A Direct Comparison Study of Asymmetric Borane Reduction of C=N Double Bond Mediated by Chiral Oxazaborolidines

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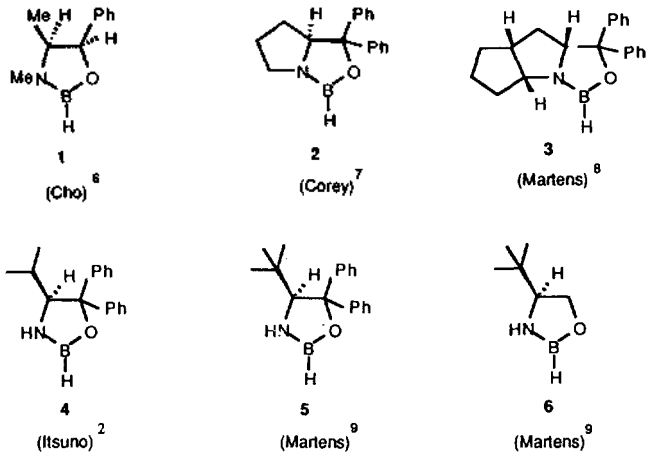
A comparison study on asymmetric borane reduction of ketoxime ethers and *N*-substituted ketimines possesing C=N double bond mediated by the selected chiral oxazaborolidines (**1-6**) was investigated. Thus, an aromatic ketoxime *O*-alkyl ether acetophenone oxime *O*-methyl ether was reduced to the corresponding amine (1-phenylethylamine **8a**) with optical yields, such as 58% ee with **1**, 86% ee with **2**, 3% ee with **3**, 99% ee with **4**, 60% ee with **5**, and 73% ee with **6**. However, the reduction of an aliphatic ketoxime derivative 2-heptanone oxime *O*-methyl ether provided low optical inductions (7-13% ee). For ketoxime *O*-trimethylsilyl ethers, the reduction of acetophenone *O*-trimethylsily ether afforded **8a** with optical yields which were 90% ee with **1**, 40% ee with **2**, 2% ee with **3**, 62% ee with **4**, 5% ee with **5**, and 60% ee with **6**. The reduction of 2-heptanone *O*-trimethylsilyl ether also gave the product amine with low optical yields (10-40% ee). In the case of *N*-substituted ketimines, the reduction of acetophenone *N*-phenylimine afforded the corresponding amine with 79% ee, 78% ee, 9% ee, 73% ee, 78% ee and 67% ee using **1**, **2**, **3**, **4**, **5**, and **6**, respectively, whereas low optical inductions (5-18% ee) for 2-heptanone *N*-phenylimine were achieved.

Introduction

One of the convenient methods for the preparation of optically active amines is asymmetric reduction of imine derivatives. However, the efficient enantioselective reduction of imines to amines with chiral hydride reagents has been relatively neglected in contrast to the large number of papers dealing with carbonyl compounds.[1] Recently, the effective asymmetric borane reductions of ketoxime *O*-alkyl ethers using a chiral oxazaborolidine (**4**, Itsuno's reagent) derived from (S)-valine as a chiral auxiliary were reported by Itsuno and co-workers.[2,3] Very recently we reported the enantioselective conversion of *N*-substituted ketimines into the corresponding amines via asymmetric reduction using chiral hydride reagents.[4]

On the other hand, asymmetric borane reductions of ketones mediated by a variety of chiral oxazaborolidiens have been extensively investigated.[5] Accordingly, it appears desirable to undertake the study on the asymmetric reduction of C=N bond mediated by these chiral oxazaborolidines. However, only a few of references regarding this enantioselective reduction have appeared in the literature. To examine the effectiveness of chiral oxazaborolidines in the asymmetric reduction, we first selected the following chiral 1,3,2-oxazaborolidines **1-6** derived from (-)-ephedrine, natural and unnatural α-amino acids, such as (S)-proline, (S)-valine, a bicyclic proline (1R, 3R, 5R)-2-azabicyclo[3.3.0]octan-3-carboxylic acid and (S)-*tert*-leucine (scheme 1) and compared their enantioselectivities by employing asymmetric borane reduction of C=N bond in the presence of the selected chiral oxazaborolidines. In this paper, the direct comparison of results obtained from the asymmetric borane reduction of oxime **7** and imine derivatives **8** chosen as representative compounds possesing C=N bond mediated by each of the six selected chiral oxazaborolidines is described.

