Figure 1. Relationship between undissociated acid concentration and specific rates of hydration of *trans*-cyclooctene and 2,3-dimethyl-2-butene in wholly aqueous H_3PO_4–$H_2PO_4^-$ buffer solutions at 52.4°; stoichiometric buffer ratio = 2, ionic strength maintained at 0.1 M with $NaClO_4$. Corrections to constant [H^+] were made by adjusting k_{obsd} to the H^+ concentration (0.014 M) of the most concentrated buffer.
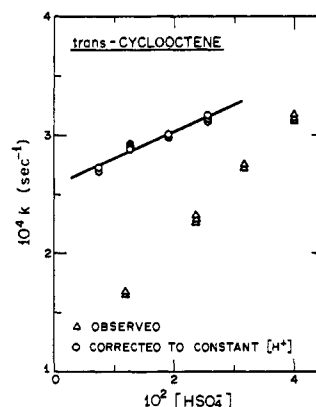

Figure 2. Relationship between undissociated acid concentration and specific rates of hydration of *trans*-cyclooctene in wholly aqueous HSO_4^-–SO_4^{2-} buffer solutions at 52.4°; stoichiometric buffer ratio = 4, ionic strength maintained at 0.1 M with $NaClO_4$. Corrections to constant [H^+] were made by adjusting k_{obsd} to the H^+ concentration (0.014 M) of the most concentrated buffer.

with decreasing buffer concentration (Figures 1 and 2). This, in itself, however, is not proof of catalysis by general acids, for neither H_3PO_4 nor HSO_4^- is a sufficiently weak acid to give dilute buffer solutions whose hydrogen ion concentration does not decrease upon buffer dilution. The experiments were therefore performed at ionic strengths no greater than 0.1 M, for which the extended Debye–Hückel formula for calculating ionic activity coefficients is valid, and exact solution compositions were thus estimated. Figures 1 and 2 show that, when the necessary corrections to constant hydrogen ion concentration are made with k_{H^+} values measured in dilute $HClO_4$ solution, marked dependences of reaction rate upon undissociated acid concentration still remain; least-squares analysis of the data gives $k_{H_3PO_4} = (6.4 \pm 0.5) \times 10^{-4}$ M^{-1} sec^{-1} and $k_{HSO_4^-} = (2.3 \pm 0.1) \times 10^{-3}$ M^{-1} sec^{-1} for *trans*-cyclooctene and $k_{H_3PO_4} = (2.46 \pm 0.03) \times 10^{-4}$ for 2,3-dimethyl-2-butene. The hydration of 2,3-dimethyl-2-butene was not examined as a function of HSO_4^- concentration, but the velocity of this reaction measured in a single HSO_4^- buffer proved to be significantly greater than that calculated for hydrogen ion catalysis alone, showing general acid catalysis in this system as well. Thus, all of the reactions investigated here are subject to catalysis by general acids.

The reason why general acid catalysis was not discovered in previous examinations[11] of aliphatic olefin hydration conducted for this purpose is now apparent. In both previous studies, large catalyst concentrations were employed to provide conveniently measurable reaction velocities, and, since buffer solutions were used, this led to high ionic strengths—in one case, as great as 3.0 M.[11b] Specific ionic interactions can be expected to come into prominence under these conditions, and it has in fact been recently demonstrated[13]

that such effects can mask general acid catalysis completely. Thus, the present results are not incompatible with previous investigations, and the operation of an A-S_E2 mechanism for the hydration of simple olefins is finally firmly established.

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Heats of Complexing of Alkali Metal Ions with a Crown Ether in Aprotic Solvents[1]

Sir:

Calorimetric results are reported here which show a large selectivity factor for the heat of complexing of dicyclohexyl-18-crown-6 ether[2] for different alkali cations and, furthermore, a considerable solvent effect on this selectivity.[3–5]

Data in Table I show dramatic differences in the complexing of the smaller cations, Li^+ and Na^+,

(1) Supported by National Science Foundation Grant No. GP-6550-X.
(2) Dicyclohexyl-18-crown-6 ether (2,5,8,15,18,21-hexaoxatricyclo[20.-4.0.0⁹⁻¹⁴]hexacosane) was generously supplied as a mixture of isomers by H. K. Frensdorff of E. I. Du Pont de Nemours.
(3) Key references to the complexing of group Ia and IIa cations by crown ethers are: C. J. Pederson, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); C. J. Pederson, *ibid.*, **92**, 387, 391 (1970); H. K. Frensdorff, *ibid.*, **93**, 600 (1971); R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, *ibid.*, **93**, 1619 (1971).
(4) The importance of macrocyclic polybasic ligands in membrane transport and other biological processes is summarized in: D. C. Tosteson, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1269 (1968); H. Lardy, *ibid.*, **27**, 1278; R. S. Cockrell, E. J. Harris, and B. C. Pressman, *Biochemistry*, **5**, 2326 (1966); P. Muller and D. P. Rudin, *Biochem. Biophys. Res. Commun.*, **26**, 398 (1967); M. Eigen, *Pure Applied Chem.*, **6**, 97 (1963).
(5) R. J. P. Williams, *Quart. Rev., Chem. Soc.*, **24**, 331 (1970).

