

Articles

Conformational Analysis of Catecholamines-Raman, High Resolution NMR, and Conformational Energy Calculation Study

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The conformational analysis has been done for catecholamines (dopamine, norepinephrine, and epinephrine) in the cationic and di-anionic states. The species responsible for adsorption on silver metal surface is anionic deprotonated at hydroxyl groups of catechol moiety, i.e., di-anionic states of catecholamines. This was deduced from Fourier-transform Raman spectra of sodium salts of catecholamines. High resolution proton NMR (400 MHz) spectra of catecholamines in basic and neutral D₂O solution show that the conformations of norepinephrine and epinephrine in the di-anionic states are preferred in gauche, but not for dopamine in the di-anionic state. However the energy difference between *trans* and gauche of catecholamines in the protonated cationic states is small enough to rotate freely through C-C bond in ethylamine moiety. The conformational calculations using an empirical potential function and the hydration shell model (a program *CONBIO*) show consistent with above experimental results. The calculations suggest that the species of catecholamines adsorbed on silver metal surface would be in favor of the gauche conformations.

Introduction

Catecholamines are found as neurotransmitters in the central and sympathetic nervous system, and as hormones in vesicles of the adrenal modulla for the regulation of heart beat rate and blood pressure. The preferred conformation and biological activity of catecholamines has been in great interest. The conformational studies have been done with X-ray analysis¹, nuclear magnetic resonance² and semiempirical potential function or molecular orbital^{3,4} calculations. The divalent metal ion⁵ chelates and the complex⁶ with substrates (e.g., ADP) of catecholamines have been studied for the pathway intermediates of the storage and transport of neurotransmitters. Catecholamines form the bidentate complex *via* two oxygen atoms of the hydroxyl groups in the catechol moiety. Catecholamines are flexible and subject to rotate in the ethylamine moiety. They may be preferred in certain conformation, for example, staggered or eclipsed. The possibility of conformational transitions, however, upon complexation with metal ions or substrates has not received much attentions so far.

The catecholamine/silver metal complex was proposed to be bidentate in the surface enhanced Raman scattering (SERS) of catecholamines on silver metal surface⁷ based on resonance Raman studies for metal catecholates^{8a}. But the active species responsible for SERS has not been clearly elucidated. Raman spectra using visible light source of catecholamines in powder state have not been available mainly because of fluorescence from impurities in the catecholamine samples. Raman scattering using infrared laser source may be considered as it can produce Raman scattering from major component in the sample. In this study Fourier transform

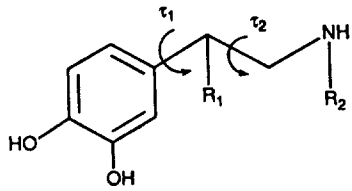
(FT) Raman spectroscopy using 1064 nm light source of sodium salts of catecholamines in powder state is applied to clarify the active species for SERS. Also the possibility of conformational transitions in the ethylamine moiety of catecholamines is pursued upon deprotonation of hydroxyl groups in catechol moiety using high resolution (400 MHz) NMR study.

Hydration has been known as one of the determining factors for the conformations and biological activities of biological molecules and their receptors. The hydration shell model has been developed to introduce hydration into conformational energy calculations⁹. In this paper the conformational energy using the ECEPP/2 empirical potential function¹⁰ and the hydration free energy using hydration shell model (a program *CONBIO*)¹¹ are evaluated for preferred conformations in the cationic, di-anionic, and zwitterion-like states of catecholamines.

Experimental Section

Dopamine · HCl (DA), (R)-(-)-norepinephrine(NE), (R)-(-)-epinephrine(E), NaOH and HCl were purchased of the highest purity from Tokyo Kasei Chemical, and D₂O (99.7%) and NaOD (40% in D₂O) were from Merck. The high pD values were adjusted by the addition of NaOD solution. All chemicals were used as received without further purification. For sodium salts of catecholamines, each of catecholamines was mixed with 3 times equivalent amounts of NaOH, and dried in vacuum with cooling. SERS on silver electrode was described elsewhere⁷.

