the system at the marginal state does not relax to the stable steady state but always oscillates on the closed trajectory.

In a forthcoming paper we shall apply the general result to a specific model, that is, the Goodwin model for protein synthesis[1] and then in detail discuss the physical and biological meanings of the results.

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Facile Reduction of Carboxylic Acid Salts to Aldehydes by Boron Hydrides, Thexylbromoborane-Dimethyl Sulfide and 9-Borabicyclo[3.3.1]nonane[†]

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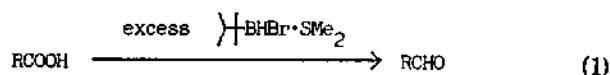*Department of Chemistry, Yeungnam University, Gyongsan 713-749*

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New methods for the reduction of carboxylic acid salts to aldehydes with 2 equiv of thexylbromoborane-dimethyl sulfide (ThxBHBr·SMe$_2$) or 9-borabicyclo[3.3.1]nonane (9-BBN) are described. Both these reagents provide the corresponding aldehydes from various sodium and lithium salts of carboxylic acids in high yields both at room temperature. Such facile reductions are explained as the simple substitution for the bromo group of ThxBHBr by a carboxylate to form thexyl-(acyloxy)borane followed by reduction with excess reagent and the formation of an ate complex followed by reduction with excess 9-BBN.
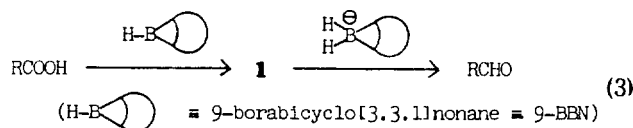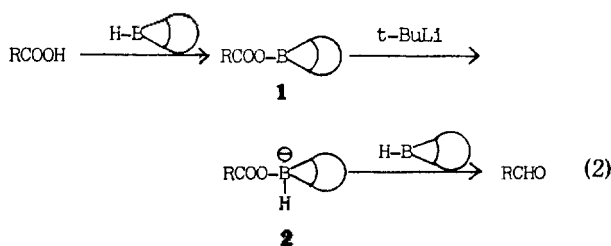
Introduction

Transformation of carboxylic acid derivatives, such as esters, amides, acid chlorides, nitriles, etc., to the corresponding aldehydes is of great importance because of their versatile utility in organic synthesis. Various useful methods for preparation of aldehydes from carboxylic acid derivatives have been developed[1], however there have been no report for the direct conversion of metal salts of carboxylic acid to aldehydes. Very recently, we have reported that thexylbromoborane-dimethyl sulfide (ThxBHBr·SMe$_2$)[2] and 9-borabicyclo[3.3.1]nonane (9-BBN)[3] can achieve the direct conversion of carboxylic acids to the corresponding aldehydes in high yields (eqs 1-3). This result intrigued us. Consequently, we have investigated to find out the new methodology for the direct conversion of carboxylic acid salts to aldehydes using such unique reducing agents.

In this paper, we describe details of such apparently first development for the direct conversion of sodium and lithium

$$RCOOH \xrightarrow{\text{excess } \text{Thx}BHBr \cdot SMe_2} RCHO \qquad (1)$$

(R=aliphatic and aromatic)

$$RCOOH \xrightarrow{\text{H-B}} RCOO\text{-B} \xrightarrow{t\text{-BuLi}} \mathbf{1}$$

$$RCOO\text{-B}^{\ominus}_{H} \quad \mathbf{2} \xrightarrow{\text{H-B}} RCHO \qquad (2)$$

$$RCOOH \xrightarrow{\text{H-B}} \mathbf{1} \xrightarrow{\text{H-B}^{\ominus}_{H}} RCHO \qquad (3)$$

$$(\text{H-B}) = 9\text{-borabicyclo[3.3.1]nonane} = 9\text{-BBN}$$

salts of carboxylic acids to aldehydes, which have already reported in a forn of communication[2a,4], including the mechanistic considerations as well as the isolation method of aldehyde products.

