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10. Physical, spectral and elemental analysis data of P4H: mp. 225°C ^{1}H NMR (CDCl$_3$), δ (ppm) −3.62 (b, 2H, N$\underline{H}$), 0.74 (t, 24H, −CH$_2$(CH$_2$)$_2$C$\underline{H}_3$), 1.25 (m, 16H, -CH$_2$CH$_2$C$\underline{H}_2$- CH$_3$), 1.60 (m, 16H, -CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 4.22 (t, 16H, -CO$_2$- C$\underline{H}_2$-), 5.18 (s, 16H 1-methylene), 10.30 (s, 4H, methine); UV (CHCl$_3$), λ$_{max}$ (nm) 475, 523, 580, 637; IR (KBr), v (cm^{-1}) 3410 (s, NH), 2960-2850 (s, CH), 1738 (s, C=O); Calcd for C$_{68}$H$_{94}$O$_{16}$N$_4$ (MW 1223), C 66.75, H 7.74, O 20.92, N 4.58, Found: C 66.84, H 7.58, O 21.02, N 4.60.
11. Physical, spectral and elemental analysis data of P4H-Cl: mp. 200°C ; ^{1}H NMR (CDCl$_3$), δ (ppm) −3.56 (b, 2H, N$\underline{H}$), 1.82 (m, 32H, -CH$_2$(C$\underline{H}_2$)$_2$CH$_2$Cl), 3.59 (t, 16H, -(CH$_2$)$_3$C$\underline{H}_2$- Cl), 4.11 (t, 16H, -CO$_2$C$\underline{H}_2$-), 5.16 (s, 16H, 1-methylene), 10.31 (s, 4H, methine); UV (CHCl$_3$), λ$_{max}$(nm) 468, 525, 578, 635; IR (KBr), v (cm^{-1}) 3412 (s, NH), 2962-2854 (s, CH), 1736(s, C=O); Calcd for C$_{68}$H$_{86}$O$_{16}$N$_4$Cl$_8$ (MW 1450), C 54.49, H 5.78, O 17.07, N 3.74, Cl 18.92, Found C 54.58, H 5.72, O 17.12, N 3.70, Cl 18.94.
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13. X-ray diffraction experiments were performed with JEOL JDX using CuKα radiation at 40 KV×15 mA. Since the quantity of the sample was small, the sample was sealed in a fine glass capillary to be irradiated by X-ray, and the capillary was set in the middle of the furnace. The incident X-ray was collimated with a pin-hol slit, and the diffraction pattern were recorded on high sensitive Kodak DEF-5 film so as to minimize the exposure time.
14. For electron microscopy, the specimen was solved in ethanol-chloroform mixture (3 : 1) and a drop of the solution was spread on a thin amorphous carbon film fixed beforehand on an electron microscopic grid. After evaporating the solution in air, the strutural changes of the specimens were examined with JEOL 2000-FX equipped with a high temperature specimen holder.

A Simple Flow Method to Study Photochemistry of Molecules Adsorbed on Ag Colloid Surface

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Enhanced surface photochemistry of molecules adsorbed on surfaces capable of producing surface-enhanced Raman has been known.[1-4] Photochemistry at surfaces may be enhanced by the same field enhancement responsible for surface-enhanced Raman scattering (SERS).

SERS spectroscopy in principle provides a powerful means for the study of surface chemical reactions, because these reactions directly results in the changes in SERS spectra of adsorbed molecules.[5,6]

Recently, Suh *et al.* have studied the kinetics of the photodecomposition of 2-pyrazinecarboxylic acid adsorbed on silver colloid surfaces using SERS as a probe.[7] They have used a capillary as the sample cell to increase the effect of irradiation. Both photochemistry and surface-enhanced Raman were monitored by focused Ar ion laser light traversing the capillary containing a sample solution, without flowing. In this case, it is possible to use SERS as a probe because the rate of the photodecomposition is relatively slow. If the rate of photochemical decomposition of a molecule adsorbed on silver colloid surfaces is relatively fast, it is almost impossible to use SERS as a probe to study the kinetics of photochemistry since SERS signal should be accumulated for a certain period to obtain reasonable signal-to-noise ratios. For a fast photochemistry, the accumulation time of Raman signal to get reasonable signal-to-noise ratio may be much longer than its photochemical reaction time.

