<sub>2</sub><sup>-</sup> is a large, polarizable anion while X<sup>-</sup> is a relatively small, strong hydrogen bond acceptor. If solvation of the large ion in the aprotic solvents were the main consideration to be made, one would expect that in the change from water to DMSO, a large anion such as AgI<sub>2</sub><sup>-</sup> would gain more stabilization than AgCl<sub>2</sub><sup>-</sup>. This is not the case. There is an alternative explanation. Solvation of any species involved in the dissociation equilibrium  $\text{AgX}_2^- \rightleftharpoons \text{Ag}^+ + 2\text{X}^-$  will favor the increased stability and formation of that species. If solvation of the ions in water are: Cl<sup>-</sup>, strong; I<sup>-</sup>, moderate; AgCl<sub>2</sub><sup>-</sup> and AgI<sub>2</sub><sup>-</sup>, weak; and in DMSO are: Cl<sup>-</sup>, weak; I<sup>-</sup>, weak; AgCl<sub>2</sub><sup>-</sup> and AgI<sub>2</sub><sup>-</sup>, very weak, then the loss in solvation (water to DMSO) would be: Cl<sup>-</sup>, large; I<sup>-</sup>, small; AgCl<sub>2</sub><sup>-</sup> and AgI<sub>2</sub><sup>-</sup>, very small. In the two equilibria



the species losing the most solvation energy by the transfer is Cl<sup>-</sup>; hence equilibrium 1 would proceed to the left to a greater extent than 2.

(9) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **90**, 2821 (1968).

(10) I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, **65**, 1020 (1961).

(11) R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **89**, 3703 (1967).

If it is true that large anions are more solvated in DMSO than are small anions, this should be reflected in the enthalpies of solvation. We have determined the heats of solution of some alkali halide salts in DMSO,<sup>12</sup> which are reported in Table I along with heats of solution of the same salts in water, enthalpies of solvation in both solvents, and the crystal lattice energies of the salts. Enthalpies of solvation were calculated in the following manner.

$$\Delta H_{\text{solv}} = \Delta H_{\text{soln}} - \text{crystal lattice energy}$$

Kinetic data for the displacement of tosylate from *n*-propyl tosylate by Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> are presented in Table II.

**Table II.** Rates of the *n*-Propyl Tosylate-Halide Ion<sup>a</sup> Reaction in DMSO and DMSO-Water (70:30) at 50°<sup>b</sup>

	Chloride, $k_2 \times 10^3$	Bromide, $k_2 \times 10^3$	Iodide, $k_2 \times 10^3$
DMSO	7.93	4.88 <sup>c</sup>	1.53
DMSO- H <sub>2</sub> O (70:30)	0.250	0.318	1.663

<sup>a</sup> From tetra-*n*-butylammonium halides. Each rate constant is the mean of duplicate determinations agreeing to 4% or less. <sup>b</sup> Measured in units of l. mol<sup>-1</sup> sec<sup>-1</sup>. <sup>c</sup> 4.78 with KBr.

Considering the lithium and potassium salts separately, it is evident in both cases that the iodide ion is more weakly solvated than is the bromide, and in the case of the lithium series (potassium chloride is too insoluble in DMSO to permit measurement) the chloride ion is the most strongly solvated. Thus, while the probable loss of solvation, in going from water to DMSO, is greatest for chloride it still appears to be the most solvated of the three halide ions in both solvents. The trend is for the solvation by DMSO (as with water) to decrease with increasing size of anion, and one might conclude that a very large transition state would be still less solvated. This trend is found to be consistent no matter which series of crystal lattice energies is employed (theoretical or experimental)<sup>13-16</sup>

(12) Although alkali chlorides and bromides have been described<sup>7</sup> as "too insoluble in DMSO to permit direct measurement," we find that LiCl, LiBr, and LiI are readily soluble in DMSO. KBr is less soluble but with proper preparation it dissolves rapidly. (The critical practitioner in the field will recognize that although KBr has a considerable solubility in DMSO,<sup>11</sup> the limited rate of solution requires that finely and uniformly subdivided material be used.) Our value of -2.7 kcal/mol for  $\Delta H_{\text{soln}}$  of KBr in DMSO is in good agreement with a calculated value of -2.75 kcal/mol obtained using the single ion enthalpies of transfer of Arnett and McKelvey.<sup>7</sup>

(13) M. Born and K. Huang, "Dynamical Theory of Crystal Lattices," The Clarendon Press, Oxford, 1954, p 36.

(14) D. Cubicciotti, *J. Chem. Phys.*, **31**, 1646 (1959).

(15) R. V. Gopala Rao, H. V. Keer, and C. Deenadas, *Indian J. Phys.*, **37**, 238 (1963).

(16) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd revised ed, Pergamon Press, Oxford, 1964, p 562.

although the differences in solvation enthalpies will vary slightly going from one set to another. From these data it is apparent that a plot of ionic radius *vs.* solvation energy in DMSO would have a slope of the same sign as that in water, and not the opposite sign as has been previously suggested.

If enthalpies of solvation parallel free energies of solvation<sup>17</sup> the above data do not support the suggestion that nucleophilic reactivity (in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ ) is increased because smaller anions are less solvated than large ones in dipolar aprotic solvents. Furthermore, there is no need for this premise. Rates of nucleophilic displacement reactions would be accelerated in dipolar aprotic solvents if unsolvated chloride ion is a sufficiently stronger nucleophile than unsolvated iodide toward *n*-propyl tosylate that the more strongly solvated chloride ion in DMSO is, nevertheless, more reactive than the less solvated iodide. In water the difference in solvation is much larger. The extremely strong chloride hydration diminishes the reactivity of the ion to less than that of the weakly solvated iodide. While a large transition state is probably less solvated in DMSO than are small anions, one cannot rule out the possibility that it may still be more solvated in that medium than in water. This idea is not required because the rates would be accelerated so long as the solvation difference between nucleophile and transition state becomes less in going from water to DMSO. Our data are consistent with this latter view in that the differences in solvation of the anions become smaller in the transfer from water to DMSO.

The interaction of substrates with the DMSO dipole, leading to a more reactive, polarized substrate species,<sup>18</sup> is not ruled out by our measured enthalpies of solution. Especially in predominantly aqueous DMSO mixtures this factor may be a major one.

## Experimental Section

**Reagents.** Primary standard grade KBr and KI were vacuum dried at 100°. Reagent lithium bromide and lithium chloride were dried under vacuum at 225 and 150°, respectively, after recrystallization from acetone-H<sub>2</sub>O. Lithium iodide was prepared from the carbonate and hydriodic acid,<sup>19</sup> and was recrystallized several times from aqueous ethanol and vacuum dried at 250°.

(17) The solubilities of the silver halides<sup>11</sup> suggest that this is the case. In both water and DMSO the solubilities are  $\text{AgCl} > \text{AgBr} > \text{AgI}$ , and the increase in solubility on transfer from H<sub>2</sub>O to DMSO is in the opposite order. Parker's "P values"<sup>11</sup> which are a measure of the relative free energy of transfer of anions (water to DMSO) are most positive for  $\text{Cl}^-$  and least for  $\text{I}^-$ , as with the enthalpies of transfer.

(18) C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964).

*Anal.* Calcd for LiI: I, 94.7. Found: 94.6.

All of the salts were transferred to the calorimeter sample holder in a drybox under prepurified nitrogen which was continuously circulated through 4A molecular sieves. The kinetic studies utilized dried commercial tetrabutylammonium halides as sources of the nucleophile. Commercial *n*-propyl tosylate was distilled and stored under nitrogen in the refrigerator. The DMSO was "Baker Analyzed" reagent and contained 0.002 or 0.05% water. To be certain that this amount of water has a negligible effect on the calorimetric values, a portion was vacuum distilled from calcium hydride and collected over 4A molecular sieves. Karl Fischer titration of a sample of this DMSO showed 10 ppm water. Calorimetry was performed on LiCl using this dry DMSO, and the values of enthalpy of solution obtained were within experimental error of those obtained using solvent directly from the bottle. A second Karl Fischer titration was performed after a calorimetric measurement had been made using the dried DMSO, and the water content was found to be only 14 ppm, which corresponds to about  $5 \times 10^{-5}$  mol of water in 70 ml of DMSO. The quantity of LiCl used was  $6.4\text{--}9.9 \times 10^{-3}$  mol. Since LiCl was in excess over water in the dry DMSO and the calorimetric values did not differ from those obtained in commercial DMSO (where water is in excess), then solvation by water occurs only to a small degree, if at all. Analysis of DMSO by gas chromatography showed 2–3 ppm dimethyl sulfide. To check concentration effects, several samples of each alkali halide were dissolved in DMSO without renewing the solvent (new solvent was used for each halide). The calorimetric results were independent of concentration in all cases.

**Calorimetry.** The calorimeter was an all-glass system with a total volume of 100 ml. The body (but not the lid) was vacuum jacketed and silvered. The vessel was fitted with ground-glass joints to hold a resistance heater, thermistor, and sample holder. A solid sample was weighed into a glass bulb and mounted in the sample holder. The vessel, with solvent, was submerged in a water bath at  $25.000 \pm 0.004^\circ$  and allowed to equilibrate while the solvent was magnetically stirred. After thermal equilibrium was reached the sample bulb was broken toward the bottom of the vessel. The thermistor signal was fed through a Leeds and Northrup dc amplifier into a recorder. Calibration for each determination was accomplished by passing a known current from a Sargent coulometric current source through the heater of known resistance. Total calibration of the calorimeter was accomplished using KCl as a standard and measuring the heat of solution in water. The average of six determinations was 4.11 kcal/mol with an average deviation of  $\pm 0.05$ , which is in good agreement with the value of 4.115 kcal/mol offered by National Standards Reference Data System NRSDS-NBS.

**Kinetic Measurements.** Solutions were mixed in 50-ml volumetric flasks, and were 0.03 *M* in tetrabutylammonium halide and 0.015 *M* in *n*-propyl tosylate. The solvent was DMSO or DMSO-water (70:30, v/v). Zero time was taken as the time of half-addition of a solution of *n*-propyl tosylate in the solvent (at 50°) to a solution of the salt in the same solvent at 50°. Aliquots of 5 ml were withdrawn periodically and added to water, and halide was determined using 0.015 *N* silver nitrate. Potentiometric titration was carried out with a Radiometer Type TTT-1 titrator, using silver and calomel electrodes, the latter isolated with a potassium sulfate salt bridge. Duplicate determinations agreed to within 4% or better.

(19) G. Tsuchihashi, M. Matsushima, S. Miyajima, and O. Simamura, *Tetrahedron*, **21**, 1049 (1965).