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Thermochemical Isotope Effects. II. CH_3OH–CH_3OD, C_2H_5OH–C_2H_5OD, and H_2O–D_2O in Selected Solvents

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Received October 23, 1974

Abstract: Standard heats of solution at 25° have been determined for the isotopic pairs methanol–methanol-*d*, ethanol–ethanol-*d*, and water–heavy water in a variety of solvents. In every case, the transfer of the deuterated compound from an inert solvent (in the case of water, from the gaseous state) to a hydrogen-bonding solvent is more exothermic than the transfer of the parent compound. The isotope effect on the enthalpy of transfer shows a rough correlation with the difference between the reduced masses of the solvent–solute pair. The isotope effect on the enthalpy of the O–H bond in methanol has also been determined.

As part of a continuing investigation of thermochemical isotope effects,[1-4] we have measured standard heats of solution of the isotopic pairs methanol–methanol-*d*, ethanol–ethanol-*d*, and water–heavy water in a variety of solvents at 25°. In a previous study[1] involving chloroform–chloroform-*d* and acetone–acetone-d_6, isotope effects on the enthalpy of transfer of chloroform from "inert" solvents to "active" solvents were interpreted as evidence that solvent–solute interactions were stronger for the deuterated compound than for the parent compound. Similar effects were observed for acetone, but interpretation in this case was clouded by possible isotope effects on the enolization of acetone in different solvents. This complication was avoided in the present study by the choice of solutes, and the results generally confirm the conclusions advanced for the chloroform–chloroform-*d* study. The trends in isotope effects for alcohols are more similar to those for acetone than for chloroform, but the only important differences between the chloroform and alcohol studies are in the position of alcohols as solvents relative to the basic solvents pyridine, tetrahydrofuran, and *p*-dioxane. This difference is compatible with the fact that alcohol solutes can form multiple hydrogen bonds with alcohol solvents and single hydrogen bonds with basic solvents, while chloroform forms single hydrogen bonds with all of these solvents.

Isotopic exchange is a more important consideration for alcohols and water as solutes than was the case for chloroform, and apparently was a complication in some of these measurements. The enthalpy of the isotopic exchange reaction between water and methanol was used to calculate the isotope effect on the enthalpy of the O–H bond in methanol.

Experimental Section

Materials. Methanol was Matheson Coleman and Bell (MCB) Spectroquality Reagent and was used without further purification. Methanol-*d* was supplied by Stohler Isotope Chemicals (SIC) with a labeled isotopic purity of greater than 99%. Conductivity grade ethanol was prepared by the method of Murr and Shiner.[5] Ethanol-*d* as supplied by SIC with an isotopic purity of greater than 99% contained a significant amount of an unidentified impurity, as detected by gas chromatography. This impurity was reduced to an undetectable level by fractional distillation from CaO on a spinning band column. Conductivity grade water was prepared with a Barnstead conductivity still. Heavy water was obtained from Savannah River Laboratory[6] with a labeled isotopic purity of

Table I. Heats of Solution and Derived Quantities at 25.0°

Solvent (S)	Isotope	Obsd	$\Delta H°$, cal/mol	b,[a] (cal kg)/mol²	σ, cal/mol	$(\Delta H_D° - \Delta H_H°)_S$, cal/mol	$\Delta(\Delta H_{D/H}°)_{I\to S}$, cal/mol[b]
CH_3OH-CH_3OD							
Methanol	D	4	3	0	1	3	−204
	H		0				
Tetrahydrofuran	D	4	845	−460	3	34	−173
	H	4	811	−702	6		
Pyridine	D	4[c]	−372	−82	1	36	−171
	H	4	−408	−42	3		
1,4-Dioxane	D	4	1310	−566	3	52	−155
	H	4	1258	−413	5		
Water	D	4	−1635	−27	12	111	−96
	H	4	−1746	−75	10		
Carbon tetrachloride	D	4	4510	−71[d]	16	207	
	H	4	4303	−57[d]	14		
$C_2H_5OH-C_2H_5OD$							
Ethanol	D	1	−1			−1	−178
	H		0				
Pyridine	D	6[c]	16	−101	1	18	−159
	H	5	−2	−82	1		
Tetrahydrofuran	D	4	1057	−296	6	27	−150
	H	4	1030	31	9		
1,4-Dioxane	D	6	1687	−815	4	42	−135
	H	4	1645	−934	5		
Carbon tetrachloride	D	4	4485	−91[d]	15	177	
	H	4	4308	−69[d]	19		
Cyclohexane	D	4	5887	−87[d]	25	172	
	H	4	5715	−72[d]	7		
H_2O-D_2O							
Methanol	D	5	−904	47	5	−186	−517[f]
	H[e]	6	−718	50	3		
2-Propanol	D	3	207	0	1	−171	−502[f]
	H	2	378	0	1		
Water	D	11	31.6	0	0.2	31.6	−299[f]
	H		0				
1,4-Dioxane	D	6	1583	−923	6	80	−251[f]
	H	5	1503	−950	4		

