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Photochemistry of cyclohexane and its excitation mechanism on metal surfaces

In our laboratory, we have investigated the photochemical activation of CH bonds of saturated hydrocarbon on metal surfaces. It has been found that methane photodissociation takes place by the irradiation of photons whose energy is much lower than the onset energy of the absorption band of methane in the gas phase. The lowering in the excitation photon energy was interpreted to be due to the hybridization between the CH anti-bonding state of methane and substrate unoccupied states.

In this thesis, I describe the photochemistry of cyclohexane on various metal surfaces. Cyclohexane is another typical saturated hydrocarbon and shows a broad and substantially redshifted absorption band of the CH stretching mode on metal surfaces, indicating the CH bonds are softened by the interactions with metal surfaces. This phenomenon is called CH-bond softening. The degree of softening depends on the metal substrate and shows some correlation with thermal reactivity. The CH softening mode of cyclohexane on Pt(111) shows the redshift of $\Delta\nu = 310 \text{ cm}^{-1}$ and cyclohexane is dehydrogenated to benzene thermally. On the other hand, the redshifts on Cu(111) and Ni(111) are 130, and 180 cm^{-1} , respectively, and cyclohexane simply desorbs molecularly when the surfaces are annealed.

Because the electronic interactions are responsible for the CH-bond softening, it is expected that same interactions lower the excitation photon energy for the transition to the CH anti-bonding state of cyclohexane on metal surfaces. Thus, the aims of this study are in the following: (1) To confirm that the photochemistry of cyclohexane on metals takes place upon UV irradiation as in the case of methane. (2) If so, to explore the photoexcitation mechanism. (3) To clarify primary photