

observed. After 5 min, 4.0 ml of the reaction mixture was removed and injected into a hydrolyzing mixture of THF-water-glycerine (1:1:1). The hydrogen evolved was 3.0 mmol, indicating that 1.0 mmol of hydride had been used per mmol of acetophenone. Therefore, 1.0 mmol of hydride had been used for reduction per mmol of acetophenone. Another 4.0 mL of the reaction mixture was also removed and hydrolyzed after 30 min. The amount of hydride used for reduction was 1.03 mmol. After 1 h, it was also 1.03 mmol. It was shown that reduction of acetophenone was over in 5 min.

Procedure for Product Analysis by GLC. The reduction of 1-methyl-1,2-cyclohexene oxide is representative. The setting-up was the same as the previous part. 1 ml of solution containing 1 mmol of 1-methyl-1,2-cyclohexene oxide and 0.5 mmol of dodecane as a internal standard in THF was placed in a 50 mL flask and then 0.65 ml of THF was introduced. The mixture was maintained at 0°C and then 2.35 ml (4.0 mmol) of KEt_3BH solution was added dropwisely. After 24 h, excess hydride was destroyed with 0.5 mL of water and oxidized by the addition of 0.8 mL of 2 N NaOH, followed by 0.8 mL of 30% H_2O_2 for 2~3 h. The aqueous layer was saturated with K_2CO_3 and subjected to GLC analysis on a 10% carbowax 20 M column, 10 ft \times 0.125 in. It was revealed that KEt_3BH reduced 1-methyl-1,2-cyclohexene oxide to 1-methylcyclohexanol (95%) exclusively.

Procedure for Competitive Reaction. The reaction of ethyl benzoate in the presence of cyclohexene oxide is representative. The experimental set-up was the same as the rate study. To a well-stirred mixture of 2 mmol of ethyl benzoate and cyclohexene oxide was added 2.14 mL (4.4 mmol) of KEt_3BH solution at 0°C. After 15 min, the remaining hydride was destroyed with 0.5 mL of water and 1 mL (1.0 mmol) of naphthalene in THF as an internal standard was added. After warming the reaction mixture to room temperature, it was oxidized by the addition of 1.0 mL of 2 N NaOH

and 1.0 mL of 30% H_2O_2 for 2~3 h. Then the aqueous layer was saturated with K_2CO_3 and the dry THF layer was subjected to GLC analysis. The column used was the same as the previous section. GLC analysis showed the formation of 95% benzyl alcohol and cyclohexene oxide remained intact.

Acknowledgement. We are grateful to the Ministry of Education, and to the Korea Science and Engineering Foundation for financial support of this work.

References

1. S. Krishnamurthy, *Aldrichimica Acta*, **55**, 7 (1974).
2. (a) H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979); (b) H. C. Brown and S. Krishnamurthy, *Aldrichimica Acta*, **12**, 3 (1979); (c) J. M. Fortunato and B. Ganem, *J. Org. Chem.* **41**, 12 (1976); (d) N. M. Yoon, K. E. Kim and J. Kang, *J. Org. Chem.* **51**, 226 (1986).
3. H. C. Brown, S. C. Kim and S. Krishnamurthy, *J. Org. Chem.* **45**, 1 (1980).
4. (a) H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95**, 1669 (1973); (b) M. P. Cooke, Jr. and R. M. Parlman, *J. Org. Chem.* **40**, 531 (1975).
5. C. A. Brown and S. Krishnamurthy, *J. Organometal. Chem.* **156**, 111 (1978). They reported the reaction is over in 0.5 h, however, in our large scale preparation, we ran the reaction for 24 h in order to insure completion.
6. Reeve, Erikson and Aluotto, *Can. J. Chem.* **57**, 2747 (1979).
7. H. C. Brown, C. P. Mathew, C. Pyun, J. C. Son and N. M. Yoon, *J. Org. Chem.* **49**, 3091 (1984).
8. C. Pyun, J. C. Son and N. M. Yoon, *Bull. Korean Chem. Soc.*, **4**, 3 (1983).
9. H. C. Brown, S. C. Kim and S. Krishnamurthy, *Organometallics* **2**, 779 (1983).