Absorption spectra were checked using HITACHI U-3400 spectrophotometer. For the conventional Raman scattering

Table 1. The Structure of the Studied Catecholamines (τ_1 and τ_2 are dihedral angles)


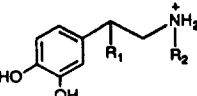
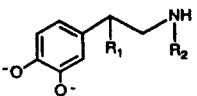
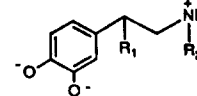
	R_1	R_2
Dopamine (DA)	H	H
Norepinephrine (NE)	OH	H
Epinephrine (E)	OH	CH ₃

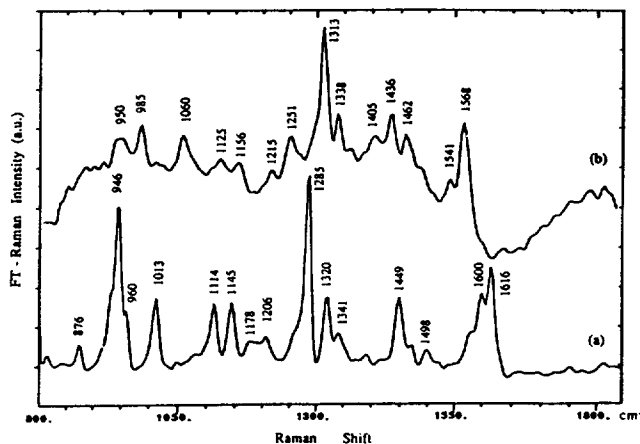
experiments, JEOL JRS 400T laser Raman spectrophotometer equipped with Spectra Physics Model 2030 Ar⁺ ion laser (about 2 watt max. total power) was employed. Each slit width of three slits was maintained at 300 μ m. The scan speed and the time constant were 100 $\text{cm}^{-1}/\text{min}$ and 0.8 sec, respectively. The laser power of 514.5 nm at samples was kept to less than 0.1 watt through narrow bandpass filter. Bomem DA3.002 spectrophotometer was applied for FT-Raman spectra. It was equipped with Quantronix cw Nd:YAG 1064 nm laser (about 3 watt max. power), liquid nitrogen cooled InGaAs detector, and back-scattering light collection optics. The laser power for obtaining FT-Raman spectra was 0.1 watt at sample to avoid decomposition. The sample powder was contained in ordinary melting point capillary tube. Spectral resolution was 10 cm^{-1} , and 1000 times coadded (takes about 20 min. running).

High resolution proton NMR spectra were recorded using JEOL-GX FT-NMR spectrometer operating at 400 MHz. Spectral resolution was 0.31 Hz and 16 times coadded for measurements. All the measurements were obtained at an ambient probe temperature of 27°C. NMR sample tube was 5 mm diameter and total amount of a sample was about 0.4 mL. Dioxane (3.57 ppm to TMS) sealed in melting point capillary tube served as an external standard reference for the shift measurements. Sample concentrations were about 1.0% in D₂O under the nitrogen atmosphere and added a trace amount of Na₂SO₃ to avoid oxidation reactions. After adding NaOD solution right before the measurements to catecholamines solution to get high pD values (about 14), the sample turned color to pale brown. But it didn't disturb getting NMR spectra because very weak bands were observed during 16 scans from oxidation products of catecholamines.

For the structures of catecholamines to calculate the ECEPP/2 potential function and hydration free energy (a program CONBIO)¹¹, PCMODEL (Serena Software, 1987) was applied running at IBM PC-XT computer. The coordinates from PCMODEL was transferred to MMPMI (QCPE 395) to get the optimum coordinates including π -electron delocalization energy. The ECEPP/2 potential function and hydration shell model were described elsewhere⁹⁻¹¹. The assignments of ring and side-chain protons of the studied catecholamines is given in Table 1 with dihedral angles, τ_1 and τ_2 . Only two conformations are considered for calculations, an extended *trans* conformation with $\tau_1 \sim 90^\circ$ and $\tau_2 \sim 180^\circ$, and a folded *gauche* conformation with $\tau_1 \sim 90^\circ$ and $\tau_2 \sim \pm 60^\circ$.

Table 2. The Structures of Catecholamines for Conformational Energy Calculations (R_1 and R_2 are the same as in Table 1. The asymmetric β -carbons of NE and E have (R)-configurations)

(Structure I)	(Structure II)	(Structure III)
		

**Figure 1.** FT-Raman spectra of cationic state (a) and sodium salt (b) of dopamine in powder state in ordinary melting capillary tube. Nd:YAG laser 1064 nm excitation, 0.1 watt power at sample, spectral resolution 10 cm^{-1} , 1000 times coadded.