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Tabe 1. Yields of Aldehydes in the Reduction of Representative Sodium and Lithium Salts of Carboxylic Acids by 9-Borabicyclo[3.3.1]nonane in Tetrahydrofuran at Room Temperature[a]

Acid salt	Yield of aldehyde[b], %	
	Na salt	Li salt
butyric	89[c]	97
hexanoic	87[c]	99(83)[d]
decanoic	88	98
stearic	99	99(91)[e]
isobutyric	91	99
isopentanoic	88	92
pivalic	93[f]	—
diphenylacetic	98(90)[e]	98
cyclopropanecarboxylic	88	84
cyclohexanecarboxylic	90	92
chloroacetic	74	72
bromoacetic	69	65
6-bromohexanoic	78	84
a-camphoric	88	89
1,10-decanedicarboxylic	94	95(90)[e]
benzoic	82	80
p-methylbenzoic	44	60
p-methoxybenzoic	38	66
p-chlorobenzoic	70	75
p-nitrobenzoic	83	80
terephthalic	99	99

[a] Reacted with 2 equiv of 9-BBN (2 equiv for monocarboxylic and 4 equiv for dicarboxylic acid salts) for 1 h with aliphatic and for 3 h with aromatic carboxylic acid salts, both at room temperature. [b] Analysis 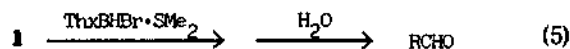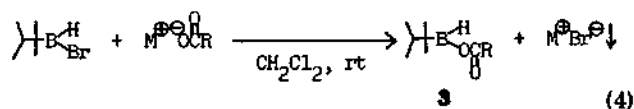with (2,4-dinitrophenyl)hydrazine. [c] Reacted for 0.5 h. [d] An isolated yield on distillation after hydrolysis. [e] Yields are based on the analytically pure products isolated after evaporation of solvent, following treatment of the bisulfite adduct with formaldehyde. [f] Reacted for 3 h.

Results and Discussion

Reduction with Thexylbromoborane-Dimethyl Sulfide (ThxBHBr·SMe₂). Thexylbromoborane-dimethyl sulfide (ThxBHBr·SMe₂), readily prepared by hydroborating 2,3-dimethyl-2-butene (tetramethylethylene) in methylene chloride[2,5] with monobromoborane-dimethyl sulfide, which in turn being easily prepared by treating borane-dimethyl sulfide with 1/2 equiv of bromine in carbon disulfide[6], appears to be an excellent reagent for the direct transformation of carboxylic acids to the corresponding aldehydes in the presence of several functionalities, including carbon-carbon double bonds.[2]

Such outstanding reducing characteristics of the reagent can also be extended to the reduction of carboxylic acid salts. This possibility comes from the simple substitution for the bromo group of the reagent by a carboxylate to form thexyl-(acyloxy)borane 3, the acyloxy group of which is then readily reduced to aldehyde by another 1 equiv of the reagent (eqs 4 and 5). This substitution reaction occurs readily in methylene chloride with precipitation of the metal bromide even under the heterogeneous conditions at room temperature.

$$\text{)HB}{<}^H_{Br} + M^{\oplus\ominus}_{O\text{-}C\text{-}R}^{O} \xrightarrow[CH_2Cl_2, \; rt]{} \text{)HB}{<}^H_{O\text{-}C\text{-}R}^{O} + M^{\oplus}Br^{\ominus}\downarrow \tag{4}$$

$$\mathbf{1} \xrightarrow{\text{ThxBHBr·SMe}_2} \xrightarrow{H_2O} RCHO \tag{5}$$

The reagent reduces both sodium and lithium salts of most aliphatic carboxylic acids 4, regardless of structural type, to the corresponding aldehydes in approximately 3 h at room temperature in yields of 85-99% (Chart 1), as shown in Table 1. Even aliphatic diacid salts 5 are converted to the dialdehydes in yields of 85-92%. In almost all cases the yields for sodium and lithium salts are similar, with no obvious generalizations to be drawn about the differences (the largest differences observed was 16%, and the average, about 5%). The reagent tolerate many organic functionalities, *viz.*, esters, acid chlorides, epoxides, halides, and nitro compounds.[5,b] For example, 6-bromohexanoic acid salts (6) provide the corresponding bromo aldehydes in yields of 72-76%. However, the most useful feature of this reagent is its reluctance to hydroborate carbon-carbon double bonds. Just as in the reduction of a,β-unsaturated carboxylic acids by this reagent[2a], the reduction of their salts, such as cinnamic (7) and crotonic (8) acid salts, gives the corresponding aldehydes in good yields, without attack on the double bonds.

