Table I. Heats of Solution in DMSO and H_2O[a]

Nonelectrolytes	$\Delta\bar{H}_s$, DMSO	$\Delta\bar{H}_s$, H_2O	$\delta\Delta\bar{H}_s$, DMSO-H_2O
Benzene	0.65 ± 0.03	0.72^b	-0.07
Toluene	0.89 ± 0.03	0.77^b	0.12
Isopropylbenzene	1.30 ± 0.04	1.06^c	0.24
Carbon tetrachloride	0.00 ± 0.03		
Chloroform	-1.32 ± 0.09		
Acetone	0.37 ± 0.03	-2.37 ± 0.04	2.74
Water	-1.28 ± 0.03	0.00	-1.28
Methanol	-0.34 ± 0.03	-1.74 ± 0.05	1.40
Ethanol	0.28 ± 0.02	-2.45 ± 0.05	2.73
1-Propanol	0.61 ± 0.04	-2.48 ± 0.05	3.09
1-Butanol	0.99 ± 0.03	-2.16 ± 0.03	3.15
2-Methyl-2-propanol	1.21 ± 0.04	-4.10 ± 0.04	5.31
Electrolytes[d]			
NaI	-11.53 ± 0.13	-1.86 ± 0.04	-9.67
KI	-6.15 ± 0.11	4.85 ± 0.03	-11.36
CsI	-2.84 ± 0.08	7.46 ± 0.05	-10.30
$NaB(C_6H_5)_4$	-14.23 ± 0.14	-4.77 ± 0.10	-9.46
$(C_6H_5)_4AsI$	3.44 ± 0.05	8.28 ± 0.09	-4.84
Et_4NI	4.86 ± 0.10	6.83 ± 0.12	-1.97
Et_4NBr	3.27 ± 0.07	1.38 ± 0.08	1.89
Et_4NCl	2.42 ± 0.05	-3.02 ± 0.07	5.44

[a] We wish to thank Mr. F. M. Jones for his assistance in obtaining these measurements. Heats expressed in kcal/mole. Errors are expressed as confidence limits at the 95% level on six to twenty separate measurements on different batches of carefully dried and purified materials. [b] R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951). [c] D. N. Glew and R. E. Robertson, *J. Phys. Chem.*, **60**, 335 (1956). [d] Alkali chlorides and bromides are too insoluble in DMSO to permit direct measurement.

Table II. Single Ion Enthalpies of Transfer from Water to DMSO[a]

Ion	$\delta\Delta\bar{H}_s$	Ion	$\delta\Delta\bar{H}_s$
K^+	-8.84^b	$(C_6H_5)_4As^+$	-2.32
Cs^+	-7.78	$(C_6H_5)_4B^-$	-2.31
Na^+	-7.15	Et_4N^+	0.55
I^-	-2.52	Br^-	1.34
		Cl^-	4.89

[a] For the purpose of placing anions and cations on the same scale, it has been assumed that $\delta\Delta\bar{H}_s((C_6H_5)_4B^-) = \delta\Delta\bar{H}_s((C_6H_5)_4As^+)$. [b] Heats expressed in kcal/mole.

aprotic solvent by a different criterion.[11] The positive heats of transfer for chloride and bromide ions indicate that water is the better solvating medium for small anions. Furthermore, the heats of transfer for the halide ions become rapidly more exothermic in the order $Cl^- < Br^- < I^-$, with I^- actually having an exothermic heat of transfer.

It is important that *these results should not be applied to* rate or equilibrium differences between these two solvents. A dramatic demonstration of the disparity that may arise between $\delta\Delta\bar{H}_s$ and the corresponding free energy of transfer is supplied by benzene. This compound is nearly insoluble in water but completely miscible with DMSO. Therefore, $\delta\Delta\bar{G}_s$ must be enormous although $\delta\Delta\bar{H}_s$ is negligible. In all likelihood this reflects the peculiar position of water among hydroxylic solvents in its interactions with nonelectrolytes. The correspondence between $\delta\Delta\bar{H}_s$ and $\delta\Delta\bar{G}_s$ should be better for transfer of small ions.[12] Our data should be of value for analyzing the effect of medium change on energies of activation between these solvents, but we know of no kinetic study to date to which they may be applied.