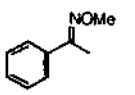
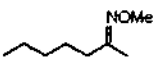


Scheme 1.

Results and Discussion

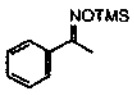
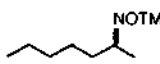
General. As representative compounds possesing C=N bond, we selected oxime ethers **7** and *N*-substituted ketimines **9**. Thus, acetophenone oxime *O*-methtyl ether (**7a**), 2-heptanone *O*-methyl ether (**7b**), acetophenone oxime *O*-trimethylsily ether (**7c**), 2-hepanone oxime *O*-trimethylsilyl ether (**7d**), acetophenone *N*-phenylimine (**9a**), and 2-heptanone *N*-phenylimine (**9b**) were chosen. The ketoxime *O*-methyl ethers **7a-7b** were prepared by condensation of the corresponding ketones with methoxyl amine[10] and ketoxime *O*-trimethylsilyl ethers **7c-7d** were obtained from silylation of oxime with trimethylsilyl chloride in the presence of triethylamine.[2a] *N*-phenyl ketimines **9a-9b** were prepared by condensation of

Table 1. Asymmetric Borane Reduction of *O*-Methyl Ethers of Acetophenone Oxime and 2-Heptanone Oxime in the Presence of Chiral Oxazaborolidines in Tetrahydrofuran at Room Temperature[a]

Compounds	Chiral oxazaborolidines	Time h	Products amines **8a-8b** yields (%)[b]	% ee[c]	abs. config.[d]
 **7a**	**1**	24	94	58 (36)[f]	S
	2	24	89	86 (58)	S
	3	72	66	3	R
	4[f]	24	100	99 (52)	S
	5	48	89	60	S
	6	24	90	73	S
 **7b**	**1**	12	93	7	S
	2	18	85	34	S
	3	48	78	4	R
	4	18	93	43	S
	5	24	85	15	S
	6	18	93	17	S

[a] All of the reductions were carried out with compounds: chiral oxazaborolidines: borane-THF (1 : 1.1 : 1.1) in THF, unless otherwise indicated. [b] Determined by GC analyses using internal standards. [c] Determined by capillary GC analyses of their MTPA amides. [d] Determined by comparison of the optical rotations and elution order of MTPA amides of optically active authentic amines. [e] The figures in parentheses indicated optical purities obtained by the presence of 10 mole % of oxazaborolidines. [f] Data taken from ref. **2a** and **2d**.

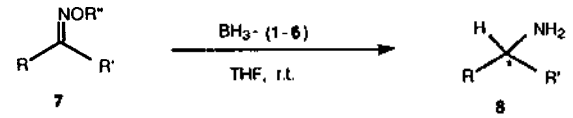
Table 2. Asymmetric Borane Reduction of *O*-Trimethylsilyl Ethers of Acetophenone Oxime and 2-Heptanone Oxime in the Presence of Chiral Oxazaborolidines in Tetrahydrofuran at Room Temperature[a]

Compounds	Chiral oxazaborolidines	Time h	Products amines **8c-8d** yields (%)[b]	% ee[c]	abs. config.[d]
 **7c**	**1**	24	95	90	S
	2	24	87	40	S
	3	72	45	2	R
	4	24	92	62	S
	5	48	85	5	S
	6	24	81	60	S
 **7d**	**1**	18	95	40	S
	2	18	85	10	S
	3	48	64	27	R
	4	18	93	27	S
	5	24	89	13	S
	6	24	87	10	S