The yields of aldehydes in the reduction of aromatic carboxylic acid salts are significantly lower than those in the aliphatic series and appear to be influenced by substituents on the aromatic ring, *cf.* benzoic, p-methoxybenzoic, and p-chlorobenzoic *versus* p-nitrobenzoic (9) and terephthalic (10) acid salts (Table 1).
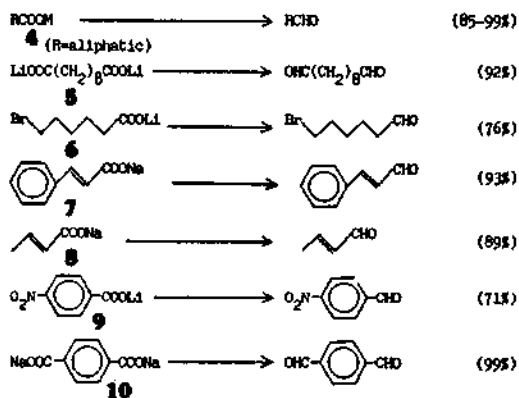

Chart 1

Reduction with 9-Borabicyclo[3.3.1]nonane (9-BBN). The commercially available 9-BBN readily reacts with carboxylic acids to form the corresponding acyloxy-9-BBNs 1 with immediate evolution of 1 equiv of hydrogen[7], the acyloxy moiety of which in turn is readily converted to the aldehyde stage through stepwise treatment of 1 with *tert*-butyllithium and 9-BBN (eq 2).[3,c] This facile reaction could be rationalized as the consecutive hydride-transfer pathway in which the hydride from 2 migrates to 9-BBN (*i.e.*, formation of 9-boratabicyclo[3.3.1]nonane, 9-BBNH) and then again the hydride from 9-BBNH species attacks the carbonyl carbon of acyloxy moiety. This interpretation has been further supported by the equally nice conversion through treatment of 1 with 9-BBNH itself (eq 3).
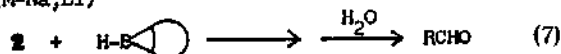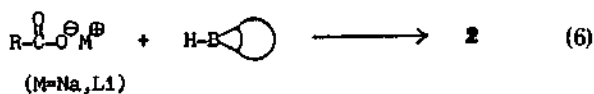
Such transformation procedure can also be applicable to the reduction of carboxylic acid salts to aldehydes. If a carboxylate and 9-BBN form an ate complex (eq 6), which is the same compound 2 formed by treatment of acyloxy 9-BBN with *tert*-butyllithium (eq 2), we can expect that in the

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Table 2. Yields of Aldehydes in the Reduction of Representative Sodium and Lithium Salts of Carboxylic Acids by Thexyl-bromoborane-Dimethyl Sulfide in Methylene Chloride at Room Temperature[a]

Acid salt	Yield of aldehyde[b], %	
	Na salt	Li salt
butyric	90	89
hexanoic	92(77)[c]	86
decanoic	87	89
stearic	92(88)[d]	92
isobutyric	88	86
isopentanoic	90	87
pivalic	85[e]	—
cyclopropanecarboxylic	87	77
cyclohexanecarboxylic	86	76
diphenylacetic	83	99(91)[d]
6-bromohexanoic	72	76
α-camphoric	88	87
1,10-decanedicarboxylic	85	9_(87)[d]
cinnamic	93	82
crotonic	89	81
benzoic	49	47
p-methoxybenzoic	42	31
p-chlorobenzoic	44	43
p-nitrobenzoic	70	71
terephthalic	99	94

[a] Reacted with 2 equiv of reagent for monocarboxylic and 4 equiv for dicarboxylic acid salts for 3 h at room temperature. [b] Analysis with (2,4-dinitrophenyl)hydrazine. [c] An isolated yield of distilled product, following treatment of the bisulfite adduct with formaldehyde. [d] Yields are based on the analytically pure products after evaporation of solvent, following treatment of the adduct with formaldehyde. [e] Reacted for 6 h.

presence of another equiv of 9-BBN the system follows the exactly same reduction pathway as the case of reduction of carboxylic acid through stepwise treatment of acyloxy-9-BBN with *tert*-butyllithium and 9-BBN.

