Electronic Effects of Icosahedral Carboranes. Retentive Solvolysis of (1,2-Dicarba-*closo*-dodecaboran-1-yl)benzyl *p*-Toluenesulfonates

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The icosahedral *closo* carboranes (dicarba-*closo*-dodecaboranes) have been described as three-dimensional aromatic systems, by analogy with the two-dimensional benzene ring,[1] and the implications of this for electronic interaction with substituents have been of particular interest since the first studies on these compounds some 30 years ago. Concerning the electronic effect of icosahedral carboranes on a substituent outside the cage, investigations of pK_a values of carboranylbenzoic acids and carboranylanilinium ions,[2] and of ^{19}F NMR chemical shifts of carboranylfluorobenzenes,[3] showed that the icosahedral carboranes behave as strongly electron-withdrawing groups in the sequence *ortho* ≫ *meta* > *para* toward carbon substituents. These investigations have also shown that the electron-withdrawing inductive effect of the carborane cage is similar to that of halogens, and that ground-state cage−ring-π interaction is not important. Nevertheless, the electron-delocalizing effect of the icosahedral carboranes, especially the electronic bonding structure of the two cage carbons in *o*-carboranes, remains ambiguous. Although the electron-delocalizing effect in the static situation has been evaluated by spectroscopic methods,[1a,4] the effect in the dynamic situation (e.g., kinetics) has not been examined. In this paper, we report the first example of kinetic investigation of a carbocation adjacent to an *o*-, *m*-, or *p*-carboranyl cage, and the discovery of a unique character of the *o*-carboranyl moiety.

To evaluate the electronic effects of the icosahedral carboranes, we focused on the hydrolysis of (1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaboran-1-yl)benzyl *p*-toluenesulfonates (**1**, **2**, **3**). The (*o*-carboranyl)benzyl tosylate **1** was prepared from 1,2-dicarba-*closo*-dodecaborane by employing tetrabutylammonium fluoride (TBAF)-promoted addition[5] with benzaldehyde followed by reaction with *p*-toluenesulfonyl chloride. The benzyl tosylates, **2** and **3**, were prepared by the reaction of corresponding lithiates of 1,7- and 1,12-dicarba-*closo*-dodecaboranes with benzaldehyde followed by reaction with *p*-toluenesulfonyl chloride.[6] (2-Methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)benzyl *p*-toluenesulfonate (**4**) was prepared from 1-methyl-1,2-dicarba-*closo*-dodecaborane[7] by a similar procedure to that used for **2**.

The kinetic experiments of the hydrolysis on the (carboranyl)-benzyl tosylates (**1**−**4**) and (1-adamantyl)benzyl tosylate (**5**) in 70% dioxane-d_{12}−D_2O were performed by NMR measurement of the decrease of starting materials. The hydrolyses of **1**−**5** gave the corresponding alcohols **6**−**10** quantitatively. The rate constants and activation parameters for the hydrolysis of **1**−**4** are summarized in Table 1. The *m*- (**2**) and (*p*-carboranyl)benzyl tosylates (**3**) showed almost the same values of rate constant and activation parameters. The k_1 values of approximately 6×10^{-6} s^{-1} at 80 °C for **2** and **3** were remarkably smaller than the k_1 value of 1.03×10^{-3} s^{-1} at 50 °C for (1-adamantyl)benzyl tosylate (**5**), in which the substituent resembles the carborane cage in molecular size and shape. This result is consistent with a strongly electron-withdrawing effect by the icosahedral carboranes in **2** and **3**, compared to the electron-donating adamantyl group in **5**. However, the hydrolysis of (*o*-carboranyl)benzyl tosylate (**1**), bearing what is thought to be the most electron-withdrawing group among the icosahedral carboranes, was 100−1000 times faster than that of **2** and **3**. The activation parameters of the hydrolysis of the *o*-carboranyl derivative were $\Delta H^{\ddagger} = 16.1$ kcal/mol, $\Delta S^{\ddagger} = -28.3$ eu. These values differ significantly from those of **2** ($\Delta H^{\ddagger} = 27.1$ kcal/mol, $\Delta S^{\ddagger} = -6.1$ eu) and **3** ($\Delta H^{\ddagger} = 26.0$ kcal/mol, $\Delta S^{\ddagger} = -9.0$ eu), suggesting that the processes involved are more "dissociative" than that of **2**. It appears that the mechanism of hydrolysis of **1** is distinct from that of **2**, and that the transition state of hydrolysis of **1** is stabilized.

A stereochemical examination of the hydrolysis of optically active (carboranyl)benzyl tosylates (**1**−**3**) provided more persuasive evidence of a distinction between the *o*-carboranyl group and the others. The optically active (carboranyl)benzyl tosylates were prepared from corresponding alcohols, which were obtained by optical resolution of the racemic alcohols (**6**−**8**) as (−)-camphonic acid esters, followed by alkaline hydrolysis. The optical purity of the optically active (carboranyl)benzyl derivatives was determined by ^{1}H NMR measurement in the presence of a chiral shift reagent: tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III). Hydrolysis of (+)-*R*-*m*- ((+)-*R*-**2**) and ((+)-*R*-*p*-carboranyl)benzyl tosylate ((+)-*R*-**3**) afforded racemic **7** and **8** under the same conditions as used for the kinetic examination. The results indicated that the hydrolyses of **2** and **3** proceed through typical S_N1 processes. However, hydrolysis of

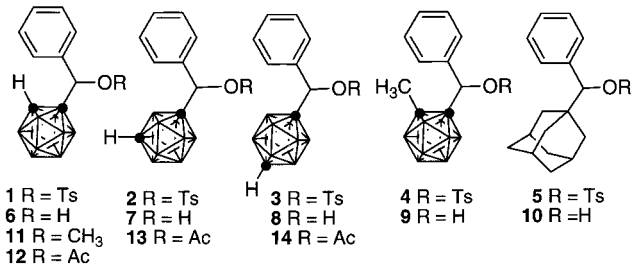

Figure 1. In the icosahedral cage structure, ● represents a carbon atom and other vertexes represent BH units.

Table 1. Pseudo-First-Order Rate Constants (k_1 s^{-1}) and Activation Parameters for the Hydrolysis of **1**−**4** in 70% Dioxane-d_{12}−D_2O

	1	**2**	**3**	**4**
temp (°C)				
50.7	5.87×10^{-5}			
60.7	1.21×10^{-4}			
70.7	2.71×10^{-4}			6.37×10^{-5}
80.7	5.24×10^{-4}	5.56×10^{-6}	6.28×10^{-6}	1.35×10^{-4}
90.7		1.80×10^{-5}	1.76×10^{-5}	2.61×10^{-4}
100.7		4.62×10^{-5}	4.82×10^{-5}	
rel rate (calcd) at 25.0 °C	1840	1.0	1.4	356
$\Delta H^{\ddagger}$ (kcal/mol)	16.1	27.1	26.0	16.9
$\Delta S^{\ddagger}$ (eu)	−28.3	−6.1	−9.0	−28.8

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Table 2. Pseudo-First-Order Rate Constants (k_1 s^{-1}) and Activation Parameters for the Acetolysis of **1**−**4** in CD_3COOD

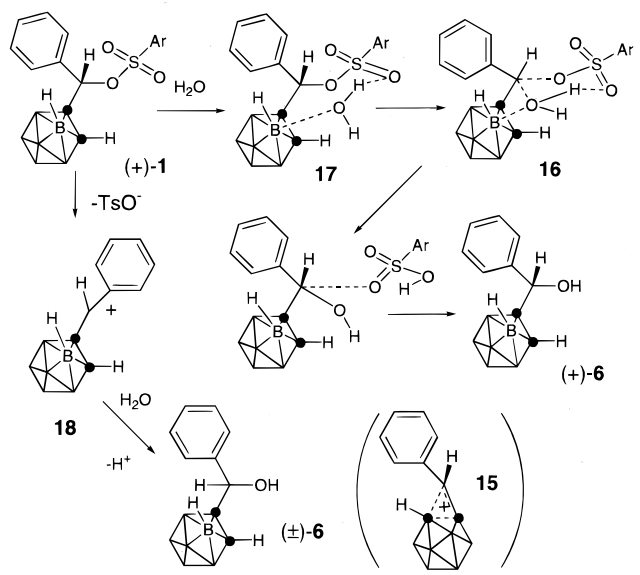
	1	**2**	**3**	**4**
temp (°C)				
100.6	1.32×10^{-5}	3.06×10^{-5}	3.92×10^{-5}	1.67×10^{-5}
108.0	2.82×10^{-5}	6.23×10^{-5}	8.36×10^{-5}	3.28×10^{-5}
115.6	5.80×10^{-5}	1.13×10^{-4}	1.39×10^{-4}	6.72×10^{-5}
rel rate (obsd) at 108.0 °C	0.45	1.0	1.3	0.53
$\Delta H^{\ddagger}$ (kcal/mol)	28.5	24.4	23.6	27.8
$\Delta S^{\ddagger}$ (eu.)	−7.0	−14.2	−15.8	−8.5