The structures studied for conformational calculations are shown in Table 2.

Results and Discussion

SERS and FT-Raman Scattering of Catecholamines.

SERS of DA, NE, and E on the roughened silver electrode are basically the same as previously observed spectra⁷. They show four distinguished bands, two intense and relatively intense two Raman bands in the range of 1000-1800 cm^{-1} region. But SERS intensity for E is weaker than the other two, DA and NE. An intense band near 1480 cm^{-1} is assigned to the stretching of the C-C bond to which two oxygens are positioned in catechol moiety^{8a}. The other intense band near 1270 cm^{-1} is due to the stretching of C-OH in catechol moiety. Other two bands are assigned to the ring vibrational modes of catechol moiety⁷.

FT-Raman spectra of the cationic state and sodium salt of DA in powder states are illustrated in Figure 1(a) and 1(b), respectively. An intense band at 1285 cm^{-1} in Figure 1(a) is assigned C-OH stretching mode of hydroxyl groups in catechol moiety. This frequency is up-shifted to 1313 cm^{-1} , C-O⁻ stretching mode of the salt in Figure 1(b). When both hydroxyl protons are deprotonated to be di-anionic, two peaks near 1260 and 1320 cm^{-1} were observed in the resonance Raman study^{8a}, which were suggested indicative of the di-anionic character of catechol moiety. Therefore two bands at 1251 and 1313 cm^{-1} in Figure 1(b) can indicate features of di-anionic catechol moiety. Two intense bands at 1616

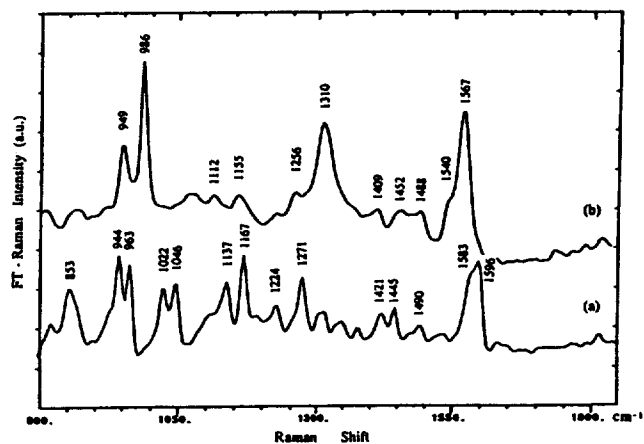


Figure 2. FT-Raman spectra of neutral state (a) and sodium salt (b) of norepinephrine in powder state. The experimental conditions are the same as in Figure 1.

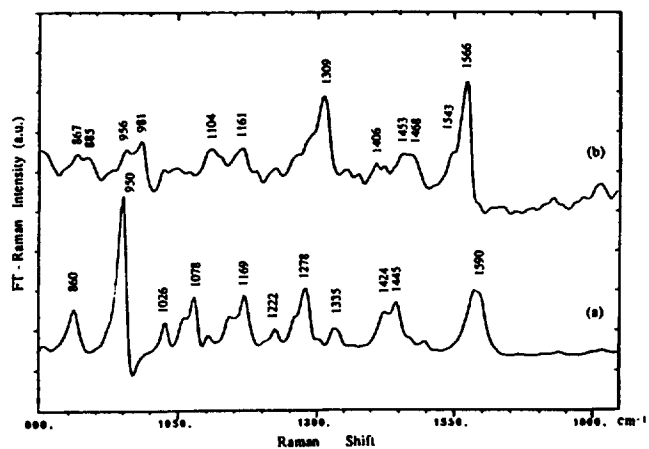


Figure 3. FT-Raman spectra of neutral state (a) and sodium salt (b) epinephrine in powder state. The experimental conditions are the same as in Figure 1.

cm^{-1} and 1600 cm^{-1} in Figure 1(a) are the ring stretching (ν_{8b} and ν_{8a} : Wilson number^{8b}) modes of catechol moiety. They are down-shifted to 1568 cm^{-1} and 1541 cm^{-1} upon deprotonation of both hydroxyl groups seen in Figure 1(b), respectively. A band at 1449 cm^{-1} in Figure 1(a) assigned to the ring stretching and deformation mode (ν_{19b} : Wilson number^{8b}) is down-shifted to 1436 cm^{-1} in Figure 1(b). These up- and down- shifts are also exactly the same way observed in Figure 2(a) and 2(b), FT-Raman spectrum of the neutral and the sodium salt of NE in powder state, and Figure 3(a) and 3(b), FT-Raman spectrum of the neutral and the sodium salt of E in powder state, respectively. The similar features between SERS of catecholamines and FT-Raman spectra of dianionic catecholamine may be one of the direct evidences for the active species adsorbed on metal surface in solution.

