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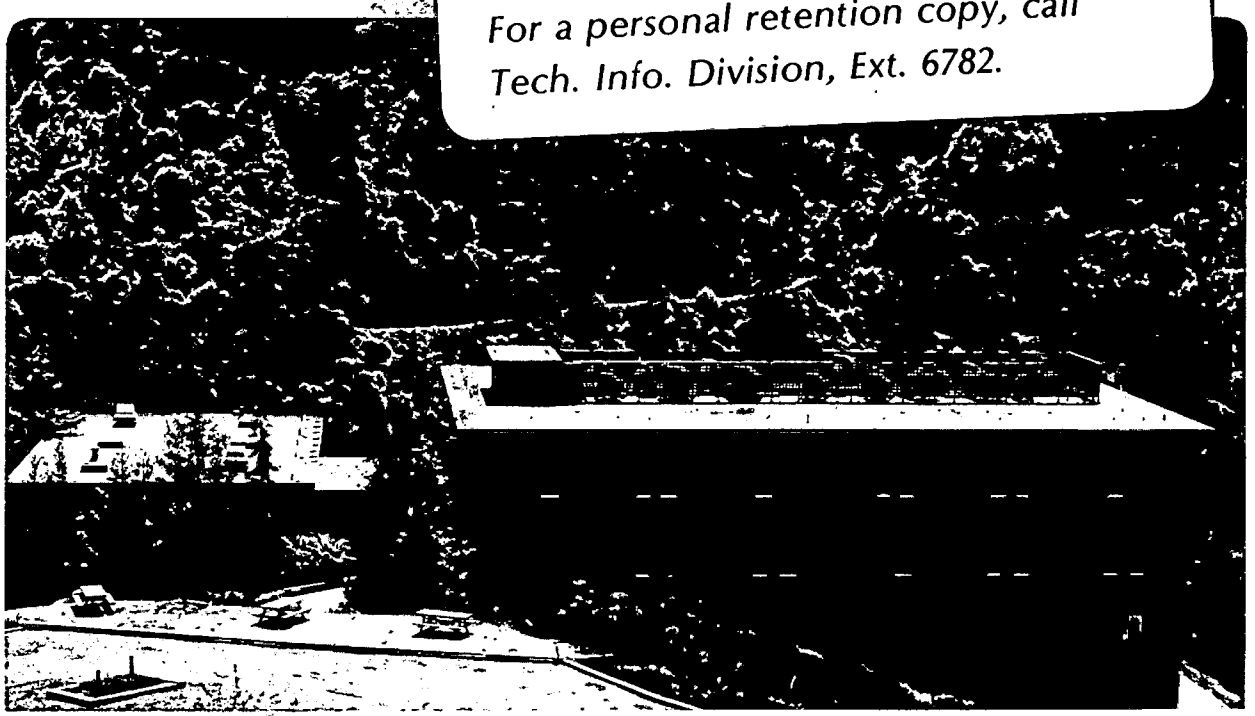

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Silane Surface Chemistry of Palladium: Synthesis of Silaethylene, Silacyclobutadiene and Silabenzene

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Abstract

The clean surface of Pd(110) proved effective in the dehydrogenation of organosilanes. After chemisorption of $(CH_3)_3SiH$ on Pd(110) at -135°C, rapid heating of the crystal led to desorption of $(CH_3)_3SiH$, $(CH_3)_2Si{=}CH_2$, H_2, and a minor amount of $\{(CH_3)_2SiCH_2\}_2$. Silacyclohexane on Pd(110) partially desorbed reversibly and partially dehydrogenated to give silabenzene, SiC_5H_6. Silacyclobutane on Pd(110) yielded silacyclobutadiene $H_2Si{=}CH_2$, and $\{H_2SiCH_2\}_2$. $(CH_3)_2Si{=}CH_2$ was also partially formed in the thermal desorption of $(CH_3)_3SiOSi(CH_3)_3$, $(CH_3)_3SiNHSi(CH_3)_3$, and $(CH_3)_3SiN_3$. The azide also formed $\{(CH_3)_2SiNCH_3\}$.

