# THERMOCHEMICAL COMPARISON OF DEPROTONATION IN KAPA (POTASSIUM 3-AMINOPROPANAMIDE) AND POTASSIUM DMSYL

Edward M. Arnett* and K.G. Venkatasubramaniam

Department of Chemistry
University of Pittsburgh
Pittsburgh, PA  15260
(Present address, Gross Laboratory, Duke University, Durham, NC  27706).

Abstract. Heats of deprotonation in solutions of the potassium salt of 1,3-diaminopropane in the parent amine as solvent indicate that it is over a million times more basic than the potassium salt of DMSO.

Thermochemical measurements which we present in Table I suggest that the superior reactivity of potassium 3-aminopropanamide as a base catalyst (1-8) reflects a high thermodynamic basicity and probably a true catalytic (kinetic) factor as well.

The search for increasingly strong superbases has firm pragmatic foundations in the enormous importance of base-catalyzed reactions. Theoretically, proton transfer comparisons through pKa measurements provide the most general of structure-energy scales. We have reported a thermochemical method for comparing the strengths of weak acids through their heats of deprotonation ($\Delta H_D$) in DMSO using the potassium salt of this solvent, K$^+$DMSYL$^-$ (9-13, 14-18). We were therefore intrigued by C.A. Brown's announcement (1) of the remarkable potency of the potassium salt of 1,3-diaminopropane as a base catalyst and wished to apply the same approach to measurement of heats of deprotonation by this salt in the neutral diamine as solvent. It is plain from comparison of columns 1 and 2 in Table I that by this criterion KAPA solutions are in fact much more basic towards the carbon acids shown than is K$^+$ DMSYL$^-$ in DMSO. When injected as an acid into KAPA, DMSO itself gives a $\Delta H_D$ of about 8 kcal/mole representing a difference of about $1.4 \times 10^6$ in equilibrium constant over the less basic medium if one may translate enthalpy differences directly into free energy ones (11) and ignore activity coefficient terms. The difference between $\Delta H_D$(KAPA) and $\Delta H_D$(DMSYL) for diphenylmethane, triphenylmethane and xanthene are 6-7 kcal/mole, again demonstrating a much greater basicity for KAPA. However, in our hands, KAPA gave no thermochemical evidence of deprotonating toluene or p-xylene but gave some evidence of attacking p-phenyltoluene. Since cesium cyclohexylamide (Cs$^+$CHA$^-$) partially

deprotonates p-phenyltoluene (19) but not toluene (to any measureable extent) it appeared that KAPA was showing thermodynamic basicity similar to that of CsCHA. To compare KAPA with KCHA, cyclohexylamine was injected into a solution of 0.1M KAPA and then into 1,3-diaminopropane to correct for any medium effect on the initial state (9). Both reactions were thermoneutral. Likewise, the attempt to form potassium diisopropylamide by injecting the neutral amine into KAPA produced negligible heat.

On the basis of the above experiments, we confirm Brown's original inference (1) that KAPA is of comparable basicity to Cs+CHA− by virtue of similar reactivities (20). Brown proposed that KAPA may assume a chelated ring structure which could favor concerted bifunctional catalysis. In view of the unusually high proton affinity of 1,3-diaminopropane (and higher $\omega$-diamine homologues) in the gas phase (21) compared to monoamines this seems reasonable. Also, since the dielectric constant of this solvent is only 9.55 (22) KAPA probably exists primarily as chelated ion pairs with relatively few free amide ions. Although this would serve to reduce the effective basicity of KAPA, the proximity of potassium ions to its basic centers could indeed support bifunctional catalysis (such as might assist the acetylene zipper reaction (2) in this solvent).

We are currently investigating the use of indicator methods, such as those used by Bordwell (23-27) and Streitwieser (28-30) for the determination of free energies of ionization in KAPA solutions.

## Experimental Section:

The samples used were either crystallized or distilled until physical properties indicated purity. DMSO was purified as described previously (9). 1,3-diaminopropane (Aldrich 99%) was dried over activated 4A Molecular Sieves, then distilled from sodium metal at reduced pressure. KAPA was prepared by adding 1,3-diaminopropane to a calculated amount of KH (1) under argon, stirred for ca. 1 hr until $H_2$ evolution subsided, then filtered through a glass frit under argon. The strength of the base solution was checked by non-aqueous titration with pure ethanol using triphenylmethane as indicator and diluted if necessary. The solution was stored under positive argon pressure and used within 36 hrs. Heat of deprotonation measurements were made as described before (9,32).