High Resolution NMR Studies of Catecholamines.

FT-NMR spectra of DA, NE, and E at $\text{pD}=6$ and at $\text{pD}=14$ are shown in Figure 4, 5, and 6, respectively. Their experimental data are summarized in Table 3, which shows only the proton chemical shifts of α - and β -protons in ethylamine moiety. Three acid dissociation constants of catecholamines

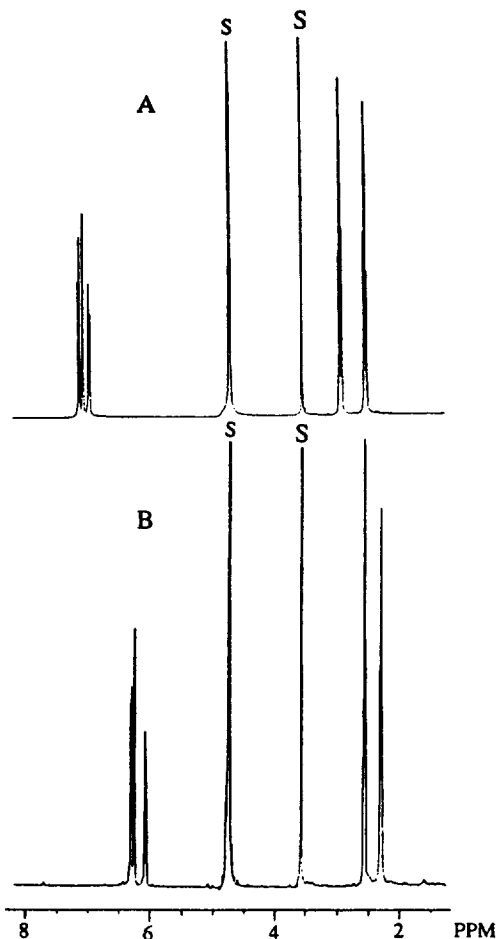


Figure 4. NMR spectra of dopamine at (A) $\text{pD}=6$ and (B) $\text{pD}=14$. s: D_2O solvent impurities, S: dioxane (3.57 ppm to TMS).

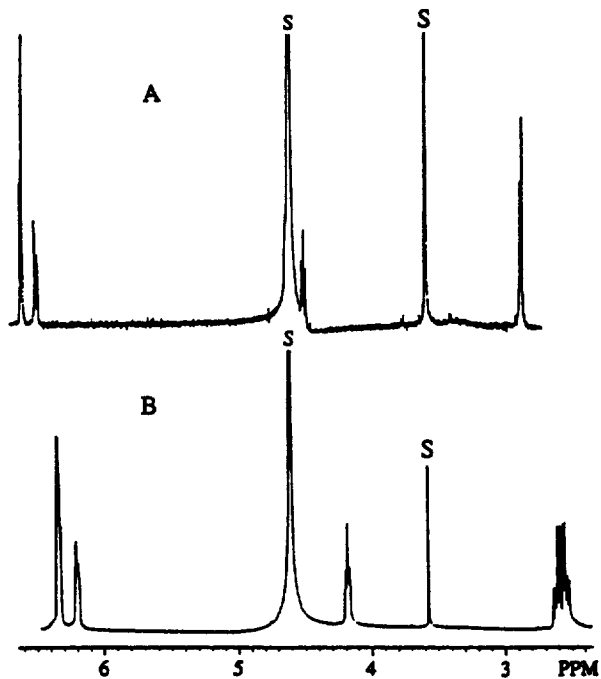


Figure 5. NMR spectra of norepinephrine at (A) $\text{pD}=6$ and (B) $\text{pD}=14$. s: D_2O solvent impurities, S: dioxane (3.57 ppm to TMS).