[a] Least-squares slope for $\Delta H^{soln} = \Delta H° + b\overline{m}^k$, $k = 1$ unless otherwise noted. [b] $\Delta(\Delta H_{D/H}°)_{I\to S} = (\Delta H_D° - \Delta H_H°)_S - (\Delta H_D° - \Delta H_H°)_I$, I = carbon tetrachloride, unless otherwise noted. [c] The first data point was omitted from the set due to trace water in the solvent. [d] $k = {}^3/_2$. [e] Determined by Mr. E. L. Taylor. [f] These values are referred to the gaseous state, I = gas.

99.75+%. Tetrahydrofuran (THF) and carbon tetrachloride were MCB Chromatoquality, pyridine and 2-propanol were MCB Spectroquality, cyclohexane and 1,4-dioxane were Fisher Certified Reagent.

Calorimetry. The calorimeter and procedures were identical to those described in our earlier paper,[1] except for a slight modification in the method of extrapolation of heats of solution of alcohols in the inert solvents carbon tetrachloride and cyclohexane. Self-association of the alcohols at high dilution in these solvents caused nonlinearity in plots of the observed heats of solution vs. molality. For these extrapolations, three equations of the form

$$\Delta H^{soln} = a + b\bar{m}^k \qquad (1)$$

were considered, with $k = 1$, $\frac{3}{2}$, and 2. Plots of ΔH^{soln} vs. $\bar{m}^k$ were generally concave downward for $k = 1$, concave upward for $k = 2$, and nearly linear for $k = \frac{3}{2}$. The curves for the isotopic pairs were roughly parallel in all of these plots, such that the isotope effect on the intercept was approximately the same for all three values of k. The value of a for $k = \frac{3}{2}$ was taken as $\Delta H°$.

Results

The values determined in this study are presented in Table I, as the standard heats of solution at infinite dilution ($\Delta H°$), dilution parameter (b), and the standard deviation (σ) of the observations about the line represented by eq 1. This table summarizes the results of 128 experiments, two of which were not used in evaluating the standard heats of solution. In the studies with pyridine as solvent, the measurement for the first increment of methanol-*d* and ethanol-*d* deviated strongly from the remainder of the set. This deviation did not occur with methanol and ethanol as solute, and the remainder of the measurements in the two sets of data were roughly parallel. We have assumed that this deviation is probably due to some degree of isotopic exchange between the deuterated alcohols and small amounts of water in the solvent, such that the first increment of added alcohol showed a much larger effect than did the following increments. The results of an additional four measurements were discarded because of differences of more than five standard deviations from the remainder of the set. Because of the very small range of compositions covered, we attach very little significance to the values of the dilution parameters (b), and these values are given only to illustrate the magnitude of the dilution effect. Values of standard deviations are indicative only of precision and not of the accuracy of the standard heats of solution. Because of solvent impurities, calibration uncertainties, etc., we regard these standard heats as accurate to about (1% + σ). However, since most of these effects are common to the heats of solution of both isotopic isomers, we consider the differences in the heats of solution of these isotopic isomers to have uncertainties comparable to the combined standard deviations of the individual heats of solution. A possible flaw in this reasoning lies in the possibility of isotopic exchange of the deuterated compounds with small amounts of water in the solvents. Because of the low concentrations of both water and the solute, the rate of this exchange is expected to be relatively slow, such that only a small amount of exchange occurs in the time period (about 3 min or less) of the calorimetric measurement. Base catalysis is expected to promote this exchange in pyridine, as was apparently observed.

