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Dimensiosolvatic Effects. III. Quantification of Dimensiosolvatic Effects by Solvolyses of 2-Bromoadamantane in Water–Alcohol Mixtures[1)]

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Solvolyses of 2-bromoadamantane in aqueous alcohols were carried out to find the selectivities, $k_{ether}/k_{alcohol}$, at various concentrations of water in an alcohol and at various temperatures. While the observed ratios contain a large error or fluctuate at low concentrations of water, they were almost constant for 1.0 : 0.8 alcohol/water mixtures. The selectivity was also independent of temperatures of the reaction. The significance of the selectivity, which is determined by the ease of solvent intervention into contact ion pairs, is discussed. *D* values, which are obtained by taking reciprocals of the selectivity for the 1.0 : 0.8 mixture, are proposed as a measure of the dimensiosolvatic effects when a solvent molecule intervenes into the contact ion pair.

While we have found that the bulkiness of solvent molecules can play an important role in reactions of ionic species and have proposed that dimensiosolvatic effects, the effects of the molecular size of solvent, must be taken into consideration for discussing reaction rates and equilibria,[2,3)] the expression of the bulkiness in terms of a definite physical meaning is a difficult problem. In attempts to quantify the dimensiosolvatic effects, we have come across an interesting but confusing problem in the literature. That is selectivity in solvolyses.

Selectivity in solvolyses of organic halides or sulfonates in binary solvents, has attracted the interests of a number of investigators.[4,5)] When one undertakes solvolyses of organic halides in ethanol–water mixtures, generally an alcohol, which is a reaction product with water, is more abundantly obtained than an ether, which is a reaction product with the alcohol, when the molar ratios of the alcohol to water is taken into consideration. The most studied is the case of water–ethanol, where an ethyl ether is less formed than an alcohol relative to the solvent composition used for the reaction, in spite of the nucleophilicity of ethanol being better than that of water.[6)]

Selectivity (*S*) is usually expressed by

$$S = k_e/k_a, \tag{1}$$

where k_a is the rate of formation of the alcohol, and k_e that of the ether. Because the solvent is a reagent in solvolyses, the product ratios reflect the molar quantities of water and ethanol (Eq. 2). Thus, when one obtains the selectivity *S*, one divides the product ratio by the molar ratio of ethanol to water (Eq. 3).

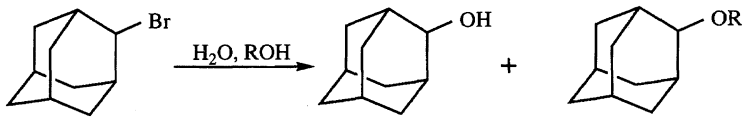
$$\text{Product ratio} = k_e[\text{ethanol}]/k_a[\text{water}], \tag{2}$$

$$S = k_e[\text{ethanol}]/k_a[\text{water}] \div [\text{ethanol}]/[\text{water}]. \tag{3}$$

The cause for this apparently anomalous phenomenon was discussed from various points of view. At the outset, the high stability of water-intervened ion pairs relative to that of alcohol-intervened ion pairs was postulated because water could form two hydrogen bonds with sulfonate anions when it intervenes into the ion pair, whereas an alcohol can form only one.[7)] However, this becomes less likely, because even halides, which can form only one hydrogen bond with water in the solvent separated ion pair (SSIP), also show similar selectivity.

Secondly, a change in nucleophilicity is postulated for the molecules trapped between the cation and the anion of an ion pair.[8)] According to the theory, for some reasons, water molecules trapped in the ion pair become more nucleophilic than ethanol in the same situation. However, this theory ignores the fact that the out-going of the trapped molecule in the ion pair is far slower than the collapse of the ion pair to produce the product.[9)] It is also difficult to explain by this theory why the selectivity changes when the structure of the alkyl part of the alcohol used for solvolyses or the leaving group in the substrate is changed. In addition, if this theory were valid, one would have to assume that two molecules of solvents, water and an alcohol, must intervene into the ion pair for competition. One could argue that solvent molecules intervene one by one. But this situation is too complex to discuss at the present time because the rate-limiting step is unknown and thus we wish to ignore this possibility.