[a-d] See the corresponding footnotes in Table 1.

ketones with aniline.[1d,11] The chiral oxazaborolidine (**1**) was prepared from borane-methyl sulfide and (IR, 2S)-(-)-ephedrine by the literature procedure.[6] The other oxazaborolidines **2-6** were generated *in situ* from borane-THF and their precursors β-chiral amino alcohols by each of the reported procedures.[7-9] The reductions were carried out with 1 equiv of borane-THF in the presence of **1-6** in THF at room temperature (*ca.* 28℃). Optical purities of product amines **8-10** were determined by capillary GC analysis of diastereoisomeric ratios of the corresponding MTPA amides.[12]

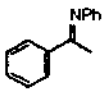
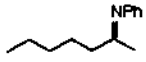
Asymmetric Borane Reduction of Ketoxime Ethers 7 in the Presence of Chiral Oxazaborolidines (1-6) in THF at Room Temperature. The reduction of the selected ketoxime *O*-methyl ethers **7a-7b** with **1**, **2**, **4** or **6** proceeded smoothly to give the corresponding amines **8** in high yields within 24 h. The reduction with **3** or **5** proceeded at a slower rate. Comparing the enantioselectivities of chiral oxazaborolidines (**1-6**) examined for the ketoxime derivatives, **2** was highly effective for aromatic ketoxime derivative **7a** to give 1-phenylethylamine (**8a**) in 86% ee, although optical yield appears somewhat lower as compared to 99% ee obtained by Itsuno.[2a] Other chiral oxazaborolidines provided good enatioselectivities with one exception of **3** for aromatic ketoxime *O*-methyl ether **7a**, such as 58% ee with **1**, 60% ee with **5**, 73% ee with **6**. Only 3% ee with **3** was obtained. However, the borane asymmetric reduction of aliphatic ketoxime *O*-methyl ether **7b** with these chiral oxazaborolidines unfortunately afforded low optical yields (7-43% ee). We also investigated the catalytic effect of the oxazaborolidines by employing reduction of **7a** with 1 equiv of borane-THF in the presence of 0.1 equiv of **1** or **2** in THF at room temperature. The reduction provided optical yields of 36% ee with **1** and 58% ee with **2**, showing high catalytic effect. In this case, somewhat low optical induction as compared to that given by the presence of 1 equiv of **1** or **2** is probably attributed to the consequence of competing noncatalyzed reduction by borane-THF. The results are summarized in Table 1.



a : R = Ph, R' = Me, R" = Me　　**b** : R = n-C_5H_{11}, R' = Me, R" = Me
c : R = Ph, R' = Me, R" = $SiMe_3$　　**d** : R = n-C_5H_{11}, R' = Me, R" = $SiMe_3$

For ketoxime *O*-trimethylsilyl ethers, such as acetophenone *O*-trimethylsilyl ether (**7c**) and 2-heptanone oxime *O*-trimethylsilyl ether (**7d**), the borane reduction of **7c** and **7d** mediated by **1**, **2**, **4** or **6** proceeded smoothly to give the corresponding amines **8a-8b** in high yields at room temperature. The reduction with **3** or **6** was somewhat slower. Comparing enantioselectivities of these chiral oxazaborolidines for reduction of **7c** and **7d**, **1** was highly effective for **7c** to give 90% ee. For **7c**, other chiral oxazaborolidines **2**, **4** and **6** afforded **8a** of 40% ee, 62% ee and 60% ee, respectively, whereas **3** and **5** provided very low optical inductions (2% ee and 5% ee, respectively). In the case of an aliphatic ketoxime derivative 2-heptanone oxime *O*-trimethylsilyl ether, low optical yields (10-40% ee) were obtained. In the reduction of ketoxime ethers using chiral oxazaborolidines derived from (1R, 2S)-ephedrine and (S)-amino acids except **3** derived from (R)-amino acid as chiral auxiliaries, absolute configurations of the products amines **8a-8b** obtained were consistently S enantiomers which were induced by *re* side

