

# Ion/Surface Reactions at Monolayers in Solution: A Combined Surface Enhanced Raman–X-Ray Photoelectron Spectroscopic Investigation of the Chemical Modification of a 2-Mercaptobenzothiazole Monolayer on Polycrystalline Au Films

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**Reaction of a methyltriphenylphosphonium (TPP) ion with a 2-mercaptobenzothiazole (MBT) monolayer on polycrystalline gold under electrochemical conditions leads to the chemical modification of the monolayer. Surface-enhanced Raman spectroscopy (SERS) has been used to study the molecular nature of the transformation. MBT, which adsorbs in the thione form on Au, gets transformed to the thiolate form upon reaction. Thermal stability of the modified monolayer is substantially lower than the corresponding pure monolayers and complete desorption of the modified monolayer occurs below 473 K. Time, potential, and solvent dependence of the reaction has been investigated. Electron transfer from the monolayer to the approaching ion in solution is suggested as the cause of the reaction. XPS investigation shows the change in the valence states of the species concerned. While the parent MBT gets oxidized, the TPP moiety gets reduced. The results suggest that modified monolayers can be made by simple electrochemical procedures and the processes are similar to the corresponding gas-phase events (1994, R. G. Cooks, T. Ast, T. Pradeep, and V. H. Wysocki, *Acc. Chem. Res.* **27**, 316). © 1999 Academic Press**

**Key Words:** self-assembled monolayers; chemical modification; 2-mercaptobenzothiazole; surface-enhanced Raman spectroscopy; X-ray photoelectron spectroscopy.

## INTRODUCTION

Chemical modifications of surfaces are important in science and technology. Modification of ultrathin molecular surfaces leading to functionalized assemblies is one of the important subject areas of chemical research today (1). Methodologies for such modifications vary from simple exposure of molecular surfaces to chemical reagents to more sophisticated methods such as low-energy ion collisions (2). Prototypical surface transformations (3) on self-assembled monolayers (SAMs) have been demonstrated with ion/surface reactions (4–6). The versatility of this methodology has prompted investigators to probe a number of such related processes toward achieving

goals such as ion and molecule trapping in SAM matrices (7, 8). Although electrochemical methods have been used for the preparation of modified monolayers (9) the subject has not been approached from the perspective of ion/surface reactions.

In an ion/surface collision, the translational energy of the incoming projectile is used to circumvent the activation barrier of a given chemical process. Since the efficiency of energy transfer is high, even endothermic processes occur with high probability (4). One of the important events when an ion approaches a surface is electron transfer from the surface, leading to an ionized surface species (2, 10). This is particularly the case for a molecular surface. Various low-energy ion/surface collision experiments have been used to understand the details of the interfacial ion processes (3–6). In an electrochemical system, an ion approaching the electrode has little translational energy and the energy transfer induced by collision cannot be a driving force in the chemical processes. Another important difference is ion solvation, which could lead to reaction between the surface and the solvent molecules instead of reaction with the ion. This would imply strong dependence of the processes on the dielectric constant of the medium. The foregoing suggests that the ion/surface reaction in electrolytic solutions would depend primarily on the difference in ionization potentials of the surface and the incoming ion. A surface having a low ionization potential would lead to efficient electron transfer (10). The ionic species so produced at the surface could be excited and that itself could be a strong driving force for a reaction.

Electron transfer at the interface could occur at a range of distances and it is probable that within the lifetime of the ionic species created at the surface, the incoming ion is in the vicinity of the surface. The same as the mechanism proposed for gas-phase ion/surface encounters, reaction between the ionic surfaces and the neutralized projectile can be one of the important means of relaxation of the excited surface species (2, 4). This reaction could occur with high efficiency, the same as similar gas-phase processes. Various aspects such as thermo-

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dynamic and entropic considerations (5) will be important in determining the product.

An important aspect of these processes is the surface sensitivity of the method. The ions can only be sensitive to the very top of the surfaces (to the top functionality in the case of a monolayer bearing a functional group), and therefore the transformations are going to be limited in this region (11). This makes the investigation of such modification extremely difficult and reliable methods have to be used for the investigation. Recently we have shown the utility of surface-enhanced Raman spectroscopy (SERS) (12–14) and X-ray photoelectron spectroscopy (XPS) (15) in investigating SAM surfaces. The development of methodologies to make SER active films (16) has also helped us in undertaking this investigation.

