The Nature of Solvent Participation in the Restriction of Rotation about Single Bonds

Sir:

In 1959 Leffler and coworkers published a series of papers on solvent effects in the racemization of optically active biphenyls.[1-4] Of particular interest was their study concerning solvent effects in the racemization of 2,2′-dimethoxy-6,6′-diphenamide (I).[4] In changing the reaction medium from acetone to acetic acid they observed a 2.6-fold increase in the rate constant, a decrease in the enthalpy of activation of 9.1 kcal/mol, and a decrease in the activation entropy of nearly 22 cal/(mol deg). For such a seemingly simple reaction to exhibit such a marked medium effect is very curious, and it would seem that a more complete understanding of this reaction would contribute significantly to the over-all understanding of solvent effects. In an effort to ascertain whether the 9.1-kcal/mol change in the activation enthalpy is due to a ground-state effect or a transition-state effect we have measured the partial molal heat of solution of I in acetone and in acetic acid. The observed heats of solution were 2.98 ± 0.74 and 1.98 ± 0.86 kcal/mol, respectively, giving an enthalpy of transfer from acetone to acetic acid of -1.0 ± 1.1 kcal/mol. Combining this with Graybill and Leffler's values for the activation enthalpies (30.6 ± 0.1 and 21.5 ± 0.2 kcal/mol for racemization in acetone and acetic acid, respectively) gives -10.1 ± 1.1 kcal/mol as the enthalpy of transfer from acetone to acetic acid for the transition state. Clearly the 9.1-kcal/mol decrease in the activation energy observed for this solvent change is due entirely to a medium effect on the transition state, the medium effect on the ground state being in the wrong direction to account for a decrease in ΔH^* for the change from acetone to acetic acid. The 9.1-kcal/mol change in activation energy observed for this change in medium is, to the knowledge of this author, the largest medium effect on the activation enthalpy which has been directly attributed to changes in the solvation of the transition state. This is in contrast with the solvolysis of *t*-butyl chloride[5] and benzyl chloride[6,7] in alcohol–water mixtures where variations in ΔH^* are attributed to changes in ground-state solvation. Likewise the increased reactivity of anions in dipolar aprotic solvents has been attributed to decreased solvation of the anions in the aprotic solvents.[8] However, it should also be noted that in the solvolysis of methyl benzenesulfonate in alcohol–water mixtures the initial and transition-state enthalpies show nearly the same solvent dependence.[6]

We are now in the process of measuring the heats of solution of I in various other solvents and are also engaged in the dissection of the activation parameters for other reactions involving rotation about single bonds. Also in progress is a study of the enthalpies of transfer for various substrates serving as models for the transition state of I. Any model of this transition state must reflect, to the extent that it resembles the transition state, the -10.1 kcal/mol calculated for the enthalpy of transfer for the transition state from acetone to acetic acid.

2-Amino-3-methoxybenzoic acid (II) was prepared by the method of Ruggli and Leonhardt.[9] Five grams of 2-nitro-3-methoxybenzoic acid (Aldrich Chemical Co.) was dissolved in 70 ml of H_2O and 30 ml of concentrated NH_4OH. A hot solution of 45 g of $FeSO_4 \cdot 5H_2O$ in 150 ml of H_2O was then added to the above solution with vigorous stirring. After 5 min the solution was filtered using a cellulose filter aid and a fritted-glass filter. The clear filtrate was evaporated down to 75 ml *via* a rotary evaporator and then made acid by the addition of 5 ml of concentrated HCl. The white precipitate which formed was recovered by suction filtration; 3.3 g of product melting at 171–172° was obtained.

2,2′-Dimethoxy-6,6′-diphenic acid (III) was prepared from II by the method of Leffler and Graybill.[3]

2,2′-Dimethoxy-6,6′-diphenamide (I) was prepared from III *via* the acid chloride as described by Adams.[10]

Calorimetry. The calorimeter used was similar to that already described by Arnett.[11] The errors reported above with the heats of solution are 95% confidence limits. The relatively large errors are due to the extremely small temperature change resulting from the solution of 100 mg of I in 175 ml of solvent. It was not practical to work with a larger sample size because of the slow rate of solution.

Acknowledgments. This investigation was aided by grants from Research Corporation, Sloan Foundation, and also by National Science Foundation Undergraduate Research Participation Grant GY-4473.

---

[1] J. E. Leffler and W. H. Graham, *J. Am. Chem. Soc.*, **63**, 687 (1959).

[2] W. H. Graham and J. E. Leffler, *ibid.*, **63**, 1274 (1959).

[3] J. E. Leffler and B. M. Graybill, *ibid.*, **63**, 1457 (1959).

[4] B. M. Graybill and J. E. Leffler, *ibid.*, **63**, 1461 (1959).

[5] E. M. Arnett, P. M. Duggleby, and J. J. Burke, *ibid.*, **85**, 1350 (1963).

[6] E. M. Arnett and D. R. McKelvey, *Record Chem. Progr.*, **26**, 185 (1965).

[7] H. S. Golinkin and J. B. Hyne, *Can. J. Chem.*, **46**, 125 (1968).

[8] D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959).

[9] P. Ruggli and W. Leonhardt, *Helv. Chim. Acta*, **7**, 701 (1924).

[10] W. Stanley, E. McMahan, and R. Adams, *J. Am. Chem. Soc.*, **55**, 706 (1933).

[11] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965).

Donald R. McKelvey, James W. Frederiksen
Robert R. Barrick, Gregory A. Teas
Department of Chemistry, Cornell College
Mount Vernon, Iowa 52314

Received August 8, 1968

Infrared and Electron Spin Resonance Study of Hydrogen Tungsten Bronze

Sir:

Glemser and Naumann[1] have shown that the so-called "tungsten blues," obtained by reduction of tungsten trioxide or tungstates, are not simple compounds but are nonstoichiometric materials, frequently in combination with starting WO_3 or H_2WO_4. Further, they were able, on reduction of WO_3, to isolate cubic $H_{0.5}WO_3$, tetragonal $H_{0.33}WO_3$, and rhombic $H_{0.1}WO_3$ and show by X-ray analysis that these were indeed analog products to the well-known sodium tungsten bronzes, Na_xWO_3.[2] More recently, Dickens and Hurditch[3] have prepared an additional hydrogen tungsten bronze tetragonal phase in the range $0.21 < x < 0.25$. In an attempt to cast more light on the state of the hydrogen in these

---

[1] O. Glemser and C. Naumann, *Z. Anorg. Allg. Chem.*, **265**, 288 (1951).

[2] For a recent review on tungsten bronzes, see P. H. Dickens and M. S. Whittingham, *Quart. Rev.* (London), **22**, 30 (1968).

[3] P. G. Dickens and R. J. Hurditch, *Nature*, **215**, 1266 (1967).