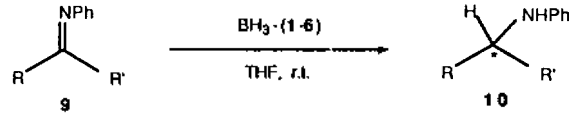
Table 3. Asymmetric Borane Reduction of *N*-Phenyl Ketimines in the Presence of Chiral Oxazaborolidines in Tetrahydrofuran at Room Temperature[a]

Compounds	Chiral oxazaborolidines	Time h	Products amines **10a-10b** yields (%)[b]	% ee[c]	abs. config.[d]
 **9a**	**1**	8	96	79 (38)[e]	R
	2	3	98	78 (37)	R
	3	2	96	9	S
	4	3	97	73	R
	5	8	94	78	R
	6	2	97	67	R
 **9b**	**1**	8	95	13	R
	2	4	91	11	R
	3	8	97	8	S
	4	8	90	18	R
	5	24	87	5	R
	6	4	97	10	R

[a-f] See the corresponding footnotes in Table 1.

attack of hydride. The results were summarized in Table 2.

On the other hand, the asymmetric borane reduction of *N*-phenyl ketimines mediated by these chiral oxazaborolidines were also carried out. Thus, both of acetophenone *N*-phenylimine (**9a**) and 2-heptanone *N*-phenylimine (**9b**) were smoothly reduced to the corresponding amines **10a-10b** in high yields. In the reduction of **9a**, all of the selected chiral oxazaborolidines with one exception provided **10a** with good enantioselectivities, such as 79% ee with **1**, 78% ee with



a : R = Ph, R' = Me b : R = n-C5H11, R' = Me

2, 9% ee with **3**, 73% ee with **4**, 78% ee with **5** and 67% ee with **6**. However, optical inductions for an aliphatic ketimine **9b** by **1-6** were very low (8-10% ee). In the reduction of **9a**, we also observed the catalytic effect of chiral oxazaborolidines. The absolute configuration of the products amines **10a** and **10b** induced by all of the chiral oxazaborolidines except **3** were R enantiomers in contrast with S enantiomers of **8a** and **8b**. The reason for the opposite configuration is so far unclear. The results were summarized in Table 3.

Conclusion

The first comparison study on asymmetric reduction C=N double bond mediated by the selected chiral oxazaborolidines **1-6** was achieved. Among the oxazaborolidines selected, **1** and **3** were highly effective for the reduction of ketoxime *O*-trimethylsilyl ether such as found for acetophenone oxime *O*-trimethylsilyl ether (90% ee) and ketoxime *O*-methyl ether such as found for acetophenone *O*-methyl ether (99% ee), respectively. These oxazaborolidines were less effective for the same 2-heptanone oxime derivatives. With the exception of **3**, all the chiral oxazaborolidines selected were effective for the reduction of acetophenone *N*-phenylimine with good enantioselectivities (67-79% ee).

Experimental

General. All glassware was dried at 140℃ overnight, assembled hot, and cooled to room temperature under a stream of nitrogen. All reactions with air sensitive materials were carried out under static pressure of nitrogen. Liquid materials were transferred with a double-ended needles.[13]

Spectra. ^{1}H-NMR spectra were conducted on Varian Gemini 300 (300 MHz) and Varian T-60 (60 MHz) spectrometers with Me_4Si as an internal standard. IR measurements were recorded on a Shimadzu IR-435 ratio recording spectrophotometer equipped with a Shimadzu data recorder. Optical rotations were measured with a Rudolph polarimeter Autopol III. Melting points were determined with a Fisher-Johns melting point apparatus.