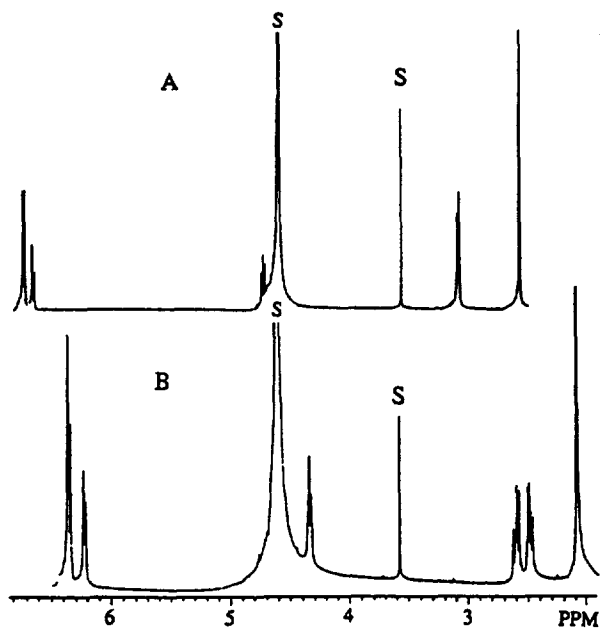


Figure 6. NMR spectra of epinephrine at (A) pD=6 and (B) pD=14. s: D₂O solvent impurities, S: dioxane (3.57 ppm to TMS).

are in the range of pK_a values, about 9, 10 and 13. These are from the ionization of two hydroxyl groups of catechol moiety, and from the deprotonation of the ammonium group of the ethylamine moiety. The pK_a value of about 13 has been known from the ionization of the second hydroxyl group. Catecholamines at pD=6 are in their cationic states at ethylamine moiety, whereas at pD=14 are di-anionic¹².

Protons of ethylamine moiety of DA in the cationic and di-anionic states belong to $AA'XX'$ system in a configuration of $Z-CH_2-CH_2-Y$. Both NMR spectral data of DA at two different pD conditions in Table 3 are composed of only two sets of triplet. They do not display the presence of any geminal coupling or any difference between AX' and $A'X$ coupling. It represents, so called, the deceptively simple spectra of apparent A_2X_2 system¹³. There may be two possible ways to explain this observation. Firstly, the population of *trans* con-

formers can be greater rather than that of *gauche* conformers. Because the structure of catechol moiety attached to ethylamine moiety is not symmetric, chemical equivalence of A and A' would not be held exactly the same. But the difference may be minimal to be observed. The other explanation is that the rotation through the C-C bond of ethylamine moiety is fast enough to discriminate the nonequivalence of A and A'. The energy barrier between *trans* and *gauche* conformer is low enough compared to the thermal motion, particularly rotation. In fact, the anti or *gauche* couplings between A or A' and X or X' in *trans* conformers is not necessarily the same as those couplings in *gauche* conformers. But these differences may not be significant to show the nonequivalence on NMR spectra by 400 MHz field strength.

Protons of ethylamine moiety of NE in the cationic and di-anionic states are ABX system in the configuration of $Z-CHX-CH_2-Y$. On the NMR data of NE in Table 3, the cationic NE shows a set of triplet and a set of doublet, apparent $AA'X$ system. Two protons on α -carbon of ethylamine moiety are diastereotopic in each rotating conformer. Therefore chemical shifts of these protons are not chemically equivalent. But this is another example of the deceptively simple spectra caused by an insignificant difference of two chemical shifts. The observed splitting, ~ 6.4 Hz, is the average of J_{AX} and $J_{A'X}$. These results do not confirm any preferred conformation of NE in the cationic state, except a rapid rotation through C-C bond in ethylamine moiety. However the di-anionic NE gives a set of distorted triplet and a set of octet, obviously ABX system. The octet in this spectrum is sufficiently good enough for first-order analysis. The geminal coupling constant, $J_{ab} \sim 13$ Hz, and two vicinal coupling constants, $J_{ax} \sim 7.2$ Hz and $J_{bx} \sim 6.3$ Hz can be obtained. The Karplus correlation, $^3J = A + B \cos \Phi + C \cos 2\Phi$, between dihedral angle (Φ) and coupling constant for vicinal protons (3J) is applied to these vicinal coupling constants using parameters by Bothner-By ($A=7$, $B=-1$ and $C=5$)¹⁴. Dihedral angles, $\Phi_{ax} \sim 40^\circ$ and $\Phi_{bx} \sim 45^\circ$ are calculated from above data. This result indicates that the *gauche* conformers are major species of NE in the di-anionic state.