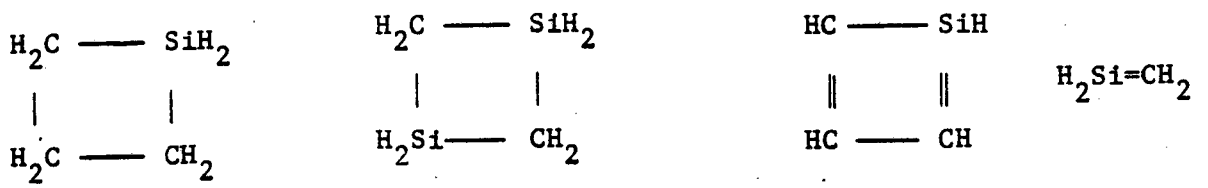
Chemisorption of cycloalkenes on metal surfaces are followed by dehydrogenation processes[1] which often give chemisorbed C_nH_n species, e.g., cyclohexene → benzene[1-3] and cyclooctadiene → cyclooctatetraene.[1] Because these transformations are facile, we have been exploring the reactions of silaalkanes with single crystal metal surfaces[4] as routes to compounds in which there are Si-C bonds of multiple bond order. With platinum and nickel, we observed either no dehydrogenation or gross degradation of the silaalkane[5]. Palladium, however, has furnished dehydrogenation syntheses of silaethylenes, silabenzene and what appears to be silacyclobutadiene.[6]

Tetramethylsilane on Pd(110) desorbed fully and intact at ∿-50°C analogous to neopentane on Pd(110) which quantitatively desorbed with a T_{max} of ∿-60°C. In sharp contrast, trimethylsilane after adsorption at -135°C underwent two competing thermal processes: (i) reversible desorption with a maximum desorption rate at -20°C and (ii) dehydrogenation to form $(CH_3)_2Si{=}CH_2$ [8,9] which desorbed with maximum rates at -40 and +90°C (the surface was essentially free of Si and C after the desorption experiment). The latter process was accompanied by H_2 desorption which also exhibited maxima at -40 and +90°C. Minor dimerization of the silaethylene also occurred: $\{Si(CH_3)_2CH_2\}_2$ desorbed to give a broad peak at ∿40°C. An unexpected feature here was desorption of silaethylene because most alkenes and alkynes <u>irreversibly</u> chemisorb on clean transition metal surfaces. Consistent with the organosilane surface chemistry, we have found that acetylene and ethylene chemisorb on Pd(110) in a partially reversible fashion.[10]

Displacement of the silaethylene, $(CH_3)_2Si{=}CH_2$, from the Pd(110) surface was effected with $P(CH_3)_3$. On dosing the crystal face with $P(CH_3)_3$ at +25°C, there was immediate displacement of the silaethylene, the dimer, $\{Si(CH_2)_3CH_2\}_2$, and trimethylsilane.

The silaethylene, $(CH_3)_2Si{=}CH_2$, was also produced in the thermal desorption experiments with $(CH_3)_3SiOSi(CH_3)_3$, $(CH_3)_3SiNHSi(CH_3)_3$, and $(CH_3)_3SiN_3$ on Pd(110). All three also exhibited partially reversible chemisorption. In the azide system, an additional and major product was $\{(CH_3)_2Si{-}N(CH_3)\}_2$.

Silacyclobutane displayed a complex Pd(110) surface chemistry. After adsorption at -135°C, silanes 1-4 were observed in the thermal desorption



1 2 3 4

with respective desorption maxima at ∿-65°, +65°, +50°, and + 70°C, respectively. Ethylene and hydrogen were observed with similar T_{max} of 60-80°C. All these species were observed in a chemical displacement reaction with $P(CH_3)_3$. Silacyclobutadiene is a new compound, and its characterization must be considered tentative in that it is based solely on mass spectrometric data. The parent ion was less intense than the parent-minus-one ion as expected for a species with one Si-H bond. Ostensibly, silaethylene was the precursor to the dimer, 2. Consistent with this presumption, the ratio of 4 to 2 increased when the heating rate was increased from 25° sec^{-1} to 75° sec^{-1}.

Silacyclohexane, initially adsorbed on Pd(110) at -135°C, also underwent two competing surface reactions: reversible desorption (T_{max} = -25°C) and dehydrogenation to give silabenzene[12], SiC_5H_6 (two T_{max} of 90 and 190°C) and H_2 (two T_{max} of 15 and 190°C). This chemistry parallels that of cyclohexene which gave benzene with a $T_{max}(C_6H_6)$ of 220°C and also of piperdine which gave pyridine with $T_{max}(NC_5H_5)$ of 115 and 155°C.[10] Silabenzene was not displaced from the surface generated from silacyclohexane at temperatures of 25-70°C.