In the following, we present a combined SERS and XPS investigation of the chemical modification of 2-mercaptobenzothiazole (MBT) monolayers in electrolytic solutions. The studies conclusively establish that ions in electrolytic solutions could drive chemical reactions at monolayers, leading to chemically transformed surfaces. Although the exact nature of chemical binding requires further investigation, the present data definitively establish the presence of such modifications. It is also suggested that electron transfer drives the reaction and simple exposure does not lead to any transformation. Kinetics of such transformations is fast enough and the process is complete within the first few minutes of the reaction. The importance of adsorbate geometry in the observed processes is underlined from the observed difference in reactivity between the monolayers grown on Au and Ag. Thermal stability of the modified surfaces is significantly different from that of the parent surfaces. An XPS investigation substantiates the SERS data and provides further proof for the chemical state of the species involved.

## EXPERIMENTAL

The monolayers were prepared by well-established methods reported in the literature (17). Briefly, 1 mM solution of the respective surfactant in absolute ethanol was exposed to the Au film overnight. The preparation of SER active films has been discussed earlier (16). The methodology involves sputter coating Au of about 2000-Å thickness on an oxidized aluminum foil in an Edwards sputter coater. Aluminum foil of 20-μm thickness was heated in air at 773 K for 5 h to make an adequately thick oxide layer. Scanning electron microscopic (SEM) investigation of the evaporated films shows corrugations of submicrometer dimensions and is shown to be excellent substrates for SERS work (16). The films after withdrawal from the solution were washed with ethanol repeatedly and used for subsequent transformations. Triphenylphosphine (PPh<sub>3</sub>) was purchased from E. Merck. MBT (C<sub>7</sub>H<sub>5</sub>S<sub>2</sub>N) was purchased from Aldrich Chemical Co. Both the chemicals were used as received. Freshly distilled solvents were used. Methyltriphenylphosphoniumiodide, [PPh<sub>3</sub>CH<sub>3</sub>]<sup>+</sup>I<sup>-</sup> (TPP), was pre-

pared as per literature procedure (18) by reacting triphenylphosphine (E. Merck) and methyl iodide (CH<sub>3</sub>I, E. Merck) in hexane.

Raman measurements were carried out with a Bruker IFS 66V FT-IR spectrometer with a FRA 106 FT-Raman attachment. A Nd-YAG laser (1064 nm, 70 mW) was used for primary excitation. Typically, 500 scans were necessary for acceptable statistics. Monolayers were washed in absolute ethanol prior to the Raman measurement. For variable temperature measurements, a home-built heater with a programmable temperature controller was used.

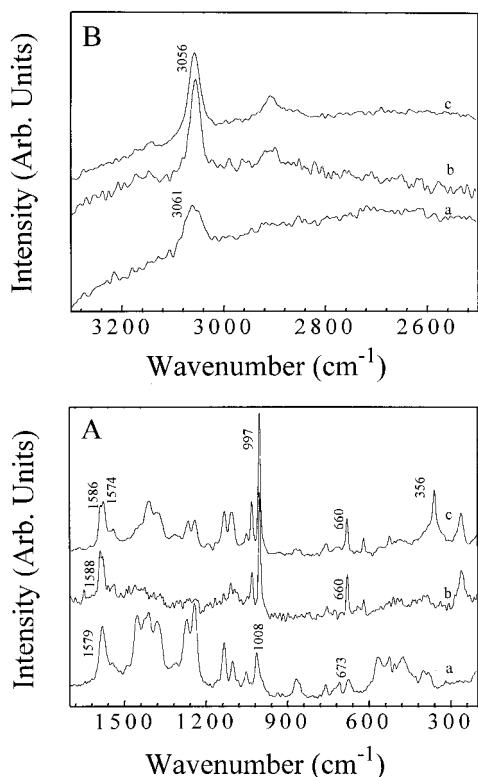
XPS measurements were conducted with a VG ESCALAB Mk II spectrometer with unmonochromatized MgKα radiation. Samples were inserted into the UHV chamber soon after they were prepared. Measurements were done under a pressure of 10<sup>-8</sup> Torr. No deterioration in the vacuum was observed during the measurement. To minimize the beam-induced damage, the X-ray flux was kept low (electron power of 70 W) during measurements. Due to poor signal quality, 20 scans of 2-min duration were necessary to achieve acceptable statistics. A pass energy of 50 eV was used for carbon, oxygen, and gold, whereas it was 100 eV for sulfur, phosphorus, and nitrogen. Severe beam-induced damages were not observed in MBT and methyltriphenylphosphoniumiodide monolayers.

The monolayers after characterization were subjected to electrochemical reaction. This was done in an electrochemical cell by keeping the monolayer as the cathode and a graphite rod as the anode. Monolayers grown on 1-cm<sup>2</sup> gold foil were used for this purpose. Solutions of 10 mM TPP in acetonitrile were used as the electrolyte. Electrochemical transformations were done by passing a current of 1 mA at a potential of -0.67 V with reference to a silver quasi reference electrode (19) for a period of 2 min. Variable time and potential measurements were conducted similarly. Monolayers after reaction were washed with acetonitrile and ethanol repeatedly and used for spectral measurements immediately.