In this communication, we report that the flow method designed to investigate the relatively fast photochemical reactions of molecules adsorbed on Ag colloid surfaces using SERS as a probe.

The schematic diagram of the flow system used is shown in Figure 1. The flow cell was a modified graduated cylinder. A stop cock was attached to the cut-out bottom of the graduated cylinder. A standard 1.5-1.8 mm Pyrex capillary tube was used as a Raman cell. To make the flow of the sample solution smooth, the tip of the outlet was dipped in a water solution whose water level was kept constant.

The driving force for the flow is the pressure difference between the outlet and the top of solution in the flow cell. Therefore, the flow rate can be written as[8]

$$F = -A_{gc}\frac{dh}{dt} = c\rho gh$$

where A_{gc} is the cell cross sectional area, h the height of solution with time, ρ the density, g the gravitational constant, and c a constant. Solving this differential equation gives the height of solution with time as

$$h = h_o \, \exp(-t/\tau_o)$$

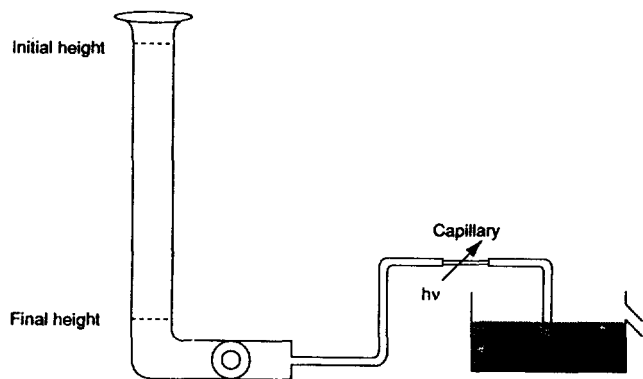where h_o is the height of solution at $t=0$ and $\tau_o = A_{gc}/c\rho g$

Figure 1. Schematic Diagram of Flow System.

Figure 2. The 3, 50, 100 and 150th SERS spectra (from top to bottom) of o-diiodobenzene adsorbed on silver colloid observed by using the flow system of Figure 1. The exciting laser was operated 488-nm at an input power of 50 mW.
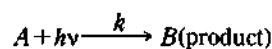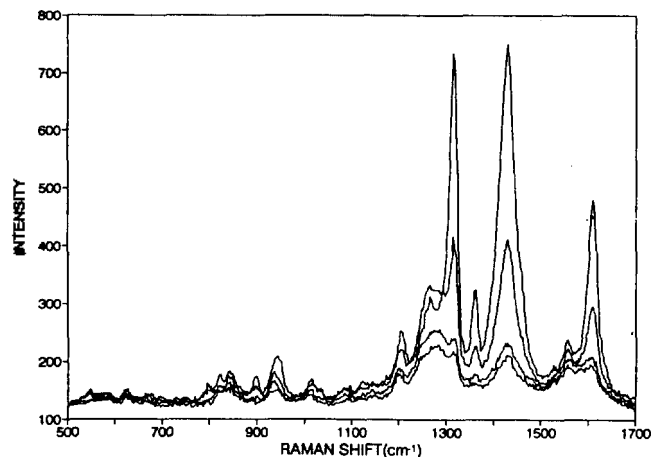
is the decay time. The flow rate becomes as

$$F = -A_g dh/dt = (A_g h_o/\tau_o)\exp(-t/\tau_o)$$

When a solution flows through in this system, the laser exposure time for the molecules within the laser beam is given as

$$t_{expose} = AD/F = (AD\tau_o/A_g h_o)\exp(t/\tau_o)$$

where A is the cross sectional area of capillary tube, and D the distance from the top of laser beam spot in the direction of flow to any position on the laser beam spot. For simplification, we have approximated that the laser beam has a square shape, not a circle, and does not have intensity gradient from the center of the laser beam to its edge.

If a photochemical reaction on colloidal surface occurs as a result of the absorption of a photon by a reactant molecule (A):

$$A + h\nu \xrightarrow{k} B(product)$$

and the reaction is first order, then the Raman intensity of a sample without flow is given as

$$S = (S_A - S_B)\exp(-kt) + S_B$$

where S_A and S_B are the Raman intensity of the reactant molecule (A) and product molecule (B), respectively. The Raman intensities S_A and S_B are functions of the concentration and Raman cross section of the molecule and the laser power used. The rate constant, k, is also a function of laser power, I.