Table I

Salt	Solvent	$\Delta H_{soln}{}^a$	$\Delta H_{complexation}{}^a$	$\Delta H_{transfer}{}^a$ H$_2$O → solvent^d	$\Delta H_{transfer}{}^a$ gas → solvent^e
LiBr	DMSO	-17.1 ± 0.1^h	No complexation^b	-5.43 ± 0.18	-209.0
NaI	DMSO	-11.40 ± 0.28	-0.48 ± 0.45^b	-9.97 ± 0.30	-177.7
KI	DMSO	-6.61 ± 0.10^i	-7.39 ± 0.40^b	-11.47 ± 0.13	-160.0
KI	DMSO		-6.52 ± 0.57^c		
KNO$_3$	DMSO	$+0.74 \pm 0.15$	-7.53 ± 0.25^b	-7.60 ± 0.18	
KB(C$_6$H$_5$)$_4$	DMSO	-0.62 ± 0.20	-7.45 ± 0.62^b		
CsI	DMSO	-2.84 ± 0.08	-6.94 ± 0.36^b	-10.81 ± 0.18	-146.4
NH$_4$I	DMSO	-9.25 ± 0.98	-4.15 ± 0.50^b	-12.53 ± 1.04	
Crown ether^l	DMSO	$+7.58 \pm 0.42$			
LiBr	Acetone		-3.87 ± 0.51^c		
NaI	Acetone	-10.4^k	-6.43 ± 0.49^c	-8.60	-176.3
NaB(C$_6$H$_5$)$_4$	Acetone	-14.3 ± 0.5	-5.99 ± 0.36^c	-9.43 ± 0.60	
KI	Acetone		-9.71 ± 0.33^c		
KB(C$_6$H$_5$)$_4$	Acetone		-9.29 ± 0.36^c		
CsB(C$_6$H$_5$)$_4$	Acetone		-8.40 ± 0.33^c		
NH$_4$I	Acetone		-9.98 ± 0.50^c		
Crown ether^l	Acetone	$+7.32 \pm 0.24$			
Crown ether^f	Acetone	$+8.57 \pm 0.27$			
Crown ether^g	Acetone	$+10.0 \pm 0.52$			
NaB(C$_6$H$_5$)$_4$	THF	-19.02 ± 0.30	-4.78 ± 0.50^b	-14.25 ± 0.40	
NaB(C$_6$H$_5$)$_4$	THF		-5.03 ± 0.53^c		
LiBr	THF	-9.85 ± 0.15	No complexation^b	$+1.82 \pm 0.23$	-201.8
Crown ether^l	THF	$+6.30 \pm 0.19$			
KI	Acetone		$-10.12 \pm 0.52^{c,f}$		
KI	Acetone		$-11.06 \pm 0.45^{c,g}$		
LiCl	H$_2$O	-8.850	No complexation^j		-211.9
NaCl	H$_2$O	0.928	No complexation^j		-185.0
KCl	H$_2$O	4.115	-3.88 ± 0.04^j		-165.8
RbCl	H$_2$O	4.130	-3.33 ± 0.01^j		-160.2
CsCl	H$_2$O	4.250	-2.41 ± 0.04^j		-151.6
NH$_4$Cl	H$_2$O	3.533	-2.16 ± 0.03^j		

^{a} All values are in kilocalories/mole at 25°; errors reported are standard deviations of four–seven measurements. ^{b} Measured by method I. ^{c} Measured by method II. ^{d} ΔH_{soln} values in H$_2$O taken from V. B. Parker, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 2 (1965). ^{e} Lattice energies from D. Cubiccotti, *J. Chem. Phys.*, **31**, 1646 (1959). ^{f} Isomer a of dicyclohexyl-18-crown-6 (from R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, *J. Amer. Chem. Soc.*, **93**, 1619 (1971)); mp 54.5–61.5°. ^{g} Isomer b of dicyclohexyl-18-crown-6 (see Izatt, *et al.*, footnote f); mp 81–83°. ^{h} From R. F. Rodenwald, K. Mahendran, J. L. Bear, and R. Fuchs, *J. Amer. Chem. Soc.*, **90**, 6698 (1968). ^{i} Our previously reported value was in error; E. M. Arnett and D. R. McKelvey, *ibid.*, **88**, 2598 (1966). ^{j} See Izatt, *et al.*, footnote f. ^{k} Estimated from extrapolation of ΔH_{soln} to infinite dilution. ^{l} Mixture of isomers.

compared to K$^+$, Cs$^+$, and NH$_4{}^+$, and that the magnitude of this difference depends on the solvent. In dimethyl sulfoxide (DMSO) where the greatest selectivity between Na$^+$ and K$^+$ (*ca.* 7.0 kcal/mol) is observed, the translation of the enthalpy difference into free-energy terms would amount to about 5.2 log K units.