Vibrational Spectroscopic Study of Benzenethiol on Silver Surface

Whi Kun Yi, Cheol Woo Park, Myung Soo Kim, and Kwan Kim*

Department of Chemistry, Seoul National University, Seoul 151. Received April 9, 1987

Vibrational spectroscopy has been applied to the benzenethiol molecule adsorbed on the silver surface. The results of infrared and Raman spectral studies have led to the conclusion that benzenethiol is chemisorbed dissociatively on the silver surface by rupture of S-H bond and the benzenethiolate formed upon adsorption is bound to silver via its sulfur atom. It seemed more likely that benzenethiol is adsorbed as being inclined to the silver surface. On contact with oxygen, the geometry of the adsorbed species appeared to bear a resemblance to that of silver benzenethiolate salt. The infrared bands of adsorbed species remained with little decrease of intensity even after the prolonged evacuation at 673 K, indicating that benzenethiol is very strongly chemisorbed to the silver surface.

Introduction

Understanding the interactions between sulfur compounds and various metals has been of a great concern in catalytic chemistry¹. Catalyst poisoning by sulfur compounds

is a serious problem in a number of applications². Despite the realization that sulfur adversely affects catalyst performance, there is little understanding of the poisoning mechanism³.

Vibrational spectroscopy has been widely used in surface and catalysis studies⁴. The most general approach of vibra-

* To whom all correspondence should be addressed.

tional spectroscopy applied to adsorbed species is transmission-absorption infrared spectroscopy which has a history dating back to 1911⁵. Terenin and his coworkers⁶ made major contributions using this approach in a systematic study of surface hydroxyl groups on oxides and interactions between adsorbed molecules and hydroxyl groups in the near infrared or overtone region. Eischens and his coworkers⁷ solved the instrumental problems associated with the investigation of dispersed, supported metal catalysts and extended infrared absorption spectroscopy to a broad range of adsorption systems of catalytic interest.

Ordinary Raman spectroscopy, the inelastic scattering of radiation in the visible frequency range, is inherently a very inefficient process and is generally less sensitive than infrared absorption when used for surface studies. In order to obtain the Raman spectrum of adsorbed species it is essential to use laser irradiation, but for supported metals this usually means excessive heating of the sample which in turn leads to desorption or decomposition of the adsorbed molecules. However, the surface-enhanced Raman scattering (SERS) method which has been developed in this last decade has provided a new avenue to applying Raman spectroscopy successfully in surface and catalysis studies⁷. With its enormous sensitivity, SERS has begun to be accepted as a useful vibrational spectroscopic technique for the study of molecule-surface interaction^{8,12}.

Following the above implications, we report here the infrared and SERS investigation of benzenethiol on silver.

Experimental

The design of the infrared cell used in this work is similar to that of Ramamoorthy et al.¹³ The homemade vacuum evaporator and the conventional vacuum apparatus were capable of maintaining a dynamic vacuum of $\sim 10^{-4}$ Nm⁻². The glass part of the latter system was heated with a heating tape. Infrared spectra were recorded with a Perkin-Elmer model 283 spectrophotometer. Raman spectra were obtained with Japan spectroscopic company model R-300 laser Raman spectrophotometer using 514.5 nm line of an Ar⁺ laser (Spectra Physics model 164-06) as an exciting source. Raman scattering was observed with 90° geometry, and scattered signal was detected using a commercial photon counting system.

Initially, γ -alumina (Morton Thiokol Incorporation), dried in air at 378 K for 72 hr, was ground to a fine powder and pressed into a self-supporting disc, 2 cm in diameter and less than 0.05 cm thick. Silver (puratronic, Morton Thiokol Incorporation) was evaporated onto the disc from a resistively heated nichrome filament in a vacuum evaporator. The thickness of the film thus obtained was 100-150 nm^{14,15}.

For the infrared measurement, the disc was placed in a stainless steel holder, which was suspended by a stainless steel wire in the infrared cell. After preparing the sample, a background spectrum was recorded. The cell was subsequently returned to the vacuum system, and benzenethiol (Aldrich Chemical Company) was added to the cell and then the cell was isolated from the vacuum system. The pressure of benzenethiol gas was monitored using a thermocouple vacuum gauge (Sargent-Welch model 1515). All observable changes were complete within 10 min when using this procedure. Before taking the spectrum, the cell was evacuated to remove any remaining gas. After recording the spectrum,