The NMR data of E in the cationic and the di-anionic

Table 3. Proton Chemical Shifts (in unit of Hz) of Ethylamine moieties of DA, NE, and E at pD=6 and pD=14, and Assignments of Protons

DA at pD=6 (assignment)	DA at pD=14 (assignment)	NE at pD=6 (assignment)	NE at pD=14 (assignment)	E at pD=6 (assignment)	E at pD=14 (assignment)
1221.5 (H α)	1033.6 (H α)	1800.8 (H β)	1678.4 (H β)	1900.9 (H β)	1740.0 (H β)
1214.2 (H α)	1026.8 (H α)	1794.3 (H β)	1672.3 (H β)	1894.4 (H β)	1733.6 (H β)
1207.5 (H α)	1020.1 (H α)	1787.6 (H β)	1665.3 (H β)	1888.0 (H β)	1726.6 (H β)
1081.2 (H β)	927.4 (H β)	1145.2 (H α)	1054.6 (H α)	1237.7 (H α)	1047.0 (H α)
1073.8 (H β)	920.6 (H β)	1139.4 (H α)	1047.6 (H α)	1231.6 (H α)	1039.4 (H α)
1066.5 (H β)	913.3 (H β)		1041.8 (H α)	1029.9 (CH ₃)	1035.1 (H α)
			1034.5 (H α)		1027.4 (H α)
			1025.0 (H α)		999.0 (H α)
			1018.9 (H α)		993.3 (H α)
			1012.2 (H α)		987.2 (H α)
			1005.8 (H α)		981.1 (H α)
					833.4 (CH ₃)

Table 4. Calculated Energies of Catecholamines (kcal/mol)

Dopamine	Structure I		Structure II		Structure III	
	<i>Trans</i> ^a	<i>Gauche</i> ^a	<i>Trans</i>	<i>Gauche</i>	<i>Trans</i>	<i>Gauche</i>
Electrostatic E.	14.96	13.90	-4.99	-3.46	-40.18	-48.91
Nonbonding E.	-3.74	-4.01	-2.81	-3.09	-3.08	-3.40
Hydration E.	-78.77	-76.51	-81.10	-80.47	-142.32	-137.42
Total Energy	-67.55 ^b	-66.62	-88.91	-87.01	-185.58	-189.73

Norepinephrine	Structure I		Structure II		Structure III	
	<i>Trans</i>	<i>Gauche</i>	<i>Trans</i>	<i>Gauche</i>	<i>Trans</i>	<i>Gauche</i>
Electrostatic E.	16.80	17.03	10.20	10.22	-25.23	-32.52
Nonbonding E.	-3.42	-4.05	-2.85	-3.33	-3.14	-3.67
Hydration E.	-87.58	-82.76	-85.50	-85.15	-147.38	-142.95
Total Energy	-74.20	-69.79	-78.15	-78.26	-175.75	-179.14

Epinephrine	Structure I		Structure II		Structure III	
	<i>Trans</i>	<i>Gauche</i>	<i>Trans</i>	<i>Gauche</i>	<i>Trans</i>	<i>Gauche</i>
Electrostatic E.	23.66	23.89	10.48	10.96	-15.61	-22.46
Nonbonding E.	-1.50	-4.83	-2.75	-3.19	-3.30	-3.98
Hydration E.	-79.57	-75.02	-85.64	-84.40	-141.34	-131.12
Total Energy	-57.41	-55.96	-77.91	-76.64	-160.25	-162.57

^a*trans* ($\tau_1 \sim 90^\circ$ and $\tau_2 \sim 180^\circ$) and *gauche* ($\tau_1 \sim 90^\circ$ and $\tau_2 \sim \pm 60^\circ$). ^bThe energy which is lower between *trans* and *gauche* conformations is in bold.

state have the same shape as those of NE shown in Table 3. For the case of di-anionic state, we can obtain the geminal coupling constant, $J_{ab} \sim 12$ Hz, and two vicinal coupling constants, $J_{ax} \sim 7.6$ Hz and $J_{bx} \sim 6.0$ Hz. The calculation of the Karplus correlation with parameters by Bothner-By ($A=7$, $B=-1$ and $C=5$) gives dihedral angles, $\Phi_{ax} \sim 37^\circ$ and $\Phi_{bx} \sim 47^\circ$. This also indicates that the preferred conformation is the *gauche* conformer in the dianionic state.