Our results may be compared with two recent studies of enthalpies of transfer from water to propylene carbonate[11] and to formamide.[13] Comparison of their data for NaI, KI, and $NaB(C_6H_5)_4$ with ours indicates that the abilities of these three dipolar aprotic solvents to solvate small cations decreases in the order DMSO > formamide > propylene carbonate.

All measurements were carried out at 25.0 ± 0.5° as described earlier.[9b] At the concentrations employed in this study (approximately 5×10^{-3} *M*), the heats of solution were found to be independent of concentration within experimental error for all compounds except tetraphenylarsonium iodide. The heats of solution for this compound in water and DMSO were found to be highly dependent upon concentration. It was therefore necessary to make measurements at various concentrations (0.5×10^{-3} *M* to 2.5×10^{-3} *M*) and extrapolate by least squares to zero concentration.

(11) Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966).

(12) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, London, 1959, p 70.

(13) G. Somsen and J. Coops, *Rec. Trav. Chim.*, **84**, 985 (1965).

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Carbonyl Neighboring Group Participation *via* Enolization

Sir:

The role of the ketonic carbonyl group in solvolysis reactions has been the topic of a recent report.[1] In this recent discussion, carbonyl participation *via* enolization was not considered to be an important factor. We wish to report evidence for the overwhelming role of enol neighboring group participation in the solvolysis of *anti*-7-hydroxynorbornan-2-one *p*-toluenesulfonate (**1**).

(1) D. J. Pasto and M. P. Serve, *J. Am. Chem. Soc.*, **87**, 1515 (1965).

Table I. Acetolysis Rates of Various 7-Norbornyl *p*-Toluenesulfonates

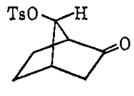
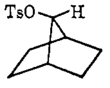
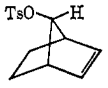
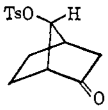
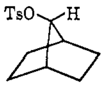
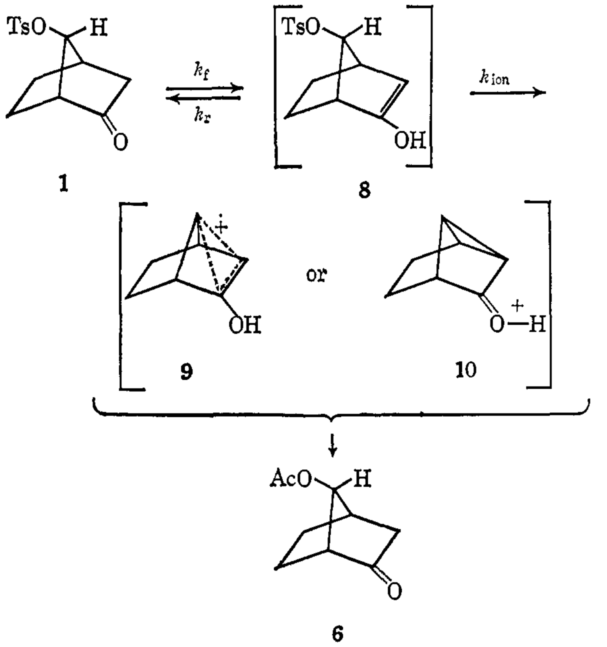
Compd	Ref	Temp, °C	Rate, sec^{-1}	ΔH^* kcal/mole	ΔS^*, eu
 **1**		90.00 ± 0.01	$(1.13 \pm 0.06) \times 10^{-5}$	22.0	−20.7
		100.00 ± 0.02	$(2.78 \pm 0.09) \times 10^{-5}$		
		110.00 ± 0.03	$(6.88 \pm 0.01) \times 10^{-5}$		
		(25)	1.28×10^{-8}		
 **4**	4	(205)	8.40×10^{-5}	35.7	−3.5
		(25)	6.36×10^{-15}		
 **5**	4	(25)	9.04×10^{-4}	23.3	5.7

Table II. Acetolysis Rates of 7-Norbornyl *p*-Toluenesulfonates in Acetic Acid-O-*d*

Compd	Temp, °C	Initial rate, sec^{-1}	Approximate final rate, sec^{-1}
 **1**	110.00 ± 0.03	$(1.31 \pm 0.02) \times 10^{-4}$	$(1.94 \pm 0.09) \times 10^{-5}$
 **4**	200.0 ± 0.1	$(5.73 \pm 0.01) \times 10^{-5}$	$(5.73 \pm 0.01) \times 10^{-5}$

Compound **1** has been synthesized by two independent routes.[2,3] Table I lists the specific rate constants and activation parameters for the solvolyses of **1**, 7-norbornyl *p*-toluenesulfonate (**4**),[4] and *anti*-7-norbornenyl *p*-toluenesulfonate (**5**)[4] in anhydrous acetic acid buffered with sodium acetate.