Since the molecules in the system flows, the laser exposure time of the molecules within laser beam varies from 0 (flow tail) to AL/F (flow front). Here L is the width of the laser beam. Therefore, the observed Raman intensity for this flow system corresponds to the average Raman intensities of molecules for which the exposure time varies from 0 to AL/F. The observed Raman intensity is given as

$$S_{obs} = \frac{1}{\tau} \int_0^\tau [e^{-kt}(S_A - S_B) + S_B]dt$$

$$= \frac{1}{k\tau}(S_A - S_B)(1 - e^{-k\tau}) + S_B$$

where $\tau = AL/F$. Substituting τ into the upper equation results in
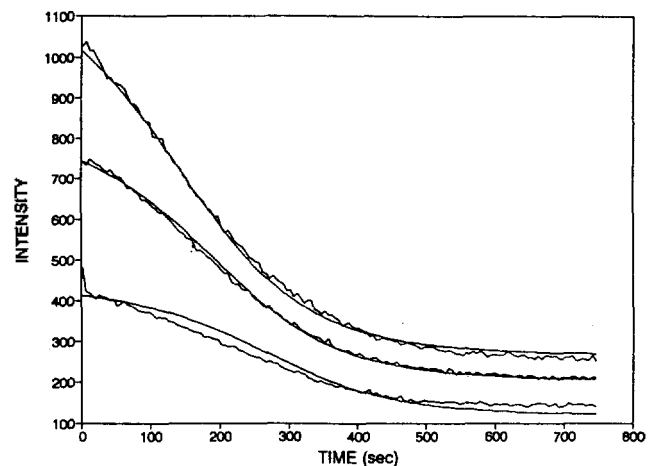
Figure 3. Time evolution of the SERS intensity at 1427 cm^{-1} excited with 488-nm Ar$^+$ laser line. Jagged lines are experimental data; smooth lines are recalculated according to the model described in the text. The laser power from top to bottom: 75, 50, 25 mW.

$$S_{obs} = \left(\frac{A_g h_o}{kAL\tau_o}\right)(S_A - S_B)e^{-t/\tau_o}$$

$$\times [1 - e^{-(kAL\tau_o/A_g h_o)e^{t/\tau_o}}] + S_B$$

Using this equation, we analyzed the SERS spectra, taken under flow conditions, of o-diiodobenzene (ODIB) adsorbed on Ag colloid surfaces aged for one month. Surface-enhanced Raman was achieved by focused Ar ion laser light traversing the capillary. SERS spectra were recorded using a Spex 1877 C Triplemate spectrometer equipped with a multichannel charge-coupled device (CCD) detector. 150 spectra were collected in sequence while flowing the sample. The accumulation time of each spectrum was 5 sec. The 3, 50, 100 and 150th SERS spectra of ODIB are shown in Figure 2.

The SERS spectra of ODIB in Figure 2 are dfferent from that of the published, which may be due to different sampling

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conditions. The sample for spectra in Figure 2 was prepared in dark, but the sample for the published one was prepared under room light.

We made a matrix using the data of 150 spectra. The data of each spectrum are arrayed in a column in the matrix. Consequently, the data of 150 spectra make 150 columns. In this case, the rows in matrix correspond to the time evolution of each channel.

Time evolution of the SERS intensity of the band at 1427 cm^{-1} with different power levels of Ar ion laser beam is shown in Figure 3. The jagged lines are experimental data and the smooth lines are calculated ones according to the equation described previously. Best fits were obtained with $k = 1200$ sec^{-1}.

In the previous model, we did not consider the effect of diffusion. The volume of the sample irradiated by laser beam is very small and the local temperature is much higher than that of surroundings due to the absorption of laser beam. Therefore, the effect of diffusion will become important when the flow becomes slow. Indeed, we could get a slightly better fitting by including a diffusion term.[7] Particularly, the fitting of the tail part of the graphs was slightly improved.

The intensities of most bands in Figure 2 decreased monotonically with increasing the exposure time of laser beam. No band growth near 1400 cm^{-1} attributable to graphite carbon was observed.[4,7] Therefore, we conclude that the ODIB on surfaces may simply leave the surface after absorption of a photon.