In addition to these drawbacks, this theory, together with the theory of stabilization by hydrogen bonding, has another shortcoming which should be taken into consideration. That is, these theories consider the stability of an intermediate but not the energy level of the transition state for the reaction.



Scheme 1.

By definition of the selectivity S, we use the ratios of rate constants. Even though one can defend the theory by saying that the energy level of the intermediate is very close to that of the transition state, the use of the transition state of the reaction, if possible, is more direct and more desirable than the discussion of the intermediate. We thus wish to discuss the factors that influence the transition state energy.

When we admit that the transition state is important, we must consider the transition structures. But this is not easy in general. As is postulated by Winstein et al.[10] and is accepted by many investigators, the solvolyses of organic halides or sulfonates can proceed via any of contact ion pairs (CIP), SSIP, or free ions. In addition we must also take into consideration the solvation of the ions produced. Therefore, discussion of solvolyses of organic halides or sulfonates in general is too complicated for delineation by simple considerations.

Halo- or arylsulfonyloxy-adamantanes provide convenient examples for studying such effects without much complexity, because they ionize by assistance of ionizing power but not by the nucleophilic assistance of the solvent, a reaction from the backside of the cation is impossible because the backside is blocked, and free ions are not formed in 2-bromoadamantane because it is a secondary halide.[11] Indeed, 2-bromoadamantane is believed to give products from the solvent-separated ion pairs exclusively, from large secondary isotope effects,[12] stereochemical retention,[13] high m values in Grunwald–Winstein equation,[14] and product analyses of solvolyses with addition of sodium azide to the system.[15]

We selected this 2-bromoadamantane for our study because the system is simple and factors that must be taken into consideration for controlling the product ratio are only a few. In addition, because 2-bromoadamantane can be assumed to undergo solvolysis reactions via SSIP exclusively, while there is a possibility that 1-bromoadamantane undergoes the reaction via free ions to some extent because of its nature being a tertiary halide, the former is a superior substrate for our objectives (Scheme 1). We limit our alcohols to only simple alkanols, because an alcohol such as 2,2,2-trifluoroethanol has additional factors which could influence the transition state for solvent intervention to CIP. Then the selectivity observed by using various alcohols should reflect a few factors affecting the product-determining step. The following points deserve mention.

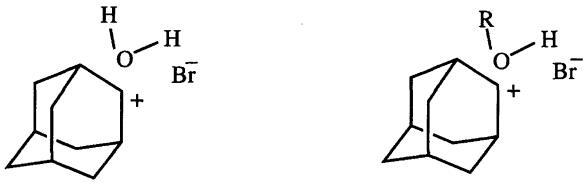
When the transition structure of 2-bromoadamantane for ionization is modeled, it must be the one in which the C–Br bond is stretched, producing some ionic character, and is stabilized by solvent molecules. However, this ionization to CIP is not the product-determining step. The product is determined by the transition state for solvent-intervention (vide infra). The barrier to solvent intervention to CIP was predicted to be present, though the barrier height is not high.[16] In this transition state for the product-determining step, typically, the solvent molecules solvate the CIP and one molecule of the solvent is to intervene into the C^+Br^- ion pair with the oxygen directing to the cationic part and the hydrogen of the OH group directing toward the anionic Br (Scheme 2). To the first approximation, we may assume that the cation–oxygen interactions and the OH–bromide interactions (and/or the electrostatic interactions between the C–Br and the O–H) are nearly the same, even if the alkyl part (or hydrogen) of ROH changes. Then the most influential factor for the intervention of water or alcohol must be the steric effects of the R part of the ROH on intervention. This discussion leads to a conclusion that the bulkier the R group, the slower the intervention of the solvent molecule into the contact ion pair.