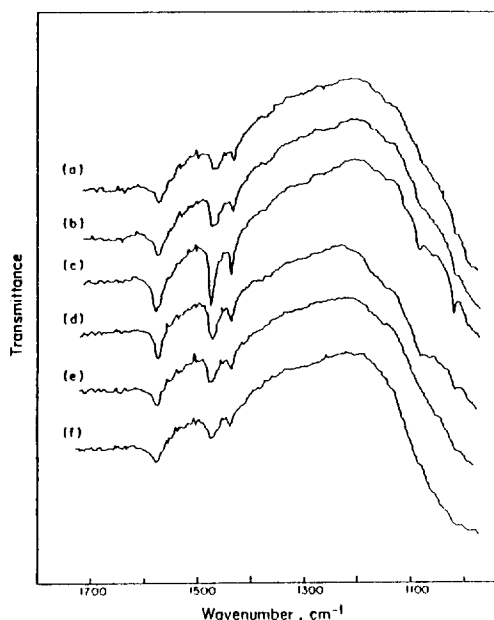


Figure 1. Infrared spectra of benzenethiol on silver at pressures of 90 mTorr (a), 150 mTorr (b), and 1 Torr (c), followed by evacuation for 1 hr at 300 K (d), 573 K (e), and 673 K (f).

the cell was returned to the vacuum system. Then, additional benzenethiol of higher pressure was admitted to the cell and the process was repeated.

Details of Raman measurement have been reported elsewhere⁸. The silver film prepared as described above was placed in a glass cell. After evacuation, gaseous benzenethiol was added to the cell and then its SER spectrum was recorded.

Results and Discussion

Figure 1(a), 1(b), and 1(c) show the infrared spectra, in the limited region 1700~1000 cm⁻¹, of benzenethiol adsorbed at 90, 150 mTorr, and 1 Torr, respectively. It has already been reported¹⁶ that no spectra of adsorbed benzenethiol appeared when the molecule was exposed solely to the γ -alumina surface without any proper heat pretreatment. Hence, the spectra shown in Figure 1 (a), 1 (b), and 1 (c) are believed to be entirely due to the adsorption of benzenethiol onto the silver surface.

A very distinct surface spectrum was obtained in contact with 90 mTorr of benzenethiol (Figure 1 (a)). The most intense bands observed are centered at 1580, 1475, and 1440 cm⁻¹ all of which can be attributed to aromatic ring-skeletal vibrations¹⁷. In specific, the band at 1580 cm⁻¹ corresponds to the ring stretching mode (8a), and the latter two bands to the ring stretching plus deformation mode assigned as 19a (1475 cm⁻¹) and 19b (1440 cm⁻¹)¹⁸.

It can be seen from Figure 1 (a), 1 (b), and 1 (c) that the infrared bands grow as the admitted benzenethiol pressure increases. However, the increase of the band intensities is far behind the pressure increment. This may indicate that 90 mTorr is more than enough for the full monolayer coverage of benzenethiol on the silver surface. It was observed that the peaks shown in Figure 1 (a) blue-shifted by 2~3 cm⁻¹ as the pressure of the benzenethiol molecule increased. The peak positions were approaching to those for the neat benzenethiol

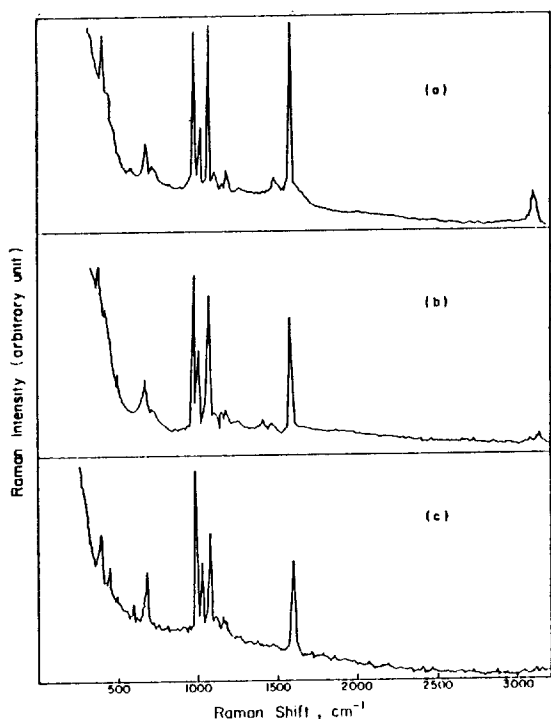


Figure 2. SER spectra of benzenethiol on silver after the exposure of 1 Torr of the molecule (a), followed by adding 70 Torr of oxygen (b). Ordinary Raman spectrum of silver benzenethiolate salt (c).

liquid, i.e., 1584 (8a), 1479 (19a), and 1443 cm^{-1} (19b). Hence, the spectra shown in Figure 1 (b) and 1 (c) are supposed as being due to the multilayer coverage of benzenethiol on the silver surface. Since the bands of adsorbed species remained with little decrease of intensity for the prolonged evacuation at the ambient temperature (see Figure 1 (d)), even the multilayer species seemed to strongly interact with the silver surface.