There are a number of remarkable features to this Pd(110) chemistry. One is the extensive degree of reversible chemisorption of unsaturated hydrocarbons like acetylene, ethylene, and of course, silaethylene and silabenzene. Secondly, these results suggest a practical synthesis of silaethylenes, silacyclobutadienes, and silabenzenes by palladium catalyzed dehydrogenation of organosilanes, an aspect now under study in our laboratories.[13] Also, this technique of metal catalyzed dehydrogenation of readily available, saturated organometallic compounds should provide not only a useful route to new compounds with multiple bonds to silicon[13] but also to new very reactive monomers with multiple bonds based on other elements such as P, Ge, Al, etc. Thirdly, we note that the saturated organosilanes in which there is at least one Si-H bond are far more susceptible to dehydrogenation than are saturated hydrocarbons; for example, cyclohexane and tetramethylsilane undergo fully reversible chemisorption on Pd(110) under ultrahigh vacuum conditions in contrast to silacyclohexane and trimethylsilane. Apparently, a primary surface interaction bond of Si-H species is through a three-center $\equiv$Si-H-$M_{surf.}$ bond: note the substantially higher desorption temperature for $(CH_3)_3SiH$ (T =-20°C) than for $(CH_3)_4Si$ (T =-50°C).

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Supplementary Material.

Thermal desorption spectra for Pd(110)-trimethylsilane, Pd(110)-silacyclobutane, and Pd(110)-silacyclohexane (6 pages). Ordering information may be obtained from any current masthead page.

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2. Gates, B.C.; Katzer, J.R.; Schuitt, G.C.A.; Chemistry of Catalytic Processes, McGraw Hill Book Company, New York, 1979, pp. 222-247.
3. (a) Tsai, M.-C.; Friend, C.M.; Muetterties, E.L. J. Am. Chem. Soc. 1982, 104, 2539-2543. (b) Tsai, M.-C.; Muetterties, E.L. J. Phys. Chem. 1982, 86, 0000.
4. See references in 3 for the equipment, techniques and procedures for these ultra high vacuum experiments. Adsorption was generally effected at -135°C and desorption studies were done usually with 25°sec^{-1} heating rates.
5. Tsai, M.-C.; Friend, C.M.; Johnson, A.L.; Muetterties, E.L., unpublished data.
6. The contrasting behavior of palladium with respect to platinum might be traced to a uniquely low Pd-Si bond energy.[7]
7. Auwiera-Matieu, A.V.; Peeters, R.; McIntyre, N.S.; Drowart, J. Trans. Faraday Soc., 1970, 66, 809-816.
8. This compound was characterized only by its mass spectrum. The essential absence of a parent minus one ion clearly indicated that this species contained no Si-H bond. This silaethylene molecule has been prepared by thermolysis of tetramethylsilane and trimethylsilane.[9]
9. (a) Fritz, G., Grobe, J.; Kummer, D. Adv. Inorg. and Radiochem., 1965, 7, 364. (b) Davidson, I.M.T.; Lamberty, C.A. J. Chem.Soc. (A) 1977, 882.
10. Gentle, T.M.; Muetterties, E.L. J. Phys. Chem. 1983, 86, 0000.
11. References to the generation of thermal processes, mass spectrum and trapping of silabenzene is given in ref. 12.

12. (a) Solouk, B.; Rosmus, P.; Bock, H.; Maier, G. Angew. Chem. Int. Ed. Engl. 1980, 19, 51. (b) Barton, T.J.; Burns, G.T. J. Am. Chem. Soc. 1978, 100, 5246.

13. Since compounds with Si-C multiple bonds readily dimerize or polymerize, the ultra high vacuum reaction conditions are ideal for observation of such compounds. However, this technique is impractical for the generation of sufficient quantities for chemical trapping experiments. We plan to examine Pd catalyzed organosilane dehydrogenation reactions under flow conditions using very short contact times and matrix or chemical trapping conditions.

Figure 1.

Shown above are the mass spectrometric intensity traces for the four compounds that thermally desorb from the Pd(110)-$(CH_3)_3SiH$ surface (heating rate of 25° sec^{-1}). The silaethylene (parent mass of 72) does not show an ion of mass 71 clearly indicating that this silicon species does not have an Si-H bond. Also the dimer $\{(CH_3)_2SiCH_2\}_2$ does not in electron impact mass spectrometry show an ion of mass 72 nor does it show substantial intensity ions for parent-minus-one or -two.