Indeed, there are several papers that suggest importance of the steric bulk of the alcohol in determining the S value.[17] t-Butyl alcohol gives the smallest S value among alcohols examined, 2-propanol follows, and then comes ethanol, methanol giving the largest S value for the solvolyses of adamantyl derivatives.[18] On the standpoint of the dimensiosolvatic effects, these results can be taken as suggesting the importance of the effects. However, the results in the literature are fragmental and S values reported by different groups of investigators are not even in agreement for the same solvolytic reactions in the same binary mixtures.[19]

This means that there is a factor that should be carefully reexamined. In addition we hoped that examining the solvent effects on the selectivity in a series of alcohols should provide a measure for the dimensiosolvatic effects. This prompted us to carry out the systematic study of the solvolyses of 2-bromoadamantane in binary mixtures of water–alcohols at various compositions and at various temperatures.

Results and Discussion

There are papers published by a group of investigators who postulate that 2 molecules of solvent intervene to form an SSIP.[20] We neglect this postulate because it is highly unlikely that two molecules intervene simultaneously and, if it were the case, product ratios must be expressed



water intervention alcohol intervention

Scheme 2.

by k_e[alcohol]$^2/k_a$[water]^2 rather than k_e[alcohol]$/k_a$[water], which is not in agreement with the observed values. It may again be possible to argue that two molecules of solvents intervene consecutively rather than simultaneously. However, we cannot discuss the effects of various factors, if two molecules intervene consecutively and which of the two steps requires more energy is unknown.

In the following discussion, we assume that only one solvent molecule intervenes to form SSIP from CIP for the reasons that have been mentioned. However, we believe the following discussion is also applicable to the cases where solvent intervention to SSIP to loosen the ion pairs is the product-determining step. Such a case has been found previously.[3)]

The rates of solvolyses of 2-bromoadamantane in various alcohols are given in Table 1. Apparently, the rates are affected by the ionizing power, Y, in conformity with the results of solvolyses in fluorinated alcohols.[11)] These results indicate that the rate-limiting step of the solvolyses is the formation of CIP. However, this step cannot be the product-determining step. The product-determining step must be the solvent intervention step toward the CIP.

We decided to use the method of Allard and Casadevall[18c)] for calculating the S value, that is, the product ratios were taken at various degrees of completion of the reaction and the values were treated statistically. The values of initial stages were abandoned because the small quantity of the products could cause large errors in the measurements and consequently in the S value: The product ratios at 30 to 60% completion of the reaction were used for the statistical treatment.

After examining the selectivity values for the alcohols at various compositions of water–alcohol mixtures, we immediately noticed that the S value varied to some extent, especially at the very low concentration of water, when the ratios of alcohol to water were changed. In addition, the S value fluctuates more than the error limits at low concentrations of water. This has been noticed by several workers, while it was specifically mentioned by Allard and Casadevall with use of 1-bromoadamantane.[18c)] The cause for this anomaly has not been discussed in detail in the literature, but we believe that the errors are caused by two factors. One is the limit of accuracy of the product ratios which are obtained by gas chromatography and another can be the change in "activity" of water in low concentrations of water in alcohol. The low concentration of water tends to give large S values with respect to high concentrations in most of the cases. Because a water cluster is destroyed under the conditions, the water molecule surrounded by alcohol molecules can be less active in intervening to the CIP than that in clusters. In terms of the present interest, the effective size of a water molecule becomes large at very low concentration. For these reasons, the S values for 1.0 : 0.4 and 1.0 : 0.8 alcohol/water mixtures only are given in Table 2. The tendency is still visible in these data.

Examining the S values in Table 2, we notice that they are almost independent of temperature. It might be argued that this tendency means the similarity in enthalpies of activation for two solvents. However, we believe that, because of the subtle difference in the enthalpies of activation for the solvent intervention, the experimental errors render it invisible. A slight increase of the S values at high temperatures may

Table 1. Kinetic Parameters for Solvolyses of 2-Bromoadamantane in Pure Alcohols[a)]

Alcohol	k_{391}/s^{-1}	$\Delta G^{\ddagger}_{391}$/kcal mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	Y
CH_3OH	2.25×10^{-6}	33.4	31.6±1.1	−4.5±2.7	−1.12
C_2H_5OH	4.01×10^{-7}	34.7	26.3±2.3	−21.4±5.5	−2.40
$CH_3(CH_2)_2OH$	1.34×10^{-7}	35.6	23.7±3.9	−30.3±9.2	—
$(CH_3)_2CHOH$	7.36×10^{-8}	36.1	23.6±2.9	−31.6±7.1	−3.42

a) 1 cal = 4.184 J.