At 25° **1** solvolyzes approximately 10^7 times faster than **4**. This rate enhancement of *ca.* ten million occurs when one might have anticipated a slight rate retardation due to the inductive effect of the carbonyl. Product analysis showed that *anti*-7-acetoxynorbornan-2-one (**6**) was the sole product of the acetolysis of **1**.[5] The combined rate data and product analysis are most consistent with the mechanism outlined below. The enol, **8**, having a close structural similarity to *anti*-7-norbornenyl *p*-toluenesulfonate (**5**), might be expected to undergo solvolysis with participation of the olefinic π electrons[4,6] to yield either the nonclassical ion,[7] **9**, or the classical ion,[8] **10**. Either ion would be expected to collapse to the observed product.



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According to our proposed mechanism, enolization would be the rate-controlling step with both k_r and k_{ion} representing relatively fast rates in comparison to k_f. Since the rate-determining step in acid-catalyzed

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(2) The tosylate **1** was synthesized from *exo,anti*-2,7-norbornanediol (**2**) [J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964)] by selective oxidation to *anti*-7-hydroxynorbornan-2-one [H. Krieger, *Ann. Acad. Sci. Fennicae, Ser. AII*, No. 109 (1962)] and subsequent conversion to **1** with *p*-toluenesulfonyl chloride in pyridine. An alternate synthesis starting with **2** involved conversion of **2** to the corresponding *exo,anti*-ditosylate, **3**, followed by selective aqueous solvolysis of **3** to *anti*-7-tosylnorbornan-2-ol. Oxidation of this hydroxytosylate with chromium trioxide in acetic acid yielded **1**. All new numbered compounds have given satisfactory analyses.

(3) Compound **1** has also been prepared by G. H. Whitham and S. C. Lewis: S. C. Lewis, Ph.D. Thesis, University of Birmingham, England, 1964.

(4) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

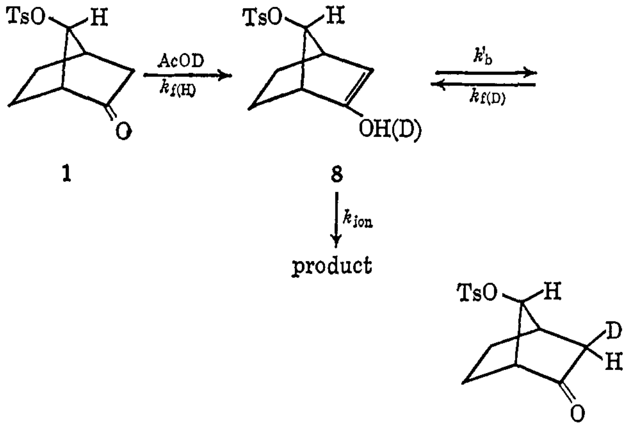
(5) Upon isolation and distillation of the acetolysis product of **1**, a 63% yield of **6** was obtained. No other products were observed by vpc analysis. However, due to the almost identical retention time of *syn*-7-acetoxynorbornan-2-one (**7**) on a variety of columns (including capillary columns), it was impossible to establish the purity of **6** beyond 97%.

(6) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

(7) S. Winstein, A. H. Lewis, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(8) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

enolization is the removal of the α-hydrogen subsequent to proton addition to the carbonyl,[9,10] it would be anticipated that a primary isotope effect would be noted in the solvolysis of **11**. Since the preparation of **11** presented certain problems, the solvolysis of **1** was carried out in acetic acid-O-*d*. If k_b and k_{ion} were of the same order, a deuterium isotope effect should be noted. Table II lists the results of acetolysis in acetic acid-O-*d*. Whereas **1** gave excellent pseudo-first-order kinetics throughout 72% reaction in regular acetic acid, in acetic acid-O-*d* buffered with sodium acetate the rate decreased almost sevenfold before a constant pseudo-first-order rate was observed. This demonstrated that there was return of the enol **8** to **11**, followed by enolization of **11** at a slower rate, $k_{f(D)}$. The over-all sevenfold decrease of rate in going from **1** to **11** was in excellent agreement with the primary deuterium isotope effect of eight observed for the acid-catalyzed enolization of perdeuterioacetone.[11] By comparison, **4** showed good pseudo-first-order kinetics on solvolysis in acetic acid-O-*d* buffered with sodium acetate. In addition to the kinetic data for deuterium incorporation *via* enolization, mass spectral analysis for the presence of deuterium in a sample of **1** recovered after 39% solvolysis showed 34% deuterium incorporation. This data firmly established the importance of enolization in the solvolysis of **1** and further indicated the significant role which enolization can play in "carbonyl participation" especially when the substrate molecule does not allow direct interaction by the carbonyl oxygen.