The results of two series of measurements performed in this study are not reported here. Heats of solution of the deuterated alcohols in acetone showed a strong nonlinear dependence on concentration, tending to approach a parallel to the unsubstituted alcohols at high concentrations, such that the results were considered unworthy of meaningful interpretation. This effect is possibly due to the presence of water, but is more likely due to isotopic exchange with acetone, perhaps involving the enol form. Heats of solution of methanol-methanol-*d* were also measured in cyclohexane, but the data showed a great deal of scatter which might be related to the very slow rate of solution. The values for methanol-*d* were in general 100-200 cal/mol more endothermic than those for methanol.

Very little data are available in the literature for comparison of these results. The standard heat of solution of methanol in water (−1746 cal/mol) is in excellent agreement with the values reported by Alexander and Hill[7] (−1735 cal/mol) and by Bertrand et al.[8] (−1756 cal/mol). The isotope effect on the heat of solution of H_2O-D_2O in 2-propanol (−171 cal/mol) is in excellent agreement with Carter's value[9] (−175 cal/mol). Our result in 1,4-dioxane (80 cal/mol) agrees with Carter's value (124 ± 70 cal/mol).

Discussion

In our earlier paper,[1] we discussed isotope effects on heats of solution in terms of solute-solute, solvent-solute, and solvent-solvent interactions, and showed that solute-solute effects and some of the solvent-solvent effects could be minimized by considering the difference between the isotope effects in "active" (S) and "inert" (I) solvents, $\Delta(\Delta H_{D/H}°)_{I\to S}$.

$$\Delta(\Delta H_{D/H}°)_{I\to S} = (\Delta H_D° - \Delta H_H°)_S - (\Delta H_D° - \Delta H_H°)_I \quad (2)$$

For ethanol and methanol, we have chosen carbon tetrachloride as inert solvent because of our erratic measurements for methanol in cyclohexane, and because the isotope effects for ethanol-ethanol-*d* are essentially the same in cyclohexane and carbon tetrachloride. Accurate measurements for the isotope effect on the heat of solution of water in inert solvents are impossible with the present calorimeter, so the results for water are referred to the gaseous state using the difference in the heats of vaporization of water and heavy water as determined by Rossini et al.[10]

$$(\Delta H_{D_2O}° - \Delta H_{H_2O}°)_I \simeq (\Delta H_{D_2O}{}^{vap} - \Delta H_{H_2O}{}^{vap})_{298} = 331 \text{ cal/mol} \quad (3)$$

Values of $\Delta(\Delta H_{D/H}°)_{I\to S}$ are given in the last column of Table I. For the alcohol-water and water-heavy water systems, a substantial portion of this effect is due to isotopic exchange, which has been assumed to be complete within the time period of the calorimetric measurement.[11] For the other systems, the isotope effect on the heat of transfer from an inert solvent to an active solvent is primarily due to differences in solvent-solute interactions, though there could also be some contributions from changes in solvent-solvent interactions due to the isotopic substitution, particularly in self-associating solvents. As was observed in our previous study,[1] the value of $\Delta(\Delta H_{D/H}°)_{I\to S}$ is negative in every case, indicating that solvent-solute interactions between solvents and solutes capable of hydrogen bonding are strengthened by deuterium substitution at a hydrogen-bonding site on the solute molecule.