Conformational Energy Calculations of Catecholamines. The *trans* conformer contains the ethylamine side chain anti-planar and perpendicular to the catechol moiety, whereas in *gauche* conformer the terminal ammonium group is oriented towards the catechol moiety. The calculated ECEPP/2 function and hydration free energy are summarized in Table 4. For three catecholamines, one can see that the *trans* conformation is preferred in the cationic state, Structure I. This is due mainly to hydration free energy by the ammonium group extended for the better hydration. However, *gauche* conformers are significantly more stable than *trans* conformers in the zwitterion-like Structure III. A major contribution to the *gauche* conformation is the electrostatic effect upon Table 4. These structures may be considered as the model species adsorbed on the metal surface. In the di-anionic state, Structure II, the *trans* conformation is preferred for DA and E, but the *gauche* conformation is in slight favor for NE. The electrostatic effect seems playing major roles for DA, but for E the hydration energy plays major roles in favour of the *trans* conformations. It is in contrast to NMR data of E in the di-anionic state that the *trans* con-

formation is preferred from calculations. Except this, the results of calculation are consistent to the interpretations of NMR results.

Conclusion

In aqueous solution of neutral, catecholamines are cationic (Structure I) and the *trans* conformation is in favor slightly. However the difference of two energies are small enough to allow a rapid rotation through the C-C bond of ethylamine moiety. When in basic medium they are di-anionic (Structure II), the *gauche* conformation is preferred for NE and E upon NMR data, but the *trans* conformation for DA. The hydroxyl group of β -carbon seems to play major roles for this different response between DA and NE or E.

The active species of catecholamines (DA, NE, and E) adsorbed on silver metal surface in solution is a bidentated complex between two hydroxyl oxygens of catechol moiety and the metal surface, i.e., zwitterion-like anion (Structure III). When adsorbed, the conformational transition occurs likely from *trans*/*gauche* rotamers mixtures to the *gauche* conformations.

Acknowledgement. One (N.S.L.) of the authors acknowledges Dr. Y. K. Do for his help to operate 400 MHz FT-NMR instrument, and for his advice and suggestions. This work was supported in part by Non Directed Research Fund, Korea Research Foundation and in part by Korea Science and Engineering Foundation.

References

- (a) R. Bergin and D. Carlström, *Acta. Cryst.*, **B24**, 1506 (1968); (b) D. Carlström and R. Bergin, *ibid.*, **23**, 313 (1967).
- T. M. Bustard and R. S. Egan, *Tetrahedron*, **27**, 4457 (1971).
- L. B. Kier and E. B. Truitt, Jr., *J. Pharmac. Exp. Ther.*, **174**, 94 (1970).
- (a) C. J. Grol, *The Chemistry of Dopamine*, A. S. Horn, J. Korf, and B. H. C. Westerink, Eds., Academic Press, pp. 7-40 (1979); (b) B. Pullman and P. Courriere, *Quantum Mechanics of Molecular Conformation*, B. Pullman Ed., John Wiley & Sons, pp. 547-570 (1976); (c) D. Carlström, R. Bergin, and G. Falkenberg, *Q. Rev. Biophys.*, **6**, 257 (1973).
- (a) K. S. Rajan, J. M. Davis, and R. W. Colburn, *J. Neurochem.*, **18**, 365 (1971); (b) K. S. Rajan, J. M. Davis, R. W. Colburn, and F. H. Jarke, *ibid.*, **19**, 1099 (1972); (c) K. S. Rajan, J. M. Davis, and R. W. Colburn, *ibid.*, **22**, 137 (1974); (d) K. S. Rajan, A. Skripkus, G. E. Marks, and J. M. Davis, *Bioinorg. Chem.*, **6**, 93 (1976).
- J. Granot and D. Fiat, *J. Am. Chem. Soc.*, **99**, 4963 (1977).
- N.-S. Lee, Y. Z. Hsieh, R. F. Paisley, and M. D. Morris, *Anal. Chem.*, **60**, 442 (1988).
- (a) L. Que and R. H. Heistand, *J. Am. Chem. Soc.*, **101**, 2219 (1979); (b) F. R. Dollish, W. G. Fateley, and F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, John Wiley & Sons, pp. 175-179 (1974).
- (a) Y. K. Kang, G. Némethy, and H. A. Scheraga, *J. Phys. Chem.*, **91**, 4105 (1987); (b) Y. K. Kang, G. Némethy, and H. A. Scheraga, *ibid.*, **91**, 4109 (1987); (c) Y. K. Kang, G. Némethy, and H. A. Scheraga, *ibid.*, **91**, 4118 (1987); (d) Y. K. Kang, K. D. Gibson, G. Némethy, and H. A. Scheraga, *ibid.*, **92**, 4739 (1988).
- G. Némethy, M. S. Pottle, and H. A. Scheraga, *J. Phys. Chem.*, **87**, 1883 (1983).
- (a) Y. K. Kang, *Conformational Analysis Programs for Biological Molecules (CONBIO)*, KRICT Research Report (1988); (b) Y. K. Kang, *Korean Biochem. News*, **10**(1), 17 (1990); (c) Y. A. Shin and Y. K. Kang, *Bull. Korean Chem. Soc.*, **12**, 61 (1991); (d) M. S. Kim, S. H. Lee, U. T. Chung, and Y. K. Kang, *ibid.*, **12**, 143 (1991); (e) J. H. Yoon, J. M. Shin, Y. K. Kang, and M. S. John, *J. Polym. Sci. Polym. Chem. Ed.*, **29**, 393 (1991).
- J. Granot, *FEBS Lett.*, **67**, 271 (1976).
- (a) R. M. Silverstein and R. T. LaLonde, *J. Chem. Ed.*, **57**, 343 (1980); (b) A. Ault, *ibid.*, **51**, 729 (1974).
- E. D. Becker, *High Resolution NMR, Theory and Chemical Applications*, 2nd Ed., Academic Press, pp. 85-107 (1980).