$$R-\overset{O}{\underset{}{C}}-O^{\ominus}M^{\oplus} + H-B \hspace{-1mm}\bigcirc \longrightarrow 2 \qquad (6)$$

(M=Na,Li)

$$2 + H-B\hspace{-1mm}\bigcirc \longrightarrow \xrightarrow{H_2O} RCHO \qquad (7)$$

Actually, this system is in equilibrium, in which the acyloxy group of ate complex thus formed is readily transformed into the corresponding aldehyde stage in the presence of excess 9-BBN. The reduction proceeds readily as the mixture of a carboxylate and 2 equiv of 9-BBN, providing a simple procedure with high yields of aldehydes, as summarized in Table 2.

Both sodium and lithium salts of most aliphatic carboxylic acid 11, such as salts of butyric, hexanoic, decanoic, stearic, isobutyric, isopentanoic, and pivalic acids, are readily converted to the corresponding aldehydes by this system in approximately 1 h at room temperature. The yields from the lithium salts are essentially quantitative, whereas the yields from the corresponding sodium salts are in the range of 87-99%, a little lower than those from the lithium salts probably due to the relatively lower solubility of sodium salts in THF

solvent. Derivatives, such as both sodium and lithium salts of diphenylacetic acid (12), also undergo the reaction well in yields of 98%. The yields of aldehydes from alicyclic carboxylic acid salts, such as cyclopropanecarboxylic and cyclohexanecarboxylic acid salts, are in the range of 84-92%. The halogeno derivatives, such as salts of chloro- and bromoacetic acids, and 6-bromohexanoic acid, provide the corresponding haloalkanals in yields of 65-84%. Dicarboxylic acid salts such as α-camphoric and 1,10-decanedicarboxylic acid salts (13) are also converted readily to dialdehydes in yields of 88-95%.

The reduction of aromatic carboxylic acid salts by this system requires 3 h at room temperature and the yields vary with the substituents on bezene ring. Thus, in the case of aromatic acid salts bearing an electron-releasing substituent such as *p*-methyl- and *p*-methoxybenzoic acid salts, the yields are around 40% for the sodium salts and around 60% for the lithium salts. However, aromatic acid salts bearing an electron-withdrawing substituent such as *p*-chloro (14) and *p*-nitrobenzoic (15) acid salts provide much higher yields of the corresponding aldehydes (70-83%). Finally, both disodium and dilithium salts of aromatic carboxylic acid, such as terephthalic acid salts (16), are readily converted to the dialdehydes in essentially quantitative yields (Chart 2).
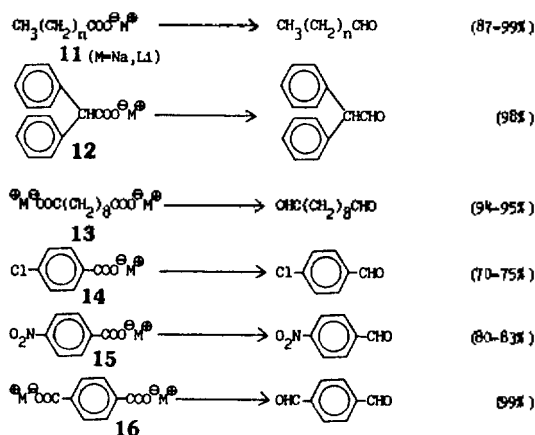
Chart 2

Isolation of Aldehyde Products. Aldehydes are notoriously unstable, and hence it is desirable to provide the practical procedure for the isolation of aldehyde products from the reaction mixture in a pure form. The widely-modified bisulfite adduct procedure, adopted for reduction of carboxylic acids with thexylchloroborane[8], appeared also to be broadly applicable to the case of thexylbromoborane (Table 1). This procedure can also be used to isolate aldehyde products from the reaction of carboxylic acid salts with 9-BBN in a pure form. However, in the case of products of lower boiling point (less than 200 °C) the distillation after stirring the reaction mixture over excess anhydrous magnesium sulfate overnight gives the quite reasonable yield of aldehyde products (Table 2).

Conclusion

Both sodium and lithium salts of carboxylic acids are readily converted to the corresponding aldehydes in very high yields either with excess thexylbromoborane-dimethyl sulfide in methylene chloride or with excess 9-BBN in THF

both at room temperature. These first-developed two methods should find additional utility of carboxylic acid derivatives in organic synthesis.