Figure 2 (a) shows the SER spectrum of benzenethiol that is obtained after the exposure of 1 Torr of the molecule to the silver surface. The bands at 2567 and 917 cm^{-1} in the neat Raman spectrum which can be assigned to the stretching and bending vibrations of S-H bond, respectively, are no longer

detected in the SER spectrum. This observation indicates that benzenethiol is chemisorbed dissociatively on the silver surface by rupture of the S-H bond. It would be worth to mention that the SER spectrum of benzenethiol shown in Figure 2 (a) is nearly the same as the SER spectrum of the molecule in aqueous silver sol. The vibrational peak positions were much the same for the two spectra, whereas the relative intensities of each peaks were more or less different. Nevertheless, the dissociative chemisorption by rupture of the S-H bond was apparent in the sol spectrum as well.

After the initial report by Fleischmann *et al.*¹⁹, the SERS effect has been the subject of intensive theoretical and experimental investigations. Although the nature of the enhancement mechanism is not yet completely understood, general consensus is being formed that the electromagnetic surface plasmon resonance and the chemical interaction between the adsorbed molecule and the metal surface play important roles^{7,20}. Regardless of which of the several proposed mechanisms is indeed correct, however, there is one common feature that the most intense enhancement occurs from the adsorbed species in the first layer. The enhancement for the higher layer species is negligible. Accordingly, although the surface infrared spectrum such as that shown in Figure 1 (c) arises from the composite multilayer species, the SER spectrum shown in Figure 2 (a) is believed as due to the first layer adsorbed species. If this argument is correct, the SER band of benzenethiol should appear at lower frequency than that of the infrared band. In fact, it was observed that the positions of the ν_{8a} , ν_{19a} , and ν_{19b} bands in the SER spectrum of benzenethiol were lower by $\sim 5 \text{ cm}^{-1}$ than those of the corresponding bands in the surface infrared spectrum. The SER spectrum of benzenethiol is thus supposed to contain more fundamental information on the interaction between the benzenethiol molecule and the silver surface than the surface infrared spectrum.

It is a well-known experimental fact that in mono-substituted benzene the frequencies of ν_1 , ν_{6a} , ν_{7a} , ν_{16b} bands are more sensitive to the mass of the substituent than others¹⁷. Indeed, it has been observed that all those bands were exclusively shifted in the SER spectrum from their positions in the neat spectrum. For example, the ν_1 band which is particularly sensitive to the substituent has shifted 20 cm^{-1}

Table 1. Relative Raman Intensities of a Few Ring Modes in the SER Spectrum of Benzenethiol and in the Ordinary Raman Spectrum of Silver Benzenethiolate, and the Relative Enhancement Factors for the SER Bands

Class	SERS		Silver Benzenethiolate	Vibrational Assignment ^c	Relative Enhancement ^d	
	Before Adding O ₂	After Adding O ₂			Before Adding O ₂	After Adding O ₂
Class I, out-of plane modes	471 ^a (8.1) ^b	471(13)	477(14)	16b	0.6	0.9
	738 (9.3)	738(8.0)	741(3.7)	11	2.5	2.2
	999 (100)	999(100)	998(100)	12	1.0	1.0
Class II, in-plane modes along z-axis	1073 (105)	1072(91)	1079(61)	1	1.7	1.5
	1182 (19)	1182(12)	1181(5.0)	9a	3.8	2.4
	1573 (108)	1572(90)	1574(47)	8a	2.3	1.9
Class III, in-plane mode along y-axis	616 (4.2)	615(18)	615(8.0)	6b	0.5	2.3

^a Frequencies in units of cm^{-1} 's. ^b Normalized peak intensities. ^c Taken from refs. (17,18). ^d Normalized to 1.0 at 999 cm^{-1} .

downward (Neat: 1093 cm^{-1} , SERS: 1073 cm^{-1}). Along with the observation that benzenethiol is chemisorbed dissociatively on silver by rupture of S-H bond, it now appears that the benzenethiolate anion formed upon adsorption is bound to the silver surface via the sulfur atom.