The lack of reliable data for hydrogen bonds involving methanol and ethanol precludes any attempt at quantitative interpretation of these isotope effects. However, in attempting various types of calculations which might allow interpretation of our results, we noticed a trend which might have physical significance. For the solutes chloroform, methanol, and ethanol, the quantity $\Delta(\Delta H_{D/H}°)_{I\to S}$ in nonexchanging solvents appears to be related to the differences in the reduced masses of the solvent-solute pairs

$$\Delta(\Delta H_{D/H}°)_{I\to S} = 3.5_5[(\mu_{H\text{-}S})^{1/2} - (\mu_{D\text{-}S})^{1/2}] \quad (4)$$

$$\mu_{R\text{-}S} = (MW)_R(MW)_S/[(MW)_R + (MW)_S] \quad R = H, D \quad (5)$$

in which $(MW)_R$ is the molecular weight of the solute, either the deuterium or hydrogen isomer, and $(MW)_S$ is the molecular weight of the hydrogen-bonding solvent. Application of eq 4 to the 14 available values for chloroform, methanol, and ethanol gives a standard deviation of 19 cal/mol and a maximum deviation of 40 cal/mol. More realistically, this correlation can be represented as a standard percentage deviation of 0.7% (maximum deviation 1.3%) between observed and predicted values of the enthalpy of transfer of the deuterated solute from an inert solvent to an active solvent, based on eq 4 and the enthalpy of transfer of the parent compound. For acetone-acetone-d_6, eq 4 predicts values which are much larger than were observed. However, acetone differs greatly from the other solutes, in that the substituted protons are not nearly so important as the carbonyl group in the hydrogen bonds of acetone, and also in the tautomerization of acetone which is expected to be strongly affected by deuteration.

Isotope Effect on the Enthalpy of the O-H Bond

By assuming that the isotopic exchange is complete within the time period of the calorimetric measurement for the solution of methanol-*d* in water and for D_2O in methanol, the enthalpy change for isotopic exchange can be calculated by two independent schemes (Schemes A and B).

Scheme A

	$\Delta H° \pm \sigma$, cal/mol
$\tfrac{1}{2}D_2O(l) + CH_3OH\cdot\infty CH_3OH \rightarrow CH_3OD\cdot\infty CH_3OH + \tfrac{1}{2}H_2O\cdot\infty CH_3OH$	−452 ± 3
$\tfrac{1}{2}H_2O\cdot\infty CH_3OH \rightarrow \tfrac{1}{2}H_2O(l) + \infty CH_3OH$	+358 ± 2
$CH_3OH\cdot\infty CH_3OH \rightarrow CH_3OD(l) + \infty CH_3OH$	−3 ± 1
$CH_3OH(l) + \infty CH_3OH \rightarrow CH_3OH\cdot\infty CH_3OH$	0

summation of these processes and enthalpy changes gives

$\tfrac{1}{2}D_2O(l) + CH_3OH(l) \rightarrow \tfrac{1}{2}H_2O(l) + CH_3OD(l)$	−97 ± 4

Scheme B

$HDO\cdot\infty H_2O + CH_3OH\cdot\infty H_2O \rightarrow CH_3OD(l) + H_2O\cdot\infty H_2O$	+1635 ± 12
$CH_3OH(l) + \infty H_2O \rightarrow CH_3OH\cdot\infty H_2O$	−1746 ± 10
$\tfrac{1}{2}D_2O(l) + \tfrac{1}{2}H_2O\cdot\infty H_2O \rightarrow HDO\cdot\infty H_2O$	+16 ± 0.1
$\tfrac{1}{2}H_2O\cdot\infty H_2O \rightarrow \tfrac{1}{2}H_2O(l) + \infty H_2O$	0

summation of Scheme B gives

$\tfrac{1}{2}D_2O(l) + CH_3OH(l) \rightarrow \tfrac{1}{2}H_2O(l) + CH_3OD(l)$	−95 ± 16

The agreement of these two independent calculations of the enthalpy of isotopic exchange provides a strong indication of the validity of the assumption of complete exchange, and also indicates the reliability of the uncertainties assigned to these isotope effects on heats of solution. Combination of these results with isotope effects on heats of vaporization (331 cal/mol for H_2O-D_2O,[10] and 116 cal/mol for methanol-methanol-*d*[12]) gives

$$\tfrac{1}{2}D_2O(g) + CH_3OH(g) \rightarrow \tfrac{1}{2}H_2O(g) + CH_3OD(g)$$
$$\Delta H^\circ = -147 \text{ cal/mol}$$