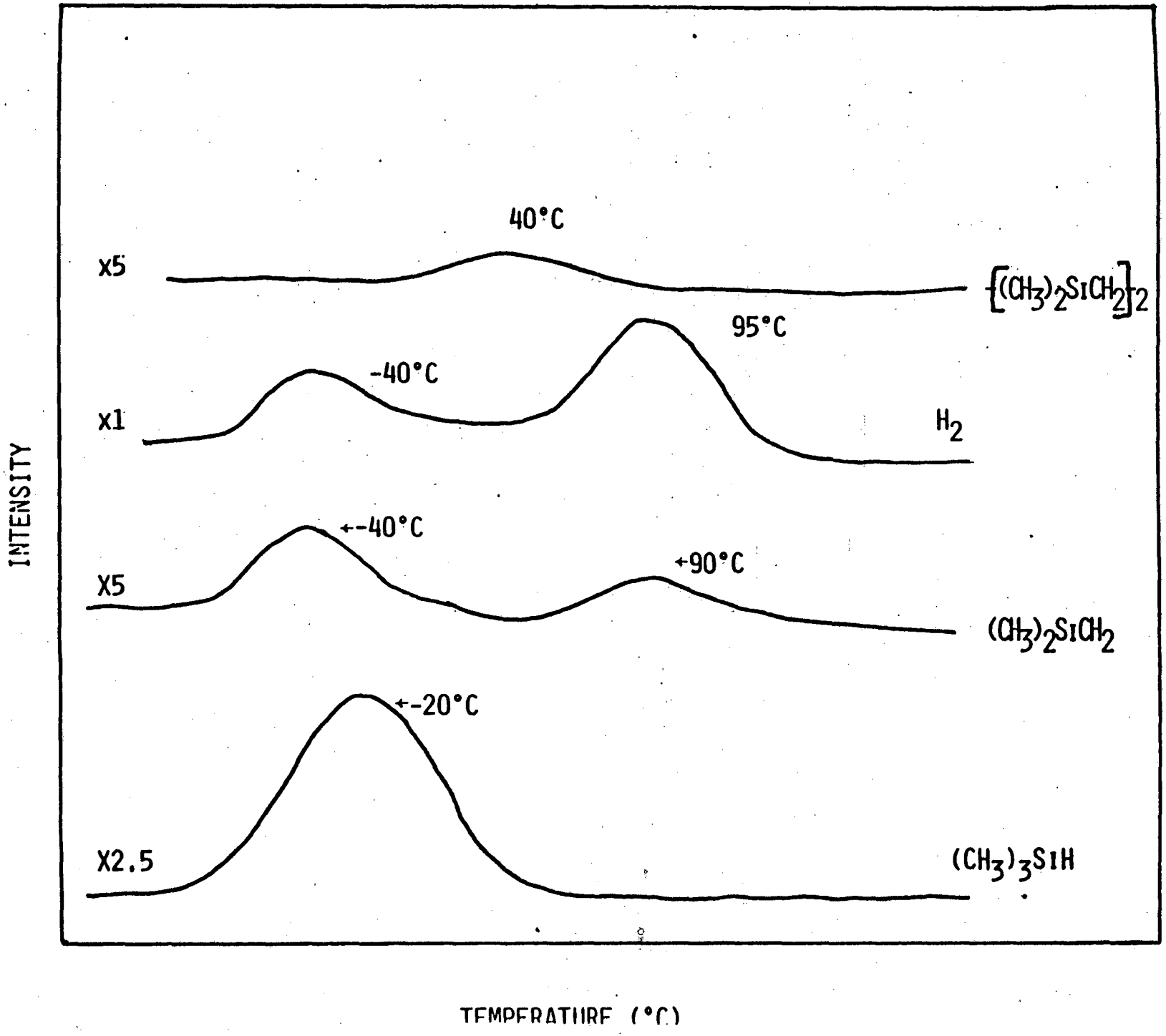

40°C
x5
$[(CH_3)_2SiCH_2]_2$
95°C
-40°C
x1
H_2
←-40°C
←90°C
X5
$(CH_3)_2SiCH_2$
←-20°C
X2.5
$(CH_3)_3SiH$
INTENSITY
TEMPERATURE (°C)

Figure 2.