Heats of complexing[6] were obtained in two ways to demonstrate thermodynamic consistency of the data, and agreement between them is found within experimental error.

In method I, the partial molar heat of solution ($\Delta \bar{H}_s$) of the salt was measured first in pure solvent and then in a solution containing at least a threefold final excess of crown ether. $\Delta \bar{H}_s$ was determined from the molar heats of solution for the introduction of a series of six small ($\sim$100 mg) increments of salt into the liquid phase using techniques and apparatus which we have described previously.[7]

In method II, $\Delta \bar{H}_s$ for the crown ether was determined in the same manner, first in pure solvent and then in a solution of the salt at least three times as concentrated as that finally reached by the crown ether after six injections of $\sim$100 mg each. In view of the high cost

of experimental macrocyclic ligands, method II is preferable except when the salt is insufficiently soluble.

Interpretation of the measured heats of solution as heats of complexing depends on two important conditions: (a) that complexing of the cation by the crown ether is either complete or undetectable, *i.e.*, that the degree of complexing of the ion by crown ether does not change significantly within the range of concentrations used here; (b) that there are no calorimetrically significant changes in equilibria between dissociated and ion-paired species (of either "solvent-separated" or "contact" varieties) within the concentration ranges of this study. Proof that both conditions are generally met was given by the constancy of the successive molar heats of solution for each solute in each solution.[8–11]

Further evidence against significant intervention of ion-pairing phenomena or adventitious water of hydration for particular salts is given by the independence of $\Delta H_{complexation}$ for any given cation from its counterion.

(6) ΔH complexation can be considered as the heat of transfer of the solute (salt in method I or crown ether in method II) from pure solvent to a solution of the other component (crown ether in method I, salt in method II) of a possible complex in the same solvent.

(7) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

(8) Note however that alkali metal salts are ion paired in acetone[9] and THF;[10] therefore, the ΔH complexation listed in Table I in these solvents may contain a heat of dissociation of the ion pair.

(9) M. B. Reynolds and C. A. Kraus, *J. Amer. Chem. Soc.*, **70**, 1709 (1948).

(10) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

(11) No concentration effect on ΔH complexation was observed in any of the solvents used by either method I or II. This implies that equilibrium constants for complex formation are greater than about 10^3.

If there are no strong ion-pairing interactions between the uncomplexed cation and its counterion, we may assume that the formation constant (and presumably the enthalpy of formation) for the crown ether complex is determined entirely by the competition between the solvent and the ligand for the cation. It is well known[12] that there are very large differences between the single ion enthalpies of transfer for different solvents. These differences are greatest between the small ions of highest charge density, Li+ and Na+, compared to the larger ions of the Ia series. It is therefore not surprising that the greatest apparent selectivity of crown ether toward large cations is found in H_2O and DMSO, the solvents in Table I, in which the smaller cations are most strongly (i.e., selectively) solvated. In less polar media, such as THF or acetone, the specific fit of the cation in the crown ether cavity must play a greater role, since all cations are less strongly held to the solvent, and the selectivity factor between them is accordingly reduced.[13]

These results suggest, since ion selectivity depends on the solvent as well as the ligand, that the ability of macrocyclic ligands to specifically affect ion transport through membranes will vary considerably depending on their molecular environment within the membrane.

(12) See, for example, G. Choux and R. L. Benoit, J. Amer. Chem. Soc., 91, 6221 (1969).

(13) K. H. Wong, G. Konizer, and J. Smid (ibid., 92, 666 (1970)) have also observed solvent effects on ion selectivity and interpreted them in a similar manner.

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The Synthesis of 2,2,3,2′,2′,3′-Hexamethylbis(1-bicyclo[1.1.0]butyl). Conjugation in a Formally Saturated System[1]

Sir:

The carbon–carbon bonds of bicyclobutane, particularly the central bond, have unusually high p character.[2] As a consequence, electronic interaction should be possible between the bicyclobutane orbitals and those of certain bridgehead substituents.[3,4] Thus, it appeared to us that bis(1-bicyclo[1.1.0]butyl) (1), a compound which has two bicyclobutane rings joined at bridgehead positions, although formally saturated, might show properties which could be considered to indicate conjugation. Increased stability relative to "isolated" bicyclobutanes need not be one such prop-

(1) Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

(2) (a) G. L. Closs and L. E. Closs, J. Amer. Chem. Soc., 83, 1003 (1961); 85, 2022 (1963); (b) M. Pomerantz and E. W. Abrahamson, ibid., 88, 3970 (1966); (c) K. B. Wiberg, Tetrahedron, 24, 1083 (1968).