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[9] C. G. Swain, A. J. Di Milo, and J. P. Cordner, *J. Am. Chem. Soc.*, **80**, 5983 (1958).

[10] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp 140–154.

[11] O. Reitz, *Z. Elektrochem.*, 43, 659 (1937).

[12] National Science Foundation Cooperative Predoctoral Fellow, 1962–1963, 1964–1966.

Geometry of the Bichloride Ion.
Preparation and Crystal Structure of Cesium Chloride · $^1/_3$ Hydronium Bichloride[1]

Sir:

West's[2] initial report of the preparation of cesium bichloride, $CsHCl_2$, by the reaction of anhydrous hydrogen chloride with a saturated aqueous solution of cesium chloride, stimulated interest in this system and led ultimately[3,4] to chemical and spectroscopic evidence that West had actually prepared $CsCl\cdot{}^3/_4H_3OCl$. We have studied the system further, making use of single-crystal X-ray techniques, and we find two distinct crystalline phases. We report here on the composition and structure of the hexagonal phase; the compound is cesium chloride · $^1/_3$ hydronium bichloride, $CsCl\cdot{}^1/_3H_3OHCl_2$.

As West reported, crystalline material is readily obtained when hydrogen chloride gas is bubbled through a saturated cesium chloride solution. The material is unstable except in the presence of HCl. Suitable crystals were transferred from the reaction vessel to X-ray capillary tubes in the presence of HCl gas, and the tubes were then sealed. Under these conditions the crystals are stable. Our initial preparation yielded an orthorhombic phase; subsequent preparations have yielded the hexagonal phase reported upon here.[5] On the basis of Weissenberg and precession photographs, taken with Mo Kα radiation, we find this phase to have Laue symmetry 6/m with lattice constants $a = 10.28$ and $c = 6.78$ A. The only systematic absences observed are for $00l$ for $l \neq 2n$; thus the most probable space groups are $P6_3/m$ and $P6_3$.

Intensity data were collected by the equiinclination Weissenberg technique for successive layers $hk0$ through $hk8$, using Mo Kα radiation. The intensities were estimated visually against a calibrated strip. After the composition of the material had been established from the structure determination, the absorption coefficient was computed and an absorption correction applied. This correction is necessarily approximate, owing to the difficulty of measuring accurately an irregularly shaped crystal which is inside a capillary tube. The data were reduced in the usual way and a three-dimensional Patterson function was computed. This function provided support that space group $P6_3/m$ is to be preferred to $P6_3$. The structure was solved by a succession of least-squares and Fourier calculations. The Cs was located in the sixfold positions (6h), and Cl atoms Cl(1) and Cl(2) were located in the six- and fourfold positions 6h and 4f, respectively. Hence the Cl/Cs ratio is 5/3. A difference Fourier computed at this point showed as its only significant feature a large peak (11 e/A^3) at position 4e, 0, 0, z, with z approximately $^1/_8$. This position is equidistant from three Cl(1) atoms, at the apex of a relatively flat pyramid. Such a position is one expected for the hydronium ion, H_3O^+, entering into three O–H–Cl bonds, an arrange-

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[1] This research was supported by ARPA through the Northwestern University Materials Research Center.

[2] R. W. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957).

[3] R. E. Vallee and D. H. McDaniel, *ibid.*, **84**, 3412 (1962).

[4] A. G. Maki and R. W. West, *Inorg. Chem.*, **2**, 657 (1963).

[5] West[2] presented evidence that his initial material belonged to the orthorhombic system. It is not clear whether subsequent studies[3,4] were carried out on the orthorhombic phase, on the hexagonal phase, or on a mixture of the two.