All the Raman spectra are presented without manipulating the intensities for the sake of meaningful comparison. This is particularly important for the temperature-dependent, time-dependent, and potential-dependent data.

## RESULTS AND DISCUSSION

MBT monolayers on Au and Ag have been the subject of an earlier report from this laboratory (14). Essential conclusions of this study were that MBT adsorbs in the thione form on Au and in the thiol form on Ag. This difference in adsorbate molecular structure also leads to variation in adsorption geometry. Whereas the molecule is adsorbed with its molecular plane perpendicular to the surface on Au, the molecular plane is parallel to the surface on Ag. The changes in surface geometry are manifested in SER spectra of the monolayers. Both the monolayers are thermally stable beyond 473 K and spectral changes are relatively few upon heating; however, due to the



**FIG. 1.** SER spectra of (a) MBT and (b) TPP monolayers on Au and (c) MBT monolayer upon reaction with TPP electrochemically. A and B represent low- and high-frequency regions of the above, respectively.

coalescence of Au grains, the absolute Raman intensity increases with temperature. A comparable effect is seen in Ag; however, this is also accompanied by small changes in adsorbate geometry.

In Fig. 1 we show the SER spectra of MBT (a) and TPP (b) monolayers on Au and that of the MBT monolayer upon reaction with TPP (c) in an electrochemical cell (conditions:  $-0.67$  V,  $1$  mA,  $2$  min). A bare TPP monolayer has not been investigated before, and hence we present an assignment of its SER spectrum in Table 1. The observed vibrations can be understood on the basis of IR and Raman spectra of phosphine systems (20, 21). Assignment of MBT bands is based on *ab initio* molecular orbital calculations (14).

The principal change we observe upon reaction of the MBT monolayer with TPP in solution is the emergence of the phenyl  $\nu_1$  mode at  $997$   $\text{cm}^{-1}$  which is absent in MBT (Fig. 1A). The two characteristic peaks seen in the reacted monolayer at  $1586$  and  $1574$   $\text{cm}^{-1}$  are due to the  $\nu_8$  modes of TPP and MBT, respectively. The intensities of these two features are similar. As a consequence of the reaction with TPP, MBT features do not reduce in intensity. Although SERS intensities can not be used for quantitative comparison, this observation may be used to argue that MBT has not desorbed as a result of reaction. It also appears unlikely, since MBT monolayers are very stable on Au (14); however, thermal stability does not imply absence

of desorption during reaction. There is a substantial shift observed in all the in-plane vibrations. The  $\nu_{\text{CC}}$  ip modes at  $1579$  and  $1451$   $\text{cm}^{-1}$  are shifted to  $1574$  and  $1440$   $\text{cm}^{-1}$ , respectively. Similar effects are also seen in the in-plane C–H bending region. This difference in the in-plane modes shows the change in the adsorbate geometry. Moreover, there is a red shift in the  $\nu_{\text{CN}}$  mode at  $1313$   $\text{cm}^{-1}$ . This, along with the increase in  $N(1s)$  binding energy in the X-ray photoelectron spectrum of the reacted monolayer (see below), may be interpreted in terms of a coordinate bond formed between the nitrogen of MBT and phosphorus of TPP. This is also sup-

**TABLE 1**  
SER Frequencies (in  $\text{cm}^{-1}$ ) of MBT, TPP, and Reacted MBT Monolayers on Au

Assignment <sup>a,b</sup>	TPP on Au	MBT on Au	Reacted MBT on Au
$\nu_{\text{CH}}$	3056	3061	3056
$\nu_{\text{CH}}$	2896	—	2898
$\nu_{\text{CC}}_{\text{ip}}$	1588	—	1586
$\nu_{\text{CC}}_{\text{ip}}$	—	1579	1574
—	—	1541	1538
$\nu_{\text{CC}}$	—	1488	—
$\nu_{\text{CC}}_{\text{ip}}$	—	1451	1440
$\nu_{\text{CC}}$	—	1408	1407
$\nu_{\text{CN}}$	—	1313	1311
$\nu_{\text{CC}}$	—	1268	1263
$\nu_{\text{CC}}$	—	1240	1238
$\delta_{\text{CH}}_{\text{ip}}$	—	—	1189
$\nu_{\text{PN}}^c$	—	—	1160
$\delta_{\text{CH}}$	—	1131	1129
$\delta_{\text{CH}}_{\text{ip}}$	1107	1100	1103
$\delta_{\text{CH}}_{\text{ip}}$	—	1050	1047
$\delta_{\text{CCC}}$	1028	—	1028
Ring deformation	—	1008	—
Ring deformation	997	—	997
$\delta_{\text{CH}}_{\text{op}}$	—	865	868
—	—	—	849
$\delta_{\text{CH}}_{\text{op}}$	—	753	753
$\nu_{\text{CS}}$	—	706	713
$\nu_{\text{CS}}$	—	673	—
$\nu_{\text{CP}}$	660	—	660
$\delta_{\text{CH}}$	609	—	616
$\delta_{\text{CNH}}$	—	563	—
—	—	—	550
$\delta_{\text{NH}}$	—	522	—
—	—	499	—
$\nu_{\text{CS}}$	—	473	—
$\phi_{\text{CC}}^d$	380	394	—
$\delta_{\text{CCC}}$	356	—	356
—	258	—	258