(3) Bridgehead carbomethoxy, phenyl, and cyano groups lead to ultraviolet absorption at longer wavelengths than would be expected if the chromophore did not interact with the bicyclobutane ring: (a) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Scherter, and J. Lavanish, Tetrahedron, 21, 2749 (1965); (b) H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, J. Amer. Chem. Soc., 93, 110 (1971); (c) H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, ibid., 93, 121 (1971); (d) W. R. Moore and G. Astrologes, unpublished observations.

(4) Based on combustion data, a claim of stabilization for 1-cyanobicyclobutane has been made: H. K. Hall, Jr., and J. H. Baldt, J. Amer. Chem. Soc., 93, 140 (1971).

1   2
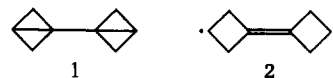
erty since joining the rings in this manner offers enhanced possibilities for ring opening. For example, we estimate that while breaking the central bond of bicyclobutane to form a diradical is endothermic by ca. 41 kcal/mol, opening both central bonds of 1 to form 2 is endothermic by only ca. 25 kcal/mol.[5]

One approach to the synthesis of 1 is through the thermal or oxidative coupling of appropriate organometallic derivatives of bicyclobutane. However, the great sensitivity of the bicyclobutane ring[7] to numerous metal cations[8] makes the possibility of rearrangement a constant hazard. We elected to study derivatives of 1,2,2-trimethylbicyclobutane (3a), a readily available compound.[9]

3a, RH
3b, RD
3c, RLi
3d, RAg
3e, RCu
3f, R₂CuLi
3g, RCH₃
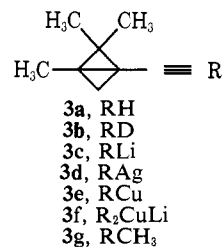
The lithium derivative 3c[9a] reacted rapidly with 1 equiv of silver iodide in ether–pentane at −80° to give the insoluble silver derivative 3d. This compound proved to be remarkably stable; it resisted all attempts to induce thermal coupling. No decomposition was noted over a period of several days at room temperature or several hours in refluxing benzene. Quenching with water resulted in the essentially quantitative recovery of 3a; when deuterium oxide was used, the expected d_1 species, 3b, was obtained. Employing tetrakis[iodo(tri-n-butylphosphine)silver(I)] to form 3d (and apparently partially solubilize it) did not noticeably affect its stability. Thus 3d does not behave like alkyl or alkenylsilver(I) compounds, which are thermally labile;[10] rather the striking stability of 3d is reminiscent

(5) These estimates are based on the heats of formation of bicyclobutane,[6a] cyclobutane,[6b] and methylenecyclobutane (estimated),[6c,d] the bond dissociation energy of a cyclobutyl–H bond,[6e] and the group parameters for calculating heats of formation of either Cox and Pilcher[6b] or Benson[6e,f] (which give slightly different absolute values, but essentially the same differences). These calculations do not include the possibility of stabilization of either the trimethylene[6g] obtained on opening bicyclobutane or 2.

(6) (a) K. B. Wiberg and R. A. Fenoglio, J. Amer. Chem. Soc., 90, 3395 (1968); (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London, 1970; (c) S. W. Benson, et al., Chem. Rev., 69, 279 (1969); (d) R. B. Turner and R. H. Garner, J. Amer. Chem. Soc., 80, 1424 (1958); (e) J. A. Kerr, Chem. Rev., 66, 465 (1966); (f) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (g) R. Hoffmann, J. Amer. Chem. Soc., 90, 1475 (1968).

(7) For a review of bicyclobutanes, see K. B. Wiberg, Advan. Alicyclic Chem., 2, 185 (1968).

(8) (a) L. A. Paquette, R. P. Henzel, and S. E. Wilson, J. Amer. Chem. Soc., 93, 2335 (1971), and preceding papers by L. A. P. cited therein; (b) P. G. Gassman, T. J. Atkins, and F. G. Williams, ibid., 93, 1812 (1971), and preceding papers by P. G. G. cited therein; (c) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, ibid., 93, 1043 (1971); (d) W. R. Moore and B. J. King, J. Org. Chem., 36, 1882 (1971).

(9) (a) W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, Tetrahedron Lett., 2365 (1970); (b) L. Skattebøl, ibid., 2361 (1970).

(10) (a) C. D. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, and J. G. Noltes, Organometal. Chem. Rev. A, 5, 215 (1970); (b) G. M. Whitesides, C. P. Casey, and J. K. Krieger, J. Amer. Chem. Soc., 93, 1379 (1971); (c) M. Tamura and J. Kochi, ibid., 93, 1483 (1971), and references cited in these three articles.