GC analysis. All GC analyses were carried out with Shimadzu GC-7A gas chromatograph and Hewlett-Packard 5890 gas chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter. Optical purities (% ee) were determined by capillary GC analysis of the corresponding MTPA amides of products amines using a Hewlett-Packard 5890 gas chromatograph equipped with a 50 m methyl silicon capillary column.

Materials. Borane-THF, (1R, 2S)-(-)-ephedrine, (S)-valine, (S)-proline, (S)-*tert*-leucine, (R)-MTPA, and the other commercially available chemical reagents were purchased from the Aldrich Chemical Co. Tetrahydrofuran was distilled over sodium benzophenone ketyl and stored in ampules under nitrogen pressure. Chiral oxazaborolidines, **1**[6], **2**[7], **3**[8], **4**[2a], **5**[9] and **6**[9] were prepared by the literature procedures. Ketoxime derivatives and *N*-phenyl ketimines used as substrates were prepared by the following methods:

Acetophenone Oxime *O*-Methyl Ether (7a).[10] To an aqueous solution (*ca.* 5 m*l*) of acetophenone (20 mmol), methoxyl amine hydrochloride (22 mmol) and sodium acetate three hydrate (22 mmol) was added 95% ethanol (*ca.* 184 m*l*) until the solution was cleared. After the reaction mixture was heated to reflux for 20 h, ethanol was evaporated *in vacuo*. The residue was extracted with ethyl ether, followed by washing with a 5% sodium bicarbonate solution and water and drying over anhydrous magnesium sulfate. After evaporation of solvent, the product was isolated by distillation: bp 95-98℃ /8 mmHg (lit.[2a] 89℃ /5 mmHg), colorless oil, 65% yield; ^{1}H-NMR (60 MHz): δ ($CDCl_3$) 7.45-6.85 (5H, m, ArH), 3.68 (3H, s, OCH_3), 1.92 (3H, s, CH_3); IR (neat), ν_{CH} (cm^{-1}): 3048, 2932, 1047, 889, 774, 689.

2-Heptanone Oxime *O*-Methyl Ether (7b). This compound was prepared, according to the same procedure described above: bp 102-104℃ /180 mmHg, colorless oil, 58% yield; ^{1}H-NMR (60 MHz): δ ($CDCl_3$) 3.93 (3H, s, OCH_3), 2.51-0.97 (11H, m, $(CH_2)_4CH_3$), 1.83 (3H, s, CH_3C=N); IR (neat). ν_{CH} (cm^{-1}): 2916, 1635, 1464, 1366, 1107, 1049, 883.

Acetophenone Oxime *O*-Trimethylsilyl Ether (7c). Trimethylsilyl chloride (33 mmol) in dry THF (12 m*l*) was added slowly to the solution of acetophenone oxime (30 mmol) in dry THF (30 m*l*) in the presence of triethyl amine

(33 mmol) at 0℃. The reaction mixture was stirred at room temperature for 8 h. The precipitate was filtered off and solvent was evaporated *in vacuo*. The product **7c** was isolated by distillation: 90-93℃/4 mmHg (lit.[2a] 105℃/2 mmHg), colorless oil, 85% yield; ^{1}H-NMR (60 MHz): δ ($CDCl_3$) 7.57-707 (5H, m, ArH), 2.17 (3H, s, CH_3): 0.00 (9H, s, $Si(CH_3)_3$); IR (neat), ν_{CH} (cm^{-1}): 3159, 2955, 1607, 1250, 990, 921, 878, 841, 754, 689.

2-Heptanone Oxime *O*-Trimethylsilyl Ether (7d). According to the same procedure described as above, **7d** was obtained: bp 74-78℃/12 mmHg, colorless oil, 79% yield; ^{1}H-NMR (60 MHz): δ($CDCl_3$) 2.85-0.93 (11H, m, $(CH_2)_4CH_3$), 2.17 (3H, s, $CH_3C=N$), 0.00 (9H, s, $Si(CH_3)_3$); IR (neat), ν_{CH} (cm^{-1}): 2942, 1631, 1457, 1247, 932, 902, 844, 748.