<sup>a</sup> <sub>ip</sub> refers to the in-plane and <sub>op</sub> refers to the out-of-plane vibrations, respectively,  $\delta$ -bending,  $\phi$ -torsional, and  $\nu$ -stretching vibrations.

<sup>b</sup> Assignments of the benzene ring modes are as per classification of Ref. 34.

<sup>c</sup> P–N stretch is observed at  $1160$  for P–N (i-Pr)<sub>2</sub> (Ref. 20, p. 350).

<sup>d</sup> Similar to the torsional bands observed in Ref. 35.

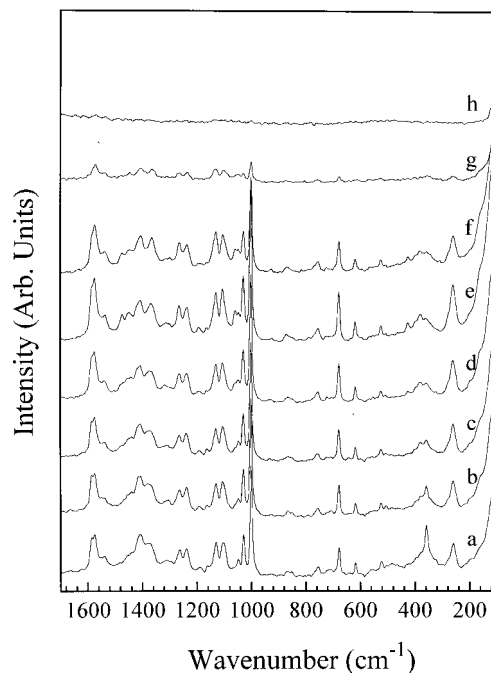
ported by the presence of a weak feature at  $1160\text{ cm}^{-1}$  attributable to a P–N stretching mode (20).

The MBT structures were changed substantially in the 400- to  $600\text{-cm}^{-1}$  region. The bands at  $563$  and  $522\text{ cm}^{-1}$ , due to  $\delta\text{CNH}$  and  $\delta\text{NH}$ , respectively, are absent in the modified monolayer. Again, the absence of the band corresponding to the  $\nu\text{C-S}$  of the thione form at  $473\text{ cm}^{-1}$  suggests the tautomerization of MBT after the reaction. An altogether absence of the MBT band at  $1008\text{ cm}^{-1}$  is observed along with the complete disappearance of the C–S band at  $673\text{ cm}^{-1}$ . It does not appear that the  $1008\text{-cm}^{-1}$  band is merged with the  $997\text{-cm}^{-1}$  band of TPP as there is no intensity at the high-frequency side of this band. Also, the width of the  $997\text{-cm}^{-1}$  band appears unaffected. These changes could be compared with those observed upon MBT adsorption on Ag (14), suggesting significant structural changes in the monolayer upon reaction. It is important to note that the MBT monolayer on Ag does not exhibit any change upon the same electrochemical process.

The spectrum in the C–H region also exhibits significant changes. The broad band observed at  $3061\text{ cm}^{-1}$  in Fig. 1B (a) is attributed to the C–H stretches of MBT. In TPP, the aromatic C–H stretching mode appears as a much narrower peak at  $3056\text{ cm}^{-1}$ . The spectrum also shows a broad peak at  $2896\text{ cm}^{-1}$ , which is due to the methyl group. Upon reaction with TPP, the spectrum in the C–H region resembles more to that of a TPP monolayer than the pure MBT monolayer. We attribute the peak at  $3056\text{ cm}^{-1}$  of the reacted monolayer as being due to the aromatic C–H stretching modes of TPP. The width of the band and the peak shape do not suggest it to be due to MBT. This again suggests changes in the adsorbate geometry of MBT upon reaction. It may be mentioned that no C–H stretching mode was observed for MBT adsorbed on Ag (14) (in the thiol form, in which case the molecular plane is parallel to the surface).