The orientation of an adsorbed molecule on the silver surface may be determined by SERS once its selection rule is known. For molecules with C_{2v} symmetry such as benzenethiolate, the image model treatment proposed by Nichols *et al.*²¹ predicts that the a_1 and a_2 vibrational modes are active for face-on adsorption, while a_1 , a_2 , b_1 , and b_2 modes are active for edge-on adsorption. According to the electromagnetic field enhancement model proposed by Moskovits²², the relative band enhancement should be in the order of $a_1 > a_2 \approx b_1 > b_2$ for face-on adsorption and of $a_1 > b_1 \approx b_2 > a_2$ for edge-on adsorption. In specific, when the rule proposed by Creighton²³ is used, the relative enhancement factors for the different modes would be $a_1 : a_2 : b_1 : b_2 = 1 : 16 : 4 : 4 : 1$ and $1 : 16 : 1 : 4 : 4$ for face-on and edge-on adsorption, respectively. Hallmark and Campion²⁴ have recently modified the image model, arriving at the same result as that predicted by Moskovits from the electromagnetic field enhancement model. In order to apply the electromagnetic field enhancement model proposed by Moskovits²² and Creighton²³, bands due to the a_2 -type vibrational mode should be prominent in both the SER and ordinary Raman spectra. It is unfortunate that there are only two bands, ν_{10a} and ν_{17a} , associated with the a_2 -type mode. Furthermore, those bands are Raman inactive. Hence, the relative enhancement for the a_2 mode is hardly determinable. Nevertheless, the relative enhancements between the b_1 and b_2 modes may be informative. It was observed for benzenethiol that surface enhancement for the b_1 mode is larger than that of the b_2 mode (see Table 1). This may indicate that benzenethiol adsorbs face-on to the silver surface. Above argument has already been used in our previous SERS study of benzenethiol in aqueous silver sol, and on that basis the molecule was tentatively assumed to lie flat on the silver sol surface²⁵.

In order to examine the orientation of an adsorbed molecule from a different point of view, we have classified the benzene ring modes into three groups, *i.e.*, out-of-plane mode and two kinds of in-plane modes. The in-plane modes are divided into two groups, depending on the vibrational axis. For benzenethiolate, the bands such as ν_{11} and ν_{16b} belong to the out-of-plane modes with the b_1 type symmetry (class I). The bands such as ν_1 , ν_{8a} , ν_{9a} , and ν_{12} belong to the in-plane modes with the a_1 -type symmetry which has the normal mode component along the molecular principal z-axis (class II). The b_2 -type mode such as ν_{6b} belongs to the in-plane vibrations along the molecular principal y-axis (class III).

The surface selection rules proposed independently by Nichols²¹, Moskovits²², Creighton²³, and Campion²⁴ have one common feature. Namely, if the benzene ring is adsorbed face-on to the silver surface, the out-of-plane modes, class I, should be more enhanced than the in-plane modes. On the other hand, if the benzene ring is adsorbed edge-on to the silver surface, the class-II in plane modes should be more enhanced than other classes.

Table 1 lists the normalized peak intensities and the intensity ratios of a few benzene ring modes in the SER spectrum with respect to the corresponding modes in the ordinary Raman spectrum of silver benzenethiolate salt. The reason

for taking the ordinary Raman spectrum of the salt as a reference is that the vibrational frequencies in the SER spectrum resemble those of the salt much more closely than those of neat benzenethiol. Such observation may reflect that the benzenethiolate anion formed upon adsorption is attached to silver atom (s) via its sulfur atom. The peak intensities shown in Table 1 were those normalized with respect to the intensities of ν_{12} mode in each Raman spectra. The SERS-to-ordinary Raman intensity ratios for each Raman peak were then computed. It is not convincingly clear from the Table whether the benzene ring lies flat or stands perpendicular to the silver surface. However, it is seen that surface enhancements for the first class modes are somewhat comparable to those for the second class modes. The third class is the least enhanced. Hence, it seems more likely that the benzene ring is leaning to one side rather than either lying flat or standing perpendicular to the silver surface.