Acetophenone *N*-Phenylimine (9a).[1c] This compound was prepared by hydrolysis of α-cyanoamine obtained from acetophenone (30 mmol), aniline (36 mmol) and potassium cyanide (30 mmol) according to the literature procedure: mp. 37-39℃ (lit.[1c] 38-39℃), 78% yield; ^{1}H-NMR (60 MHz): δ ($CDCl_3$) 6.74-8.26 (10H, m, ArH), 2.23 (3H, s); IR (KBr), ν_{CH} (cm^{-1}): 3075, 1626, 1590, 1479, 1445, 1361, 1227, 782, 759, 690.

2-Heptanone *N*-Phenylimine (9b).[11] To a flask equipped with Dean-Stark condenser were charge 2-heptanone (100 mmol), aniline (110 mmol), *p*-toluenesulfonic acid (0.6 mmol) and 70 m*l* of benzene. The reaction mixture was heated to reflux for 4 h, cooled to room temperature, and the washed with a saturated sodium bicarbonate solution, followed by washing with brine and drying over anhydrous magnesium sulfate. After evaporation of solvent, the product was isolated by distillation *in vacuo*: bp 122℃/0.5 mmHg; yellowish oil; 41% yield; ^{1}H-NMR (60 MHz): δ ($CDCl_3$) 6.4-8.16 (5H, m, ArH), 1.78 (3H, s), 0.89-263 (11H, m); IR (KBr), ν_{CH} (cm^{-1}): 3053, 2948, 1660, 1593, 1484, 1364, 1239, 793, 743, 694.

Asymmetric Borane Reduction of Ketoxime *O*-Methyl Ethers in the Presence of Various Chiral Oxazaborolidines. Asymmetric borane reduction of acetophenone oxime *O*-methyl ether (**7a**) in the presence of **2** is representative. Into a flask equipped with a side arm, a magnetic stirrer and a stopcock adapter were introduced THF solution of **2** (3 mmol; 0.5 M; 6 m*l*) and borane-THF (3 mmol; 1.0 M; 3 m*l*). After stirring for 1 h at room temperature, **7a** in THF solution (2.7 mmol; 1 m*l*) was added to the reaction flask. The reaction mixture was stirred at room temperature (*ca.* 25-28℃). After 24 h, excess hydride was destroyed with *c*-HCl, THF was removed *in vacuo* and the residue was washed with ethyl ether. The residue was basified with C-NaOH at 0℃ and extracted with ethyl ether. The ether layer was dried over anhydrous potassium carbonate. GC analysis showed the formation of 1-phenylethylamine (**8a**) in 89% yield. After **8a** being isolated by bulb-to-bulb distillation (74-76℃/14 mmHg), the optical purity determined by capillary GC analysis for its MTPA amide[12] obtained by treatment of (R)-MTPA chloride was 86% ee, S.

Asymmetric Borane Reduction of Ketoxime *N*-Phenylimines in the Presence of Various Chiral Oxazaborolidines. Asymmetric borane reduction of acetophenone *N*-phenylimine (**9a**) in the presence of **2** is representative. To a solution of **5** (0.5 mmol; 0.5 M; 0.5 M; 1 m*l*) in THF was added borane-THF (1 mmol; 1.0 M; 1 m*l*) in THF at 0℃. Stirring for 1 h at room temperature, **9a** (0.5 mmol) in THF (1 m*l*) was added a room temperature. The reaction mixture was stirred at room temperature for 8 h and then excess hydride was decomposed by addition of 1 M HCl solution. After THF was removed *in vacuo*, the reaction mixture was cooled to 0℃, basified with 3 M NaOH, and extracted with ethyl ether. The extract was washed with brine and dried over anhydrous potassium carbonate. GC analysis indicated the presence of *N*-phenyl 1-phenylethylamine (**10a**) in 94% yield. After evaporation of solvent, the product was further purified by column chromatography on silica gel using chloroform as eluent. This was converted into its MTPA amide by treatment of (R)-MTPA chloride. Capillary GC analysis of the diastereomeric ratio of the amide shows 78% ee, R.