A bare TPP monolayer exhibits only a few features typical of an aromatic molecule. All of these features are due to the ring modes or the methyl group, which are not expected to shift as a result of reaction. Note that the reaction site is the phosphorus atom. The only exception is the band at  $356\text{ cm}^{-1}$  of TPP, attributed to  $\delta\text{CCC}$ , which shows substantial intensity enhancement. Although the origin of this is unclear, it is seen that in the bare TPP monolayer, this band is relatively less intense. The observed changes in the MBT structures and the almost comparable intensity of the MBT and TPP structures in the modified monolayer, particularly the ring deformation modes around  $1586$  and  $1574\text{ cm}^{-1}$ , suggest that a chemical reaction has occurred at the surface. The data does not support co-adsorption, as will be shown below. The fact that a similar experiment with the MBT monolayer on Ag did not result in the appearance of TPP features also rule out co-adsorption.

To understand the changes in more detail, a variable temperature measurement was undertaken (Fig. 2). The modified monolayer desorbs completely around  $423\text{ K}$ , whereas MBT monolayers on both Au and Ag are stable well beyond  $473\text{ K}$



**FIG. 2.** Variable temperature SER spectra of a modified MBT monolayer. (a) 298, (b) 323, (c) 348, (d) 373, (e) 398, (f) 423, (g) 448, and (h) 473 K.

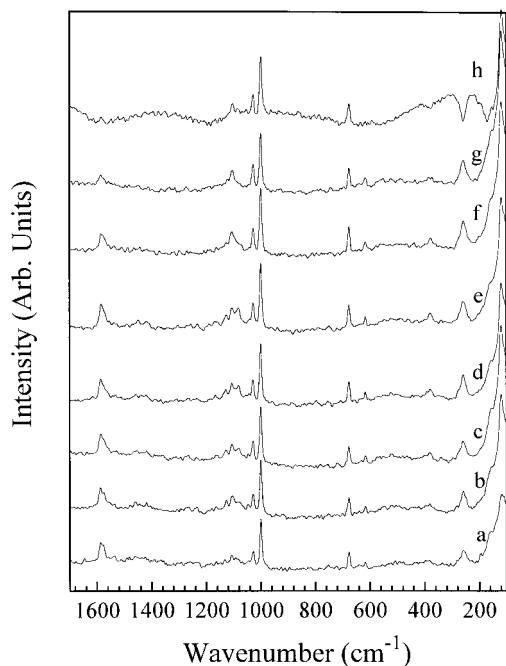
(14). Important changes occur in the spectra upon heating; this includes the emergence of a band at  $1058\text{ cm}^{-1}$  above  $348\text{ K}$  and the gradual increase in intensity of structures at  $1450\text{ cm}^{-1}$ . The TPP structure at  $356\text{ cm}^{-1}$  gradually broadens and multiple peaks occur. Along with these changes, the  $\nu_8$  band of TPP at  $1586\text{ cm}^{-1}$  gradually reduces in intensity. All of these could be attributed to the gradual disappearance of TPP from the surface. Prior to desorption, structural changes occur which are manifested as the disappearance of certain peaks and broadening of certain others. Significant changes are not observed in the C–H region (not shown) up to a temperature of  $398\text{ K}$ . Beyond this temperature, black body radiation (21) masks the features. The observed changes of reacted monolayers differ from the behavior of the pure TPP monolayer itself (Fig. 3). The band at  $356\text{ cm}^{-1}$  does not show any significant change or broadening in contrast to the corresponding band of the modified monolayer. No systematic changes are observed upon increasing the temperature and the monolayer is stable up to a temperature of  $473\text{ K}$ .

The foregoing suggests that the reacted monolayer is chemically different from those of the constituents. The data can not be interpreted in terms of physisorption of TPP on MBT or in terms of TPP adsorption in possibly vacant MBT sites. Note that MBT monolayers on Au and Ag as well as the TPP monolayer on Au do not desorb even at  $473\text{ K}$ . The MBT part of the spectrum in the reacted monolayer is substantially different from the parent monolayer. Also, in a pure TPP monolayer the band at  $356\text{ cm}^{-1}$  is relatively less intense, whereas it is a major feature in the spectrum of the reacted monolayer.