It is very unfortunate that the two approaches considered above do not lead to a unanimous decision on the molecular orientation. However, considering the observation which is to be discussed later that the surface enhancements for the first and third class modes increase upon the oxygen exposure while those for the second class modes decrease, it is very tempting to say that benzenethiol is somewhat tilted with respect to the silver surface in the absence of oxygen. As a reference, it would be worth to mention here that the second class modes were more enhanced than others under the silver sol environment compared with the present case. Although the orientation of the adsorbed benzenethiol molecule may not be conclusively determined from the surface infrared spectrum, the observation that the in-plane vibrations of benzenethiol are strongly active seems to be informative. There have been several suggestions that selection rules exist in infrared reflection-absorption spectroscopy for molecules adsorbed on metal surfaces²⁶. Physical arguments were used to demonstrate that only those molecular vibrations having nonzero dipole moment derivative components perpendicular to the surface would be infrared active²⁷. According to this rule, only the in-plane vibrations of benzenethiol should be infrared active when the adsorbed molecules are all lying perpendicular to the metal surface. On the other hand, provided the molecules are all to lie flat on the surface, only out-of-plane molecular vibration modes can be infrared active. It is noticeable that all the bands appeared in the surface infrared spectra of this work can be attributed to the in-plane vibrational modes. Hence, it seems likely that perpendicular (or inclined) orientation is more plausible than flat one for the multilayer species.

As mentioned previously, benzenethiol adsorbed was not removed by evacuation at the ambient temperature (see Figure 1 (d)). Moreover, the bands of adsorbed species remained with little decrease of intensity even when evacuation has been performed at 573 K (Figure 1 (e)) and 673 K (Figure 1 (f)) although such bands at 1023 (ν_{18a}) and 1089 cm^{-1} (ν_1) became nearly unnoticeable at 573 K. In addition, no appreciable band shift occurred from such a treatment. Hence, it seems that even the multilayer species are very strongly chemisorbed to the surface.

The disappearance of some bands at 573 K may, however, indicate that certain kinds of reaction would occur at that temperature. It has been shown²⁸ from the thermal desorption experiment that benzenethiol adsorbed on the nickel surface decompose into various chemical species at

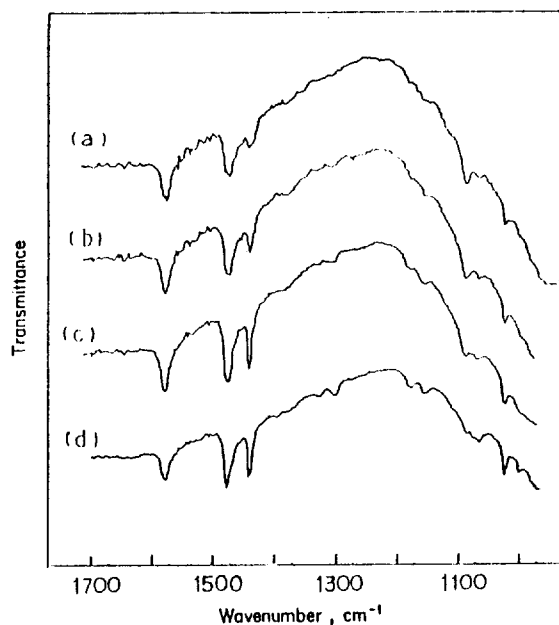


Figure 3. Infrared spectra of benzenethiol on silver after the exposure of 1 Torr of the benzenethiol molecule followed by 10 min evacuation (a) and taken at 10 min (b), 1 hr (c), and 12 hrs (d) after the introduction of 70 Torr of oxygen into the infrared cell.

the temperatures above 550 K. Preliminary experiment exhibited that benzenethiol is more strongly chemisorbed to the silver surface than to the nickel surface. Also, it appeared that the decomposition of adsorbed sulfur-containing species would occur more readily on the nickel surface in comparison with the case on the silver surface. Nevertheless, we could not completely exclude the possibility that some decomposition reactions might indeed occur under above condition on the silver surface. More detailed thermal desorption experiment should of course be carried out to get more firm information on the possible surface reactions.

It is somewhat interesting to observe that noticeable spectral changes occur as oxygen is introduced at the ambient temperature into the measurement cell. Figure 3 (a) shows the surface infrared spectrum taken after the exposure of 1 Torr benzenethiol followed by 10 min evacuation. Figure 3 (b), 3 (c), and 3 (d) correspond to the infrared spectra obtained, respectively, at 10 min, 1, and 12 hrs after adding 70 Torr of oxygen into the infrared cell. No appreciable band shift occurred. However, it was clearly seen that the peak at 1443 cm^{-1} (ν_{19b}) grew with time. Furthermore, the ν_{14} , ν_{15} , and ν_{18b} bands centered at 1327 , 1157 , and 1070 cm^{-1} , respectively, became more distinct upon the introduction of oxygen. Interestingly, above bands belong to the b_2 -type vibrations.