Experimental Section

All glassware used was dried throughly in a drying oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and manipulations of air- and moisture-sensitive materials were carried out under a dry nitrogen atmosphere. Further special experimental techniques are described elsewhere.[9]

All chemicals were commercially products of the highest purity which were carefully purified by standard methods before use. Tetrahydrofuran (THF) was distilled from benzophenone-sodium ketyl.

The yields reported in all cases are of analytically pure compounds unless otherwise mentioned.

GLC analyses were carried out using a Varian Model 1400 FID chromatograph equipped with a Hewlett-Packard 3390 A Integraor/Plotter.

Preparation of Thexylbromoborane-Dimethyl Sulfide (ThxBHBr·SMe₂) in CH₂Cl₂. Monobromoborane-dimethyl sulfide (1.5 mol) in 66 ml of CH_2Cl_2 and 15 ml of Me_2S was placed in an oven-dried, 500-ml flask fitted with a side arm and a bent adaptor connected to a Hg bubbler. The flask was immersed in an ice-water bath, and to this was added 196 ml of precooled 2,3-dimethyl-2-butene (1.65 mol) dropwise over a period of 1 h *via* a double-ended needle. The reaction mixture was stirred for an additional 2 h at 0 °C, followed by stirring overnight at room temperature. The resulting CH_2Cl_2 solution was found to be 3.34 M in ThxBHBr·SMe₂, and ¹¹B NMR showed a clean doublet centered at δ 5.16 (J_{BH} = 123 Hz).

Reduction of Carboxylic Acid Salts with ThxBHBr· SMe₂ and Isolation of Products. The following procedure for the reduction of lithium diphenylacetate is illustrative. An oven-dried, 20-ml flask, fitted with a side arm and a bent adaptor connecter to a Hg bubbler, were placed 1.09 g of lithium diphenylacetate (5 mmol) and 1.7 ml of CH_2Cl_2. Into the reaction mixture was injected 3.33 ml of the 3 M reagent (10 mmol), and the slurry was stirred for 3 h at room temperature. Analysis of the whole reaction mixture with (2,4-dinitrophenyl)hydrazine indicated a yield of 99%.

The following procedure is for the larger scale reaction. In the assembly previously described were placed 10.9 g of lithium diphenylacetate (50 mmol) and 17 ml of CH_2Cl_2. Into the reaction mixture was injected 33.3 ml of the 3 M reagent solution (100 mmol), and the slurry was stirred for 3 h at room temperature. The reaction mixture was then hydrolyzed with 50 ml of cold water by stirring vigorously for 1 h at room temperature. The mixture was saturated with NaCl. After neutralization with a small amount of NaHCO₃, the separated organic layer was poured into 75 ml of a saturated aqueous NaHSO₃ solution, and 70 ml of THF was added. The mixture was stirred for 1 h, by which time the crystalline bisulfite adduct of diphenylacetaldehyde had precipitated. The solution was cooled in an ice-water bath to ensure complete crystallization of the adduct, which was then collected by filtration and washed with 3 × 25 ml of pentane. The adduct was placed in 40 ml of water, and then 50 ml of THF and 8 ml of a 37% CH₂O solution were added. The mix-

ture was stirred for 1 h and saturated with MgSO₄·7H₂O. The organic layer was separated and dried. Evaporation of volatiles gave 8.93 g of analytically pure diphenylacetaldehyde (91%), n_D^{20} 1.5892.

Reduction of Carboxylic Acid Salts with 9-BBN and Isolation of products. The following procedure for the reduction of sodium diphenylacetate was used for quantitative analysis of yields. An oven-dried 50-ml flask, fitted a side arm and a bent adaptor connected to a Hg bubbler, was charged with 0.70 g (3 mmol) of sodium diphenylacetate. A 0.5 M solution 12 ml of 9-BBN in THF (6 mmol) was injected. and the slurry was stirred for 1 h at room temperature. Analysis with (2,4-dinitrophenyl)hydrazine indicated a yield of 98%.