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Revised Reversible and Totally Irreversible Zones for the Linear Sweep Voltammetry at a Planar Electrode

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Digital simulation program for one-dimensional geometric systems of electrochemical phenomena was developed. The accuracy of the digital simulation is discussed by comparing with the known solutions. Applying this program to the linear sweep voltammetry at a planar electrode for the electrode reaction, O+ne→R, the accurate current functions for the reversible and totally irreversible charge transfer systems were obtained. Comparing these current functions with the simulated voltammograms for various other values of α (0.1 to 1.0) and Λ (10^{-5} to 10^{5}), the revised zones that are different from those proposed by Matsuda and Ayabe for the reversible and totally irreversible systems are proposed. For α≥0.1, the reversible zone is in $\Lambda \geq 10^{1.7}$ and the totally irreversible zone is in $\Lambda \leq 10^{-1.7}$, where $\Lambda = k^{\circ}/[D_o^{1-\alpha} D_R^{\alpha} (nF/RT)v]^{1/2}$.

Introduction

The Fick's first law of flux and the mass conservation law, instead of the differential equations of the Fick's second law, can be easily implanted into a computer code to obtain the dynamic currents for complex electrochemical phenomena in any geometries. This method is called as the digital simulation[1] that should be distinguished from the numerical calculation to solve the integro-differential equations or the serial form of analytical solutions. Except a few cases of electrochemical diffusion problem[2], the analytical solutions for the differential equations representing the Fick's second law cannot be obtained with ease. Even the analytical solution is available, it might be the serial form of integral functions like Bessel functions[3], so that the tedious numerical calculation hinders the access to the accurate real numerical values. Then, digital simulation method is preferred because of detouring the mathematical complexity as well as less computer calculation time. To decrease the simulation time but not to sacrifice the accuracy, the various techniques were developed. Among them, the exponentially expanding space grid[4,5] and the Crank-Nicholson method[1,6] were employed in this work. In the simulation of chronoamperometry, the exponentially expanding time grid was also employed successfully.

In this report, the simplest electrode reaction, O+ne→R, at a planar electrode is considered to focus on the accuracy of the simulation. This will provides firm base to leap into the more complex problems, for example, the complex electrode reactions at the various geometric systems of planar, spherical, cylindrical, disk, multiple bands, and ring electrode systems. Primarily, the accuracy of the simulation was checked by comparing with the analytical solution of diffusion controlled chronoamperometric currents, *i.e.*, Cottrell equation, at a planar electrode. In case of linear sweep voltammetry, assuming the true peak current can be obtained by the infinite number of space grids and potential step grids, the true peak current can be obtained by extrapolating the bilinearly changing peak current values depending on the square of the space grid size and the square of the potential step size. Secondarily, the current functions of the reversible and totally irreversible systems for the linear sweep voltammetry at a planar electrode were also compared with that of Nicholson and Shain[7] or Suzuki[8]. Since the current functions of this work are believed to be more accurate, the revised tables of these functions are presented. Finally, the voltammograms for various values of α (0.1 to 1.0) and Λ (10^{-5} to 10^{5}) are obtained to compare with these two current functions. The voltammogram of specific value of α and Λ is compared with those of above tabulated functions. If the deviations from the current function of the reversible system or that of the totally irreversible system in all the simulated potential range are same in 1% error range, then that α and Λ value is included in the reversible system or the totally irreversible system. In this way, two distinctive zones are obtained as $\Lambda \geq 10^{1.7}$ for the reversible system and Λ $10^{-1.7}$ for the totally irreversible system. These are different from those proposed by Matsuda and Ayabe[9], where Λ≥15