In the thermal desorption experiment for Pd(110)-silacyclobutane (initial adsorption of -135°C), there were detectably six molecules that desorbed. Shown above are the mass spectral intensities of the ion characteristic of these species with exception of ethylene (ethylene desorbed at ∿60-80°C). In these plots, mass 2 is for H_2, mass 67 for silacyclobutadiene, mass 86 for $\{SiH_2CH_2\}_2$ and mass 44 for the parent ion of $H_2Si{=}CH_2$ and a fragmentation ion for a silacyclobutane. The low temperature (-65°C) maximum is ascribed to silacyclobutane reversibly desorbing and the high temperature (+75°C) maximum to silaethylene. In this experiment, the heating rate was 75°C sec^{-1}. In an experiment performed with a heating rate of 25°C sec^{-1}, more dimer $\{SiH_2CH_2\}_2$ and less silaethylene were formed. In the case of the dimer $\{SiH_2CH_2\}_2$, the parent ion intensity is less than those for the parent ion-minus-one, -two,-three and -four.

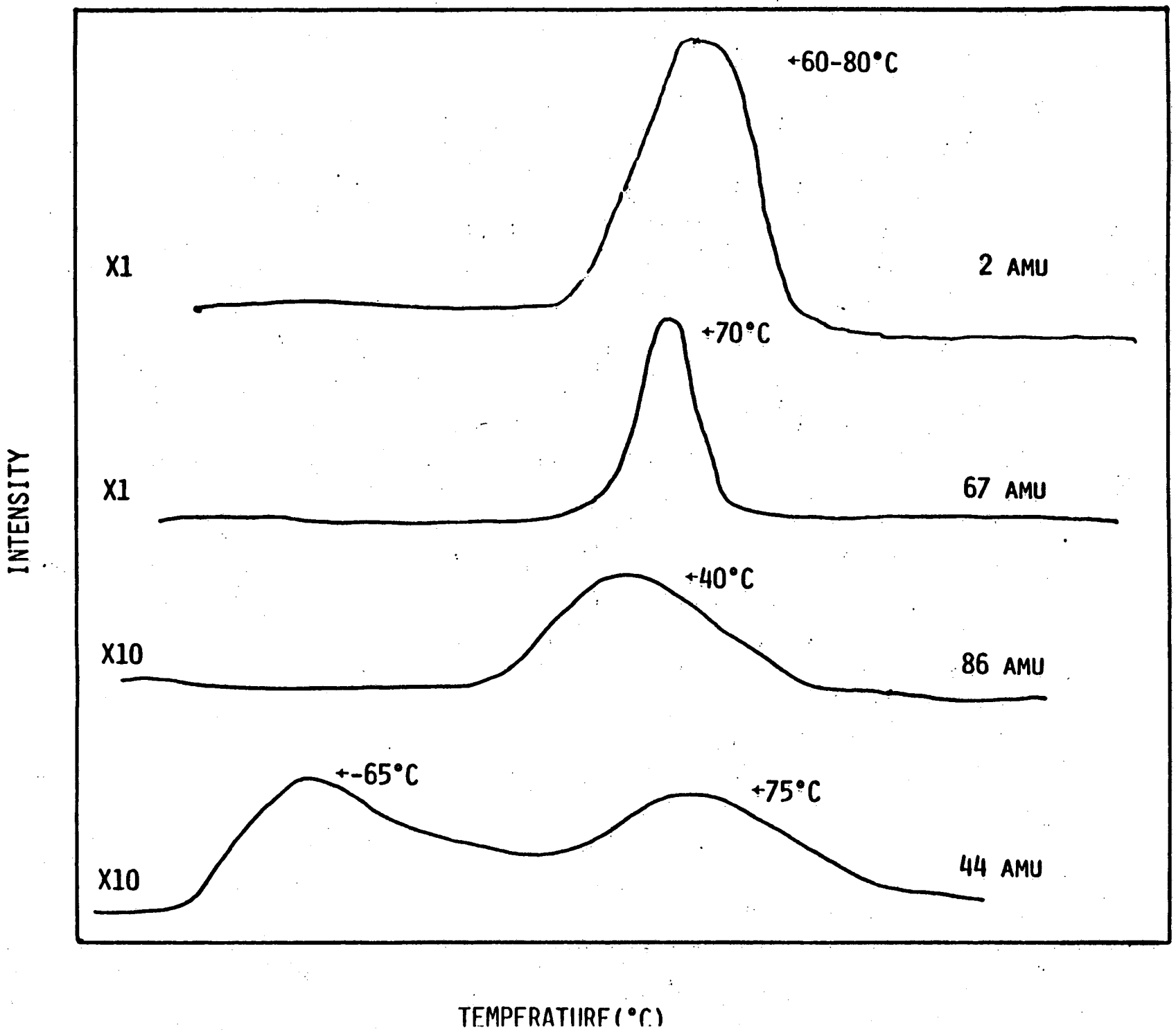
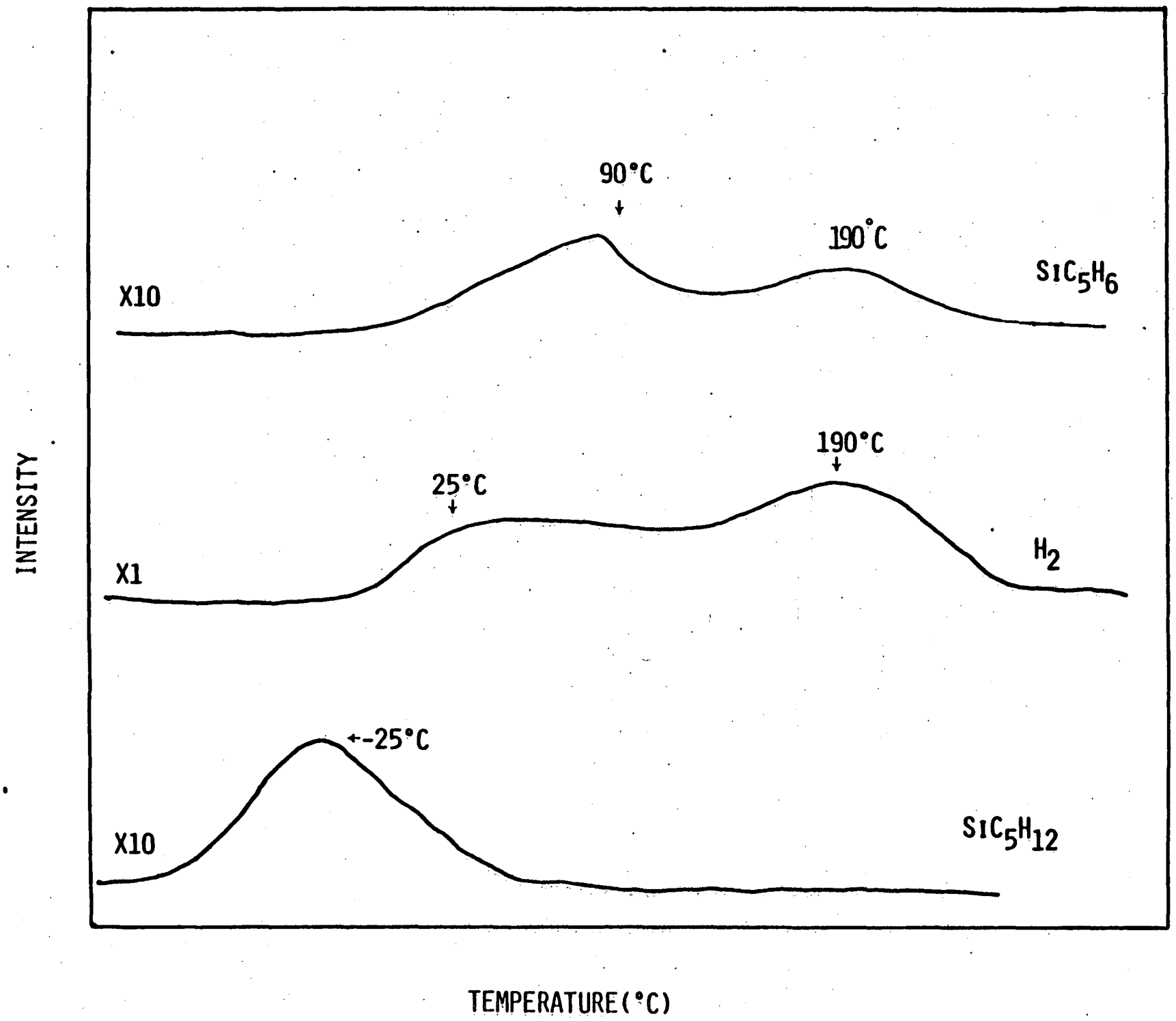

+60-80°C
X1
2 AMU
+70°C
X1
67 AMU
+40°C
X10
86 AMU
+-65°C
+75°C
X10
44 AMU
INTENSITY
TEMPERATURE (°C)

Figure 3.

Illustrated above is the results of a thermal desorption experiment (heating rate of 25°C sec^{-1}) for Pd(110)-silacyclohexane.


90°C
190°C
X10
SiC_5H_6
190°C
25°C
X1
H_2
←-25°C
X10
SiC_5H_{12}
INTENSITY
TEMPERATURE(°C)

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