In conclusion, we have shown that flow method is very useful to study the photochemistry of molecules adsorbed on Ag colloid surfaces. Particularly, the flow method can give us more advantage to use a multichannel detection system.

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Reactions of Polyhedral Boron Hydrides with Transition-Metal Acetylide: Synthesis Characterization of the New Metallaborane Clusters nido-5-Me$_2$S-6-Cp(CO)$_2$FeHC=CPh-B$_{10}$H$_{11}$ and nido-9-Cp(CO)$_2$FeHC=CPh-6-SB$_9$H$_{10}$.

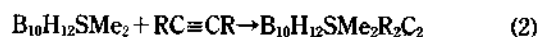Yeon-Sok Cho, Jae-Jung Ko[†], Youhyuk Kim[‡], and Sang Ook Kang*

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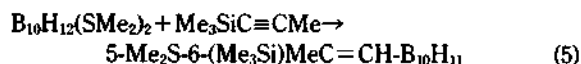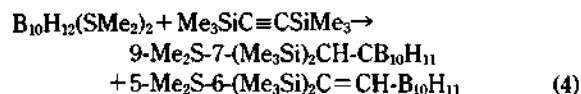[‡]*Department of Chemistry, College of Natural Sciences, Dankook University, Chung-nam 330-714, Korea*

The reaction of decaborane(14) B$_{10}$H$_{14}$ with an alkyne in the presence of dimethyl sulfide is a well-established route to *ortho*-carborane 1,2-C$_2$B$_{10}$H$_{12}$ and its derivatives.[1] Previous studies[2] have suggested that this reaction involves the initial formation of bis(dimethylsulfide) decaborane(12) B$_{10}$H$_{12}$(SMe$_2$)$_2$, which can then dissociate a dimethylsulfide unit, yielding a reactive B$_{10}$H$_{12}$SMe$_2$ species. Further reaction of this B$_{10}$H$_{12}$SMe$_2$ intermediate with an alkyne then leads to the direct insertion of a two-carbon acetylenic unit into the cage along with dissociation of the remaining SMe$_2$ and H$_2$ loss to yield the final product.

$$B_{10}H_{12}(SMe_2)_2 \rightarrow B_{10}H_{12}SMe_2 + SMe_2 \tag{1}$$

$$B_{10}H_{12}SMe_2 + RC \equiv CR \rightarrow B_{10}H_{12}SMe_2R_2C_2 \tag{2}$$

$$B_{10}H_{12}SMe_2R_2C_2 \rightarrow 1,2\text{-}R_2C_2B_{10}H_{10} + H_2 + SMe_2 \tag{3}$$

Also, reactions of B$_{10}$H$_{12}$(SMe$_2$)$_2$ with the silylated acetylenes, bis(trimethylsilyl) acetylene and (trimethylsilyl) propyne,[3] have been studied and did not yield the expected *ortho*-carborane derivatives but instead gave either alkenyldecaborane or monocarbon carborane products.

$$\begin{aligned} B_{10}H_{12}(SMe_2)_2 + Me_3SiC &\equiv CSiMe_3 \rightarrow \\ 9\text{-}Me_2S\text{-}7\text{-}&(Me_3Si)_2CH\text{-}CB_{10}H_{11} \\ + 5\text{-}Me_2S\text{-}6\text{-}&(Me_3Si)_2C = CH\text{-}B_{10}H_{11} \end{aligned} \tag{4}$$

$$\begin{aligned} B_{10}H_{12}(SMe_2)_2 + Me_3SiC &\equiv CMe \rightarrow \\ 5\text{-}Me_2S\text{-}6\text{-}&(Me_3Si)MeC = CH\text{-}B_{10}H_{11} \end{aligned} \tag{5}$$

We have investigated the reactions of decaborane(14) B$_{10}$H$_{14}$ and thiaborane(11) SB$_9$H$_{11}$ with the transition-metal acetylide Cp(CO)$_2$Fe(CCPh), and observed that, in contrast to the results discussed above, these reactions do not result in the formation of *ortho*-carborane derivatives. Instead, hydroboration of the acetylene accompanied by dimethyl sulfide group migration is observed to yield 5-(dimethylsulfide)-6-alkenyldecaborane(14) as the major product. Another single product, apparently resulting from the hydroboration of a single carbon of the acetylenic unit into the thiaborane cage, was also isolated in good yields in the reaction of transition-metal acety-

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