(+)-*R*-(*o*-carboranyl) benzyl tosylate ((+)-*R*-**1**, 100% ee.) afforded (+)-*R*-**6** in a 71% ee.[8] Similarly, methanolysis of (+)-**1** proceeded with similar rate constants (at 60 °C) to those of the hydrolysis to afford (+)-*R*-(*o*-carboranyl)benzyl methyl ether ((+)-*R*-**11**) in a 73% ee.[9]

When the rate of reaction is greater than expected, and the configuration at a chiral carbon is retained and not inverted or racemized, mechanisms such as intramolecular neighboring-group effects or an intermolecular S_Ni mechanism can be anticipated. To examine the behavior of these solvolyses, we performed acetolysis of the (carboranyl)benzyl tosylates (**1**−**4**) in CD_3COOD. The results were distinct from those in the case of hydrolysis and methanolysis. The rate constants and activation parameters for the acetolysis are summarized in Table 2. The *m*- (**2**) and *p*-carboranylbenzyl tosylates (**3**) showed almost the same rate constants as in the case of the hydrolysis. However, the acetolysis of *o*-carboranylbenzyl tosylate (**1**) was slower than that of **2** and **3**. The activation parameters of the acetolysis of the *o*-carboranyl derivative ($\Delta H^{\ddagger} = 28.5$ kcal/mol, $\Delta S^{\ddagger} = -7.0$ eu) were quite different from those in the case of hydrolysis ($\Delta H^{\ddagger} = 16.1$ kcal/mol, $\Delta S^{\ddagger} = -28.3$ eu). Further, acetolysis of the optically active carboranyl tosylates (**1**−**3**) afforded racemic products (**12**−**14**). The results indicated that the acetolyses of **1**−**3** proceed through typical S_N1 processes. The significant mechanistic change upon changing the solvent from D_2O to CD_3COOD suggested that neighboring-group participation by the electron-delocalized C−C bond in *o*-carboranes, such as formation of a nonclassical carbocation **15**, could be excluded.

We propose a mechanism involving a six-membered cyclic structure **16** (intermolecular S_Ni mechanism) as shown in Scheme 1. The first step of the reaction is interaction between the oxygen atom of nucleophile, which is hydrogen-bonded to sulfonate, and the 3-position boron atom in the carborane cage (such as **17**). It is well-known that deboranation of *o*-carborane by nucleophiles such as alkoxides,[10] aliphatic amines,[11] and fluoride anion[12] affords

Scheme 1



the *nido*-7,8-$C_2B_9H_{12}^-$. The nucleophilic attack occurs at the 3- or 6-position boron atom, since these are the most electron-deficient borons in the carborane cage. Although the deboronation proceeds in the case of *m*-carborane, the reaction rate is much lower than that in the case of *o*-carborane.[11,13] Recently, the hydrogen-bonding character and CH−π interaction of C−H on the *o*-carborane cage have been discussed in the field of supramolecular chemistry.[14] Participation of 2-C−H, however, should be excluded in this case, because the hydrolysis rate of (2-methyl-*o*-carboranyl)benzyl tosylate (**4**) was similar to, but somewhat slower than that of **1** and the activation parameters were similar to those of **1**. These results can be interpreted in terms of steric hindrance of the 2-methyl group to formation of the transition state. The structure **17** would afford the six-membered cyclic transition state **16**, in which the oxygen on the side of sulfonate may be placed on the opposite side (6-position). Thus, the transition state may be highly stabilized, and a considerable loss of entropy is involved, i.e. $\Delta S^{\ddagger}$ is negative. Then elimination of sulfonic acid would give the retentive product. This process is consistent with the alteration of the mechanism to an S_N1 process in the case of acetolysis of **1**, because acetic acid is too weak a nucleophile to interact with boron in the carborane cage. Partial recemization in the hydrolysis can be interpreted in terms of a contribution of the usual S_N1 process via the carbocation **18**, as in the hydrolysis of **2** and **3**.

The exceptional kinetic features and retentive nucleophilic substitution of (*o*-carboranyl)benzyl tosylate compared with other carboranyl derivatives is noteworthy, and should be helpful for analyzing the electronic bonding structure of the two cage carbons in *o*-carboranes and for investigating fundamental theoretical features of carboranes.

Supporting Information Available: Details of synthesis, spectral data for compounds **1**−**14**, and experimental procedures of the kinetic examination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The absolute configuration of **1** was determined by X-ray crystallography of (+)-*R*-(1,2-dicarba-*closo*-dodecaboran-1-yl) *p*-bromobenzenesulfonate.

(9) Methanolysis of **2** and **3** at 60 °C was too slow to allow determination of the kinetic parameters.

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