Table 2. Temperature Dependence of S Values for the Solvolyses of 2-Bromoadamantane in Aqueous Alcohols

Alcohol	Alcohol/Water Molar ratio	120 °C	130 °C	135 °C	140 °C	145 °C	150 °C
CH_3OH	1.0 : 0.4	0.60±0.02	0.60±0.02	0.60±0.02	0.60±0.02		
	1.0 : 0.8	0.73±0.05	0.67±0.06	0.60±0.03	0.61±0.04		
CH_3CH_2OH	1.0 : 0.4		0.83±0.04	0.81±0.04	0.80±0.04		0.85±0.03
	1.0 : 0.8		0.60±0.05	0.66±0.06	0.54±0.02		0.54±0.04
$CH_3(CH_2)_2OH$	1.0 : 0.4		0.36±0.01	0.47±0.20		0.36±0.04	0.45±0.04
	1.0 : 0.8		0.40±0.03	0.38±0.05	0.39±0.02	0.40±0.07	0.40±0.03
$(CH_3)_2CHOH$	1.0 : 0.4		0.48±0.01	0.47±0.20		0.41±0.10	0.52±0.14
	1.0 : 0.8		0.39±0.04	0.38±0.16	0.38±0.02	0.41±0.03	0.40±0.05
$(CH_3)_3COH$	1.0 : 0.4	0.18±0.01	0.16±0.01	0.17±0.01	0.14±0.01		0.11±0.01
	1.0 : 0.8	0.13±0.01	0.10±0.01	0.10±0.01	0.10±0.01		0.07±0.01

Table 3. *D* Values of Alcohols[a)]

Alcohols	H_2O	CH_3OH	C_2H_5OH	$CH_3(CH_2)_2OH$	$(CH_3)_2CHOH$	$(CH_3)_3COH$
D	1.0	1.5	1.7	2.5	2.6	10

a) For definition of *D* values, see text.

support this statement.

Because the *S* values fluctuate at low concentrations of water in alcohols, we propose that the values at or close to the 1 : 1 molar concentrations be taken as characteristic to the alcohol. In the present data, the alcohol/water mixtures of 1.0 : 0.8 correspond to this concentration. The *S* values still fluctuate but are reasonably constant.

We propose to use the reciprocal of the averages of *S* values for 1.0 : 0.8 alcohol/water mixtures, at all temperatures shown in Table 3, as measures of dimensiosolvatic effects when a solvent molecule intervenes into CIP to form SSIP. It would be more convenient if a value is larger for a bulky *t*-butyl group than that of a small alkyl group. This value for *t*-butyl alcohol happened to be 10. By definition, the value for water must be 1.0. Thus we can scale the effective bulkiness of solvent molecules from 1 to 10. We wish to call these *D* values because these scale dimensions of molecules. Examining the data in Table 3, we notice a few interesting points.

The first is that methanol and ethanol give almost the same *D* values. This result implies that the bulkiness of the alkyl group is relatively unimportant in solvent intervention into CIP. This requires improvement of the approximation which has been made. We believe this is due to the high basicity of the ethanolic oxygen atom relative to that in methanol which stabilizes the cationic center. McManus and Zutaut have pointed out that electrophilicity of the hydroxylic group in fluorinated alcohols can be important in facilitating the solvent intervention with respect to the alkanols.[18b)] In our case, the acidity of various alcohols is weak and does not vary significantly, because they are all alkanols, or it is even decreased slightly when an alkyl part becomes large. A more important change should occur in the nucleophilicity of alcohol–oxygens. We conclude, therefore, that the nucleophilicity of an alcohol is playing some roles in facilitating the solvent intervention.