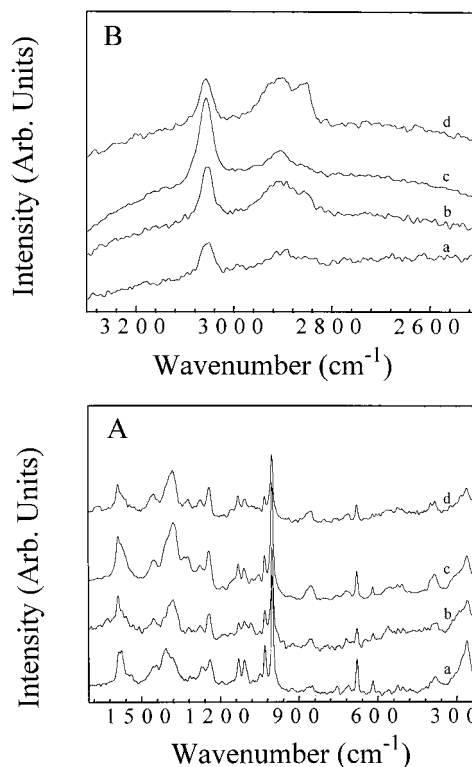
Thus, it is seen that the spectrum of the modified monolayer is not the sum of the bare TPP and MBT spectra. There is a possibility that the cause of the changes observed is due to the changes in the microenvironment of the metal surface rather than due to reaction; however, this is unlikely to lead to lasting effects in the spectra as seen here. It may be added that we have not found any change in the spectrum of the modified monolayer, even after several days.

To ascertain the fact that electron transfer is the reason for the reaction, MBT monolayers upon direct immersion in TPP solutions were subjected to Raman spectroscopic investigations. No observable changes were seen up to an exposure of several hours to the solution. Overnight exposures, however, resulted in the emergence of weak TPP features.

Several controlled experiments were performed to understand various aspects of the reaction. In Fig. 4, we present the time dependence data in which MBT monolayers were reacted with TPP solutions under the same electrochemical conditions for various times. It is to be noted that the MBT monolayer used is different in each measurement and, therefore, a small difference in MBT features is expected between the spectra. Looking at the TPP features, one can see that the band at  $997\text{ cm}^{-1}$  is relatively constant in intensity, so also the peak at  $660\text{ cm}^{-1}$  due to TPP. Again, SERS intensities are not suggested here as a means of quantitation. Note that the spectral data are presented in the same intensity scale. No manipulation has been done on the raw data except that the y axis has been offset for clarity. The absence of marked changes between spectra



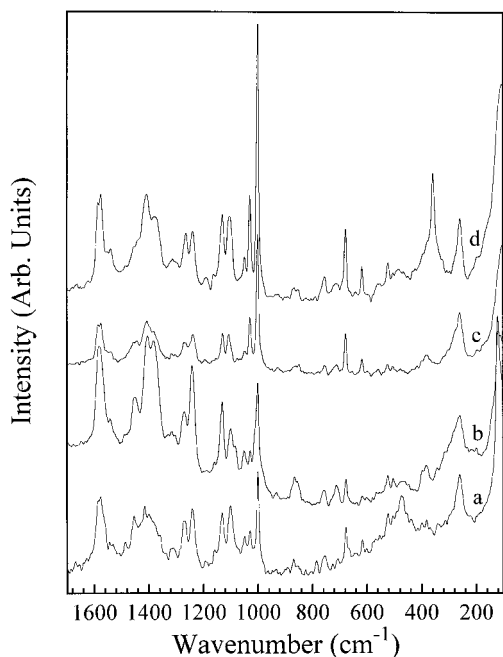
**FIG. 3.** Variable temperature SER spectra of TPP monolayer. (a), (b), (c), (d), (e), (f), (g), and (h) represent 298, 323, 348, 373, 398, 423, 448, and 473 K, respectively.



**FIG. 4.** (A) Time-dependent SER spectra of modified MBT monolayer. Reaction times were (a) 2 min, (b) 4 min, (c) 6 min, and (d) 10 min. In all these reactions, the potential was kept constant at  $-0.67\text{ V}$ . (B) Corresponding C–H regions.

under identical conditions shows similarity of the transformation. These results may be used to argue that the chemical transformation is complete within the first few minutes of reaction. In Fig. 4B, we show the corresponding C–H region. An interesting aspect is the gradual increase in intensity of the aliphatic C–H modes as time increases. Correspondingly, the aromatic C–H peak decreases in intensity, suggesting methyl for phenyl substitution at the surface within TPP. This could be due to the geometrical constraints, which lead to methyl for phenyl exchange. The data conclusively establishes that there is no co-deposition or overlayer formation, which would have resulted in an overall increase in TPP features with time.