Combination of this result with standard heats of formation[13] of $H_2O(g)$, $D_2O(g)$, H(g), and D(g) gives

$$CH_3OH(g) + D(g) \rightarrow CH_3OD(g) + H(g)$$
$$\Delta H^\circ_{298.15} = -1.9_2 \text{ kcal/mol}$$

which represents the isotope effect on the enthalpy of the O-H bond in methanol. This is slightly larger than the average isotope effect on the O-H bond in water which can be calculated from standard heats of formation.[13]

$$\tfrac{1}{2}H_2O(g) + D(g) \rightarrow \tfrac{1}{2}D_2O(g) + H(g)$$
$$\Delta H^\circ_{298.15} = -1.77 \text{ kcal/mol}$$

Acknowledgment. We thank the Research Corporation for financial support of this work.

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A Critical Examination of the Applicability of $J_{^{13}CH}$ as a Criterion for the Presence of σ Bridging in Cyclopropylcarbinyl Cations

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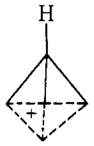
Received November 24, 1974

Abstract: The proposal that changes in the geometry caused by σ bridging may be detected by increases in the value of $J_{^{13}CH}$ has been subjected to critical scrutiny in the cyclopropylcarbinyl cations. From comparisons of the methine coupling constants in such ions with the corresponding coupling constants in neutral compounds, it is concluded that the observed values are consistent with the presence of adjacent positive charge. However, the values of $J_{^{13}CH}$ for cyclopropylcarbinyl, 180, for methylcyclopropylcarbinyl, 190, and for dimethylcyclopropylcarbinyl, 187, fail to reveal the large increase in the value for the primary ion as anticipated for the formation of a σ bridge. Consequently, of the two NMR criteria proposed as diagnostic for σ-bridged cations, one (^{13}C chemical shifts) has been interpreted as supporting a σ-bridged structure for cyclopropylcarbinyl, whereas the other ($J_{^{13}CH}$) appears in better accord with the formulation as open equilibrating cations.

The fast rates of solvolysis of cyclopropylcarbinyl systems were originally attributed to the stabilization accompanying the formation of a σ bridge through space with one or both of the far carbon atoms of the cyclopropane ring[2,3] (**1**, **2**).



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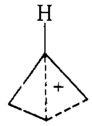

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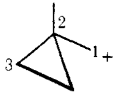
In the case of secondary (**4**) and tertiary cyclopropylcarbinyl cations (**5**), NMR studies[4] have led to the conclusion that



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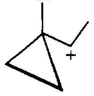

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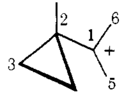

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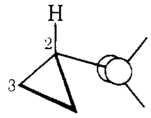
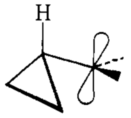
these ions exist in the bisected arrangement, so that such σ bridges must be absent. The formation of a σ bridge from a bisected structure (**6**) requires rotation of the cationic group about the C_1-C_2 bond (**7**) with movement of the cationic carbon (C_1) toward the center of the C_3-C_4 bond (to form the tricyclobutonium ion (**1**)) or toward either C_3 or C_4 (to form a bicyclobutonium ion (**2**)).



6



7

On the other hand, certain differences in the observed and calculated ^{13}C shifts for the primary ion (**3**)[5-7] have led to the conclusion that this ion exists as a σ-bridged species.[4c,8] Consequently, in this ion it is proposed that rotation of the cationic ethylene group occurs (**6** → **7**) with formation of a σ bridge with one of the methylene carbons of the cyclopropane ring (C_3, C_4).

An increase in the $J_{^{13}CH}$ value of the methine group has also been proposed as a criterion diagnostic of the formation of a σ bridge.[8] Such σ-bridge formation should result in movement of C_1 toward the cyclopropane ring. In neutral molecules, a similar decrease in the dihedral angle and increase in strain is reflected in major increases in the coupling constants[9] as shown by **8**, **9**, and bicyclobutane itself