The second point is that 1-propanol and 2-propanol exhibit almost the same *D* value. This has two significances. One is that the alkyl groups, propyl and isopropyl, can be of almost the same steric bulk by taking an appropriate conformation, as in the case of *A* values in cyclohexane derivatives.[21)] On the other hand, it is known that when a long chain has to pass a loop, such as the case of internal rotation in *m*- or *p*-cyclophanes, the longer the chain, the bulkier the effective size.[22,23)] Probably these two factors, in addition to the effect of methyl group(s), contribute to make the observed steric bulk of the propyl and the isopropyl group.

The third point is that the *t*-butyl group is definitely a large group. However, the relative size of the *t*-butyl group in the solvent intervention is rather small compared to the *A* value of the cyclohexane derivatives. We attribute this again to the fact that solvent intervention is assisted by the nucleophilicity of the alcoholic oxygen and, at the transition state for the solvent intervention, the alkyl group has not been buried completely between the cation and the anion.

Comparing these values for a series of alcohols, we believe that the theory which assumes the change in nucleophilicity can be ruled out. It can be argued that the general decrease of the selectivity on going from a less substituted alcohol to an alcohol with more methyl-substituent(s) is an indication which favors the change of nucleophilicity of the solvent molecule when trapped into an ion pair. However, if this theory were correct, the tendency of decreasing the selectivity should have fit a smooth curve when one increases the methyl-substituent one by one. The abrupt decrease in *t*-butyl alcohol must be an indication that the steric factor is important.

Finally, the effective size of the alkanols is determined by the steric bulkiness, the hydrogen-donating ability in hydrogen-bond formation (and/or electrostatic interaction), and cation-stabilizing effect of the oxygen atom. The *D* value in Table 3 should be taken as a result of these factors, in which the steric bulkiness plays the major role.

Experimental

^{1}H NMR spectra were recorded on a Varian Gemini-300 spectrometer, operating at 300.1 MHz, and mass spectra on a JEOL JMS-303HF spectrometer by the electron-impact method.

Materials. 2-Bromoadamantane was commercially available (Tokyo Kasei) and was used as received.

2-Methoxyadamantane. To a solution of 4.0 g (21 mmol) of silver tetrafluoroborate in 10 mL of dry methanol was added dropwise a solution of 2.0 g (9.3 mmol) of 2-bromoadamantane in 30 mL of methanol over a period of 40 min under a nitrogen atmosphere in the dark. The mixture was stirred for 2 d at room temperature and the precipitate was removed by filtration after the completion of the reaction. The solvent was evaporated and the residue was submitted to silica-gel chromatography with hexane eluent to give a pure product in 30% yield. It was an oil. ^{1}H NMR ($CDCl_3$) δ=1.46—2.03 (14H, m), 3.34 (3H, s), 3.34 (1H, br s). This compound was identical with the authentic specimen reported in the literature.[24)]

2-Ethoxyadamantane. This compound was prepared similarly from ethanol, 2-bromoadamantane, and silver tetrafluoroborate in 62% yield. It was an oil and identical with the authentic specimen.[25)] ^{1}H NMR ($CDCl_3$) δ=1.21 (3H, t, J=7.0 Hz), 1.45—2.06 (14H, m), 3.43 (1H, br s), 3.49 (2H, q, J=7.0 Hz).

2-Isopropoxyadamantane. This compound was prepared similarly from 2-propanol, 2-bromoadamantane, and silver tetrafluoroborate in 39% yield. It was obtained as an oil. High resolution mass spectra: Found: *m/z* 194.1703. Calcd for $C_{13}H_{22}O$: M, 194.1670. ^{1}H NMR ($CDCl_3$) δ=1.14 (6H, d, J=6.1 Hz), 1.46—2.03 (14H, m), 3.50 (1H, br s), 3.69 (1H, sept, J=6.1 Hz).