## References and Notes

1. C.A. Brown, Chem. Commun., 222 (1975).

2. C.A. Brown and A. Yamashita, J. Amer. Chem. Soc., 97, 892 (1975).

3. C.A. Brown and E.I. Negishi, Chem. Commun., 318 (1977).

4. C.A. Brown and A. Yamashita, Chem. Commun., 959 (1976).

5. C.A. Brown, Synthesis, 754 (1978).

6. C.A. Brown, J. Org. Chem., 43, 3083 (1978).

7.  H. Hommes and L. Brandsma, Recl, Trav. Chim. Pays-Bas, <u>96</u>, 160 (1977).

8.  S.R. Macaulay, J. Org. Chem., <u>45</u>, 734 (1980).

9.  E.M. Arnett, T.C. Moriarity, L.E. Small, J.R. Rudolph and R.P. Quirk, J. Amer. Chem. Soc., <u>95</u>, 1492 (1973).

10. E.M. Arnett, L.E. Small, R.T. McIver, Jr., and J.S. Miller, J. Amer. Chem. Soc., <u>96</u>, 5638 (1974).

11. E.M. Arnett, L.E. Small and D.E. Johnston, Faraday Symp. Chem. Soc., No. 10 (1975).

12. E.M. Arnett, L.E. Small and D.E. Johnston, J. Amer. Chem. Soc., <u>98</u>, 7346 (1976).

13. E.M. Arnett and L.E.  Small, J. Amer. Chem. Soc., <u>99</u>, 808 (1977).

14. C.D. Ritchie and R.E. Uschold, J. Amer. Chem. Soc., <u>89</u>, 2960 (1967).

15. C.D. Ritchie and R.E. Uschold, J. Amer. Chem. Soc., <u>89</u>, 2752 (1967).

16. C.D. Ritchie and R.E. Uschold, J. Amer. Chem. Soc., <u>89</u>, 1721 (1967).

17. C.D. Ritchie and R.E. Uschold, J. Amer. Chem. Soc., <u>90</u>, 2821 (1968).

18. C.D. Ritchie, "Solute Solvent Interactions", J.F. Coetzee and C.D. Ritchie, eds., Marcel Dekker, New York, 1969, pp. 219-294.

19. A. Streitwieser, Jr., and F. Guibe, J. Amer. Chem. Soc., <u>100</u>, 4532 (1977).

20. Brown has argued that KAPA is more convenient to prepare and handle.

21a. M. Mautner, P. Hamlet, E.P. Hunter and F.H. Field, J. Amer. Chem. Soc., <u>102</u>, 6394 (1980).

21b. R. Yamdagni and P. Kebarle, J. Amer. Chem. Soc., <u>95</u>, 3504 (1973).

22. A.M. Hartstein and S. Windwer, J. Phys. Chem., <u>73</u>, 1549 (1969).

23. F.G. Bordwell, Pure α Appl. Chem., <u>49</u>, 963 (1977).

24. W.S. Matthews, J.E. Bares, J.E. Bartmess, F.G. Bordwell, F.J. Cornforth, G.E. Drucker, Z. Margolin, R.J. McCallum, G.J. McCollum and N.R. Vanier, J. Amer. Chem. Soc., <u>97</u>, 7006 (1975).

25. W.N. Olmstead, Z. Margolin and F.G. Bordwell, J. Org. Chem., <u>45</u>, 3295 (1980).

26. F.G. Bordwell, D. Algrim and N.R. Vanier, J. Org. Chem., <u>42</u>, 1819 (1977).

27. D. Algrim, J.E. Bares, J.C. Branca and F.G. Bordwell, J. Org. Chem., <u>43</u>, 5024 (1978).

28. A. Streitwieser, Jr., J.I. Brauman, J.H. Hammons, and A.H. Pudjaatmaka, J. Amer. Chem. Soc., <u>87</u>, 384 (1965).

29. A. Streitwieser, Jr., E. Ciuffarin and J.H. Hammons, J. Amer. Chem. Soc., <u>89</u>, 63 (1967).

30. A. Streitwieser, Jr., J.H. Hammons, E. Ciuffarin and J.I. Brauman, J. Amer. Chem. Soc., <u>89</u>, 59 (1967).

31. For some very recent papers on the subject see:  (a) paper No. Orgn 33 by A.D. Denniston and N.H. Anderson, (b) paper No. Orgn 34 by C.A. Brown and A.I. Yamaichi (both papers presented at the A.C.S. Conference at Las Vegas, August, 1980).

32. E.M. Arnett, W.G. Bentrude, J.J. Burke and P. McC. Duggleby, J. Amer. Chem. Soc., <u>87</u>, 1541 (1965).

Table I. Comparison of Some Thermodynamic Properties for Deprotonation in Several Alkali Superbase Systems.

| Acid | 1. $\Delta H_D^{DMSYL}$ Kcal/mole | 2. $\Delta H_D^{KAPA}$ Kcal/mole | 3. $\Delta^a$ | 4. $pK_{DMSO}$ | 5. $pK_{CsCHA}^b$ |
|---|---|---|---|---|---|
| 1. Toluene | 0.0 | 0.0 | 0 | 42c | 41.2d |
| 2. p-Xylene | 0.0 | 0.0 | 0 | - | - |
| 3. p-Phenyltoluene | 0.0 | -1.32 | 1.32 | - | 38.95d |
| 4. Diphenylmethane | -6.56 ± .18 | -12.5 ± .2 | 5.94 ± .27 | 32.1e | 33.45f |
| 5. Triphenylmethane | -9.4 ± .4 | -16.2 | 6.8 | 30.6e | 31.45f |
| 6. Xanthene | -8.34 ± .2 | -15.1 | 6.8 | 30.09 | - |
| 7. Fluorene | -18.2 ± .4 | -19.9 | 1.7 | 22.69 | 23.04f |
| 8. Cyclohexylamine | 0.0 | 0.0 | 0.0 | - | 41.6d |
| 9. Diisopropylamine | 0.0 | -0.18 ± .04 | 0.18 | - | - |
| 10. DMSO | 0.0 | -8.10 ± .47 | 8.10 ± .47 | 35.1e | - |

Explanations:

$\Delta H_D$ = heat of deprotonation (i.e. the heat of solution of the acid in KAPA minus its heat of solution in 1,3-diaminopropane).

(a): column 1 minus column 2

(b): statistically corrected, per hydrogen

(c): ref. 27

(d): ref. 19

(e): ref. 25

(f): ref. 30

(g): ref. 23