The exact role of oxygen is not certain. Since hardly should occur any reaction between the benzenethiol and oxygen molecules at the ambient temperature, it is supposed at the present time that reorientation of the adsorbed species may occur on the silver surface. Such a possibility would be supported by the SER spectral changes. After recording the SER spectrum shown in Figure 2 (a), 70 torr of oxygen was introduced into the Raman cell. Figure 2 (b) shows the SER spectrum taken at 24 hrs after the oxygen introduction. Once again, no significant band shifts occurred. However, as can be seen from Figures 2 (a) and 2 (b), the relative band intensities changed upon the introduction of oxygen. Table 1 in-

cludes also the normalized peak intensities and the intensity ratios of a few benzene ring modes in the SER spectrum shown in Figure 2 (b) with respect to the corresponding modes in the ordinary Raman spectrum of silver benzenethiolate salt shown in Figure 2 (c). It is seen from the Table that the surface enhancements for the first and third class modes increase upon the oxygen exposure, whereas the enhancements for the second class modes decrease. This may reflect that the benzene ring inclines toward the silver surface as oxygen is introduced into the adsorbed system.

It would be interesting to notice that the infrared (Figure 3 (d)) and SER (Figure 2 (b)) spectra resemble more closely to the infrared (not presented) and ordinary Raman spectra (Figure 2 (c)) of silver benzenethiolate salt, respectively, than to the spectra obtained before adding the oxygen gas. This may suggest that the adsorbed species assumes very similar geometry to that of silver benzenethiolate salt upon being contacted with O_2 . It has been reported²⁹ that, for $[Ag_5(C_6H_5S)_7]^{2-}$, benzenethiolate group is bound to two silver atoms, and the angle between the Ag-S-Ag plane and the benzene ring is 111° . It appears thus that, in the absence of O_2 , the adsorbed molecule is neither perpendicular nor flat to the silver surface. Somewhat inclined geometry seems to be rather plausible.

Although the exact role of oxygen is uncertain, the admitted oxygen molecules may react with the silver atoms. Gonzalez-Elipse *et al.*³⁰ have studied the oxygen effect on a highly dispersed TiO_2 supported silver sample. Since TiO_2 exhibited a strong metal-support interaction³¹, Ag^+ ions existed on the support. When the sample was put into contact with oxygen, the silver aggregates were destroyed, and Ag^{2+} ions were generated. Even though the system employed in this work is quite different from that used by Gonzalez-Elipse *et al.*, the possibility that oxygen produces Ag^+ (and Ag^{2+}) ions also in the present system cannot be completely excluded. The anion formed upon adsorption of benzenethiol on the silver surface may enhance such an oxidation reaction. The Ag^+ ions should assume the geometry of the adsorbed species to resemble that of silver benzenethiolate salt. In order to understand the exact nature of the oxygen effect, more detailed experimental information should, of course, be provided.

In summary, vibrational spectroscopy has been applied to the benzenethiol molecule adsorbed on the silver surface. The results of infrared and Raman spectral studies have led to the conclusion that benzenethiol is chemisorbed dissociatively on the silver surface by rupture of S-H bond and the benzenethiolate formed upon adsorption is bound to silver via its sulfur atom. It seemed more likely that benzenethiol is adsorbed as being inclined to the silver surface. On contact with oxygen, the geometry of the adsorbed species appeared to bear a resemblance to that of silver benzenethiolate salt. Although we could not present decisive evidence, oxygen was supposed to produce the silver cations. From the observation that the infrared bands of adsorbed species remained with little decrease of intensity even after the prolonged evacuation at 673 K, it was concluded that even the multi-layer species are very strongly chemisorbed to the silver surface.

Acknowledgement. This work was supported in part by the Ministry of Education as a free research project.