2-Propoxyadamantane. This compound was similarly pre-

Table 4. Rates of Solvolysis of 2-Bromoadamantane in Various Solvents at 0.01 mol L^{-1} Concentration

Solvent	$(k \times 10^6)$ s^{-1} (temperature/°C)
CH_3OH	2.31 (120), 5.76 (130), 10.0 (135), 16.2 (140), 27.6 (145), 39.6 (150), 68.3 (155)
C_2H_5OH	0.429 (120), 0.912 (130), 1.96 (140), 4.02 (145), 4.68 (150), 7.38 (155)
$CH_3(CH_2)_2OH$	0.423 (135), 0.613 (140), 0.903 (145), 1.28 (150), 1.52 (155), 2.64 (160)
$(CH_3)_2CHOH$	0.0752 (120), 0.137 (130), 0.209 (135), 0.457 (145), 0.651 (150), 0.960 (155)
$(CH_3)_3COH$	0.103 (140), 0.0450 (150), 0.543 (160), 0.102 (170), 0.483 (180)

pared from 1-propanol, 2-bromoadamantane, and silver tetrafluoroborate in 53% yield. It was an oil. High resolution mass spectra: Found: *m/z* 194.1632. Calcd for $C_{13}H_{22}O$: M, 194.1670. ^{1}H NMR ($CDCl_3$) δ=0.94 (3H, t, *J*=7.4 Hz), 1.44—2.06 (14H, m), 1.64 (2H, sext, app *J*=6.9—7.4 Hz), 3.38 (2H, t, *J*=6.7 Hz), 3.40 (1H, br s).

2-*t*-Butoxyadamantane. Preparation of this compound by the method described in the literature, which is rather laborious, ended in a poor yield.[26] However, the use of the method described for preparation of 1-*t*-butoxyadamantane[27] afforded much better results.

To a solution of 2.0 g (9.3 mmol) of 2-bromoadamantane and 2.0 g of pyridine in 12 mL of dry 2-methyl-2-propanol was added dropwise a solution of 2.0 g (9.7 mmol) of silver perchlorate over a period of 30 min. The mixture was refluxed for 2 d and then sodium bromide was added to destroy any excess of silver perchlorate. The reaction mixture was treated as above and the desired product was obtained in 79% yield as an oil. This compound was identical with the compound reported in the literature.[26] ^{1}H NMR ($CDCl_3$) δ=1.16 (9H, s), 1.41—2.13 (14H, m), 3.53 (1H, br s).

Solvolyses. 2-Bromoadamantane (21.5 mg or 1.00×10^{-4} mol) and 10.7 mg (1.00×10^{-4} mol) of 2,6-dimethylpyridine were dissolved in an appropriate solvent mixture to make up 0.01 mol L^{-1} solutions in a 10 mL volumetric flask. The solution was placed in a glass tube and the tube was sealed. Eight such tubes were placed in a thermostatted oil bath (Yamato Thermoelite Model BH-71) at an appropriate temperature (130—190 °C) and were opened after appropriate times: For aqueous methanol it was 2 h and more and for aqueous *t*-butyl alcohol 12 h and more. The error of temperature setting is estimated to be ±0.1 °C. The rate constants are compiled in Table 4.

Analysis of the Products. The reaction was quenched by immersing the tube in an ice-bath and the tube opened. The sample solutions were directly submitted to gas chromatography. The gas chromatographic apparatus was a Hitachi G-3000 equipped with an OV-1 capillary column of 25 m×0.25 mm poly(dimethylsiloxane). The carrier gas was He. The area of the peaks for the products was read directly from the machine. Calibration curves were drawn for every product and the observed intensities of the peaks were compared with the curves. The peaks for 2-adamantanol and 2-alkoxyadamantane were identified by injecting the known compound with the reaction mixture. The analyses were repeated three times and the data are presented as averages of the three. For one solution, the amount of ether obtained from 8 samples were plotted against the amount of 2-adamantanol and the best fit line afforded the selectivity.

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