Preparation and Characterization of the Paramagnetic Rhenium Complex, $(\text{CO})_4\text{ReL}_2$ [$\text{L}_2 = 2,3\text{-Bis(diphenylphosphino)maleic anhydride}$]

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Received September 4, 1991

The paramagnetic complex of $(\text{CO})_4\text{ReL}_2$ [$\text{L}_2 = 2,3\text{-Bis(diphenylphosphino)maleic anhydride}$] was prepared both by the photochemically induced homolytic splitting of $\text{Re}_2(\text{CO})_{10}$ with L_2 and by the chemical reduction of $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$. The $(\text{CO})_4\text{ReL}_2$ compound was characterized by ESR spectrum. The spectrum exhibits three group of sextets arising from one $^{185,187}\text{Re}$ nucleus ($I=5/2$) and two equivalent ^{31}P nuclei ($I=1/2$). Infrared, ESR, and cyclic voltammetric data are reported for all of the complexes prepared in this study.

Introduction

Paramagnetic 19-electron complexes play a vital role in the organometallic chemistry because many reactions have been found in which these complexes are involved as intermediates whenever metal radicals are formed¹. The isolation and characterization of the paramagnetic complexes are relatively rare due to the instability of transient species². However, ligands with low-energy, conjugated π^* orbitals such as quinones³, α -diimines⁴, nitrosyls⁵, substituted pyridines⁶, and 2,3-bis(diphenylphosphino)maleic anhydride⁷ are capable of stabilizing 19-electron organometallic complexes. The relative stability of the complexes can be attributed to the ability

of the ligands to delocalize the extra electron. Therefore, the term "18+ δ complex" is used to describe 19-electron organometallic complexes which are essentially 18-electron complexes with reduced ligands⁸.

Recently, Fenske^{7b} reported the 19-electron complexes, $\text{Co}(\text{CO})_3\text{L}_2$ and $\text{Mn}(\text{CO})_4\text{L}_2$ [$\text{L}_2 = 2,3\text{-Bis(diphenylphosphino)maleic anhydride}$], by the reaction of $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$ with L_2 , respectively. The 19-electron complexes showed that the unpaired electron is delocalized over the transition metal atom and the π^* system of the L_2 ligand. The ease of the formation of complexes, $\text{Co}(\text{CO})_3\text{L}_2$ and $\text{Mn}(\text{CO})_4\text{L}_2$, by chemical reaction prompted us to study the 19-electron complex, $\text{Re}(\text{CO})_4\text{L}_2$. However, the reaction of $\text{Re}_2(\text{CO})_{10}$ and L_2 even