References

- N. B. Hannay, Ed., *Treatise on Solid State Chemistry*, Vol 6, Plenum Press, New York (1983).
- J. Oudar, *Catal. Rev. Sci. Eng.* **22**, 171 (1980).
- M. V. Mathieu and M. Primet, *Compt. Rend. Sect II* **299**, 419 (1984).
- W. N. Delgass, G. L. Haller, R. Kellerman, and J. H. Lunsford, *Spectroscopy in Heterogeneous Catalysis*, Academic Press, New York (1979).
- W. W. Coblenz, *J. Franklin Inst.* **172**, 309 (1911).
- L. H. Little, Ed., *Infrared Spectroscopy of Adsorbed Species*, Chap. 9, Academic Press, New York (1966).
- R. K. Chang and T. E. Furtak, Eds., *Surface Enhanced Raman Scattering*, Plenum Press, New York (1982).
- T. H. Joo, K. Kim, and M. S. Kim, *Chem. Phys. Lett.* **112**, 65 (1984).
- H. S. Kim, M. S. Kim, and K. Kim, *Bull. Kor. Chem. Soc.* **6**, 61 (1985).
- T. H. Joo, K. Kim, H. Kim, and M. S. Kim *Chem. Phys. Lett.* **117**, 518 (1985).
- T. H. Joo, K. Kim, and M. S. Kim, *J. Phys. Chem.* **90**, 5816 (1986).
- T. H. Joo, M. S. Kim, and K. Kim, *J. Mol. Struct.* in press.
- P. Ramamoorthy, A. Kosci and R. D. Gonzalez, *J. Appl. Spectrosc.* **33**, 310 (1979).
- D. W. Boo, W. S. Oh, M. S. Kim, H. Lee, and K. Kim, *Chem. Phys. Lett.* **120**, 301 (1985).
- D. W. Boo, K. Kim, and M. S. Kim, *Bull. Kor. Chem. Soc.* **7**, 55 (1986).
- W. K. Yi, C. W. Park, M. S. Kim, and K. Kim, *Bull. Kor. Chem. Soc.* **8**, 345 (1987).
- F. R. Dollish, W. G. Fateley, and F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley, New York (1974).
- G. Varsanyi, *Vibrational Spectra of Benzene Derivatives*, Academic Press, New York (1969).
- M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 163 (1974).
- E. J. Zeman and G. C. Schatz, *J. Phys. Chem.* **91**, 634 (1987).
- H. Nichols and R. M. Hexter, *J. Chem. Phys.* **75**, 3126 (1981).
- M. Moskovits, *J. Chem. Phys.* **75**, 3126 (1981).
- J. A. Creighton, *Surface Sci.* **124**, 209 (1983).
- V. M. Hallmark and A. Campion, *J. Chem. Phys.* **84**, 2942 (1986).
- T. H. Joo, H. Kim, M. S. Kim, and K. Kim, 57th Annual Meeting of the Korean Chemical Society, Abstracts, 301 (1986).
- R. M. Hexter and M. G. Albrecht, *Spectrochim. Acta* **35A**, 233 (1979).
- H. S. Pearce and H. Sheppard, *Surface Sci.* **59**, 205 (1976).
- K. Klostermann and H. Hobert, *J. Catal.* **63**, 355 (1980).
- I. G. Dance, *Aust. J. Chem.* **31**, 2195 (1978).
- A. R. Gonzalez-Elipe, J. Soria, and G. Nunuera, *J. Catal.* **76**, 254 (1982).
- S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.* **100**, 170 (1978).

Photochemical Rearrangement of Chloranil

Sung Sik Kim*, Dong Yeol Yoo, and In Ho Cho

Department of Chemistry, Chonbuk National University, Chonju 520

Sang Chul Shim

Korea Advanced Institute of Science and Technology, Seoul 131. Received April 10, 1987

Irradiation of a solution of chloranil and cycloheptatriene, or 1,3-cyclohexadiene, in dichloromethane yielded unexpected photorearrangement products as the major product, while chloranil with cyclohexene gave the photorearrangement product as well as 1:1 adduct.

Introduction

The photochemical addition of p-quinones to olefinic compounds has been the subject of some interest.¹⁻⁴ Photodimerization of p-quinone gives either cyclobutanes or spirooxetanes depending on the nature of the quinone. Cyclooctene forms spiro-oxetane(**1**) by photoaddition to chloranil.³ An excess of cyclooctene and chloranil in benzene gives 2:1 adduct (**2**) as the major product.³ The photoreaction of chloranil with 1,5-cyclooctadiene afforded the expected oxetane(**3**).⁵ Irradiation of chloranil and