In Fig. 5, we present the potential dependence of the reaction keeping the ion concentration and reaction time the same. A gradual increase in the TPP features, particularly the peak at  $997\text{ cm}^{-1}$ , is observed with the potential, whereas the MBT features remain roughly the same in intensity. Note that each sample is different and SERS intensities do vary significantly from sample to sample. Like in the earlier case, absolute Raman intensities are presented here also. The observed changes could be understood if one assumes that electron transfer is the principal cause of the reaction. An increase in potential leads to an increase in ion mobility and the number of electron transfer events increases in a given time. The C–H



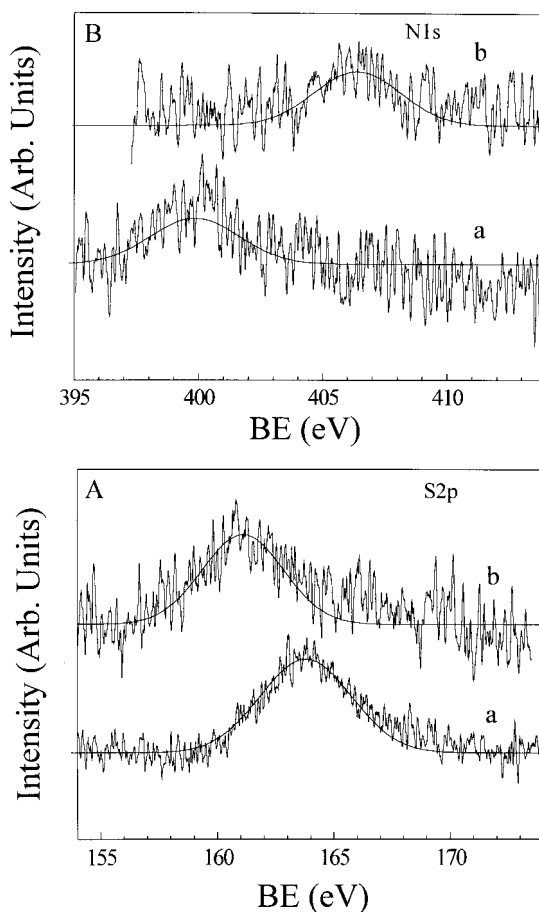
**FIG. 5.** The potential dependence of the reaction on the SER spectra of the modified MBT monolayer. Potentials were (a)  $-0.02$  V, (b)  $-0.35$  V, (c)  $-0.67$  V, and (d)  $-1.40$  V. In all these reactions, the time duration was 2 min.

region shows corresponding change (not shown). Unlike in the case of time dependence, methyl for phenyl exchange is not manifested. This suggests that the exchange occurs at a longer time scale than the surface reaction. There is, however, a possibility of MBT desorption at higher potentials and those sites may be occupied by TPP. The intensity of the  $356\text{-cm}^{-1}$  band and the relatively intense MBT features seem to suggest that this is rather negligible.

To understand the dependence of solvents on the reaction, the modifications were carried out in three solvents: water, methanol, and acetonitrile under the same conditions. In the SER spectra (not shown) an increase in intensities of the peaks corresponding to TPP is observed with a decrease in the dielectric constant of the medium. Particularly, intensity of peaks at  $997\text{ cm}^{-1}$  increase as we go from water to acetonitrile. The experimental results could be explained in terms of increased solvation with an increase in the dielectric constant. As the solvation shell surrounding the ion is large, the proximity of the ion created at the surface to the solvent molecules increases and consequently reaction between the surface and the electrolyte becomes less probable within the lifetime of the surface species.

The observed chemical transformations were investigated by XPS. In Fig. 6A, we present the  $S(2p)$  photoelectron spectra of MBT monolayers before and after the reaction. The spectrum before reaction shows a single  $S(2p)$  feature at  $164\text{-eV}$  binding energy (BE). This binding energy is slightly higher than the  $\text{RS}^-$  thiolate structure, which occurs at  $162\text{ eV}$  (22). Both thiolate and thiol forms of sulfur should occur in the range of

$162\text{--}165\text{-eV}$  BE. The observation of a peak at  $164\text{ eV}$  is in accordance with the presence of the thione form (14). After reaction, the peak shifts to a lower BE of  $161\text{ eV}$ . However, the structure is significantly broader than the unmodified monolayer and there could be other species contributing to the  $S(2p)$  intensity. It is known that thiol monolayers are susceptible for X-ray-induced damage leading to oxidized sulfur species (23). The major structure at  $161\text{-eV}$  BE is attributed to the thiolate sulfur of the thiol form of MBT. This large shift in BE is important evidence supporting chemical modification. The broadening is attributed to the greater difference between the BEs of the two sulfur forms in the molecule. Significant changes are seen in the  $P(2p)$  photoelectron spectra of the monolayers (not shown). Whereas the pure TPP monolayer shows a marginally high  $P(2p)$  BE of  $133.3\text{ eV}$ , in the reacted monolayer the structure is observed at  $132\text{ eV}$ . It may be mentioned that in triphenyl phosphine (*not phosphonium*) monolayer, the  $P(2p)$  peak is observed at  $132.7\text{-eV}$  BE, close to the value of the pure TPP monolayer. Although the difference in BEs is not large, it may be suggested that, upon