The following procedure was used for a larger scale reaction. In the assembly previously described, 11.7 g of sodium diphenylacetate (50 mmol) was added. A 0.5 M 9-BBN solution 200 ml in THF (100 mmol) was injected and the slurry was stirred for 1 h at room temperature. The reaction mixture was hydrolyzed with 30 ml of 2 N HCl solution for 1 h at room temperature and then saturated with sodium chloride. The separated organic layer was poured into 75 ml of a saturated aqueous sodium bisulfite solution. The mixture was stirred for 1 h, by which time the crystalline bisulfite adduct of diphenylacetaldehyde has precipitated. The solution was cooled in an ice-water bath to ensure complete crystallization of the bisulfite adduct, which was then collected by filtration and washed with 3 × 25 ml of pentane and dried. The sol solid adduct was placed in 40 ml of water and then 50 ml of THF and 8 ml of a 37% formaldehyde solution were added. The mixture was heated to 90-95 °C for 1 h with stirring and cooled to room temperature followed by saturation with MgSO₄·7H₂O. The organic layer was separated and dried. Evaporation of volatile gave 8.82 g of analytically pure diphenylacetaldehyde (90%), n_D^{20} 1.5892.

The following procedure for the isolation of hexanal is illustrative for the case of aldehyde products of relatively lower boiling point (less than 200 °C). In the assembly previously described was placed 6.11 g of lithium hexanoate (50 mmol). 200 Ml of 0.5 M 9-BBN in THF solution (100 mmol) was injected and the slurry was stirred for 1 h at room temperature. The reaction mixture was hydrolyzed with 30 ml of 2 N HCl solution for 1 h and then saturated with sodium chloride. The separated organic layer was stirred vigorously over excess anhydrous magnesium sulfate overnight and subjected to fractional distillation: 4.02 g of hexanal (83%), bp 131-132 °C.

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XPS Studies of CO Adsorption on Polycrystalline Nickel Surface

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The chemisorption of CO molecules on polycrystalline nickel surface has been studied by investigating the resulting chemisorbed species with the X-ray photoelectron spectroscopy at temperatures between 300K through 433K. It is found that the adsorbed CO molecules are dissociated by the simple C-O bond cleavage as well as by the disproportionation reaction at temperatures above 373K. The former type dissociation is more favored at low coverages and at elevated temperatures. The isotherms of CO chemisorption are obtained from the xps intensities of C 1s peaks, and then the activation energy of the dissociative adsorption is estimated as a function of the CO exposure. These activation energies are extrapolated to zero coverage to obtain the activation energy of chemisorption in which thermal C-O bond cleavage takes place. The value obtained is 38.1 kJ/mol.

Introduction

The chemisorption of carbon monoxide on transition metal surfaces has been extensively studied in connection with many catalysis, such as the Fischer-Tropsch synthesis and the exhaust gas purification.[1-3] It is generally accepted that elements to the left of a line connecting Co and W on the periodic table display dissociative adsorption while elements of the other side display molecular adsorption.[4-7] Nickel is, however, found to be exceptional in that it adsorbs CO molecule dissociatively at moderately high temperatures (T > 500K),[8-14] while it adsorbs CO undissociatively at low temperatures (T ≤ 300K).[15-20]

Benziger *et al.*[18] reported the result of molecularly adsorbed CO on the on-top site as well as on the bridged-site of nickel surface in the temperature range of 190K through 280K with the temperature programmed reflection absorption infra-red spectroscopy. Blyholder[21] proposed a molecular or-

bital model for the CO chemisorption bond in order to explain their IR spectra. Barber *et al.*[19] also observed the similar type of molecular adsorption with SIMS in the temperature range of 77K through 390K, and partial dissociation of adsorbed CO molecules when the temperature is raised above 390K. According to thermal desorption measurements, however, the molecularly adsorbed CO is stable up to ca 450K.[8,16,20] For example, Ertl *et al.*[20] observed a single non-dissociative TDS peak at 440K from Ni(111) surface when the CO coverage is less than 0.33, and an extra shoulder on the lower temperature side of this single peak when the coverage exceeds 0.33; Wedler *et al.*[16] observed a similar result with three nondissociative peaks at 170K, 310-360K, and 460-490K, respectively.

The adsorbed CO molecule becomes unstable and dissociates to leave atomic carbon and oxygen species on the substrate surface if temperature is elevated. The dissociation is known to take place by a disproportionation reaction and/