**FIG. 6.** (A)  $S(2p)$  region of the XPS of the (a) unreacted MBT and (b) modified MBT monolayers. Note the shift in the peak positions. (B)  $N(1s)$  region of the XPS of the (a) unreacted MBT and (b) modified MBT monolayers.

reaction, the TPP moiety has undergone reduction, leading to a small shift in the BE.

The C(1s) features of all monolayers occur around 285-eV BE (not shown). The N(1s) region of unreacted and reacted MBT monolayers are shown in Fig. 6B. The N(1s) peak of MBT occurs at 400-eV BE, characteristic of adsorbed amine systems (24). Upon reaction, the peak shifts to a value of 406 eV, suggesting that the phosphine moiety binds to the nitrogen. Structurally, also, this is the most probable binding site. It is important to see that no other N(1s) structures are observed, indicating that all the molecules on the surface have undergone reaction. Note that there is no shift observed for tautomerization on the metal surface and in both the cases (MBT on Au and Ag) the N(1s) peak is observed at 400 eV (14). To ascertain the absence of electrolyte deposition in the modified monolayer, the I(3d) region of the photoelectron spectrum was measured. Whereas an intense I(3d) was observed for the pure TPP monolayer, the peak was very weak for the reacted MBT monolayer (figure not shown). Note that it is impossible to avoid contact with the electrolyte upon immersion and subsequent removal from the cell, prior to and after the reaction, respectively. The weak I(3d) in the spectrum of the reacted monolayer is attributed to this contact. Note that the I(3d) cross section is much higher than those of P(2p), S(2p), and N(1s). The Au (4f<sub>7/2</sub>) BE in both the parent and reacted MBT monolayers was 84.0 eV, indicating that the substrate was unaffected during the modification.

The results presented above confirm the chemical changes occurring in the monolayer. They also establish that the electron transfer at the electrolyte–electrode interface is the driving force for the reaction. Issues associated with electron transfer at the monolayer–electrolyte interface has been the subject of intense investigation (25–33). Electron tunneling from the underlying substrate is suggested to be the most probable pathway, although the involvement of the adlayer has also been suggested. The reactions proposed to occur here might also be the result of electron transfer, as in the case of corresponding gas-phase processes (2). Upon ion/surface encounter in the gas phase between a polyatomic ion and the molecular surface such as a monolayer, electron transfer from the monolayer to the gas-phase ion leads to the formation of an ionized surface species. Consequent to the momentum transfer associated with the ion/surface impact, the gas-phase ion and/or the molecular surface is subjected to dissociation. The activated surface species thus created can undergo reaction with the neutralized projectile or its fragments, leading to chemically modified surfaces (6). Although this is the prominent mechanism proposed, there can be another concerted pathway for the reaction, wherein electron transfer and reaction occur simultaneously (5). The former mechanism can also occur without any distinct charge separation. Parallels can be drawn between ion/surface encounter in solution and the corresponding gas-phase processes. However, momentum-transfer-induced transformation is not important here; electron transfer from the valence state of

the adsorbed molecule could occur the same as that in gas-phase processes, leading to reaction. It is indeed probable that electron transfer occurs from the frontier metal states, and in fact there is no thermodynamic reason why electron transfer should occur from the deeper lying adsorbate states. This emphasizes the importance of concerted processes.

The dependence of the potential and dielectric constant of the medium on the proposed reaction support the electron transfer mechanism. The fast kinetics observed also suggests such a process. The shift in the XPS BEs upon reaction are also indicative of the ion-induced reaction. It is clear from XPS that the phosphonium ion is the cause for the reaction. The reaction does not lead to simple deposition of the entire electrolyte. Although the chemical nature of the modified surface is an open question, covalent interaction between the species is established. Thermal stability data suggest that neither physisorption nor ion deposition is the cause of observed changes. The integrity of the monolayer, even after prolonged exposure to a laboratory atmosphere, also point to the chemical reaction that occurred.

In conclusion, ion/surface reactions in electrolytic solutions have shown to result in chemically modified monolayers. The reaction does not lead to desorption of the monolayer nor does it change the underlying substrate chemically. This prototypical surface reaction could be explained as a result of electron transfer between the electrolyte and the monolayer. Extension of such reactions to other systems could lead to molecular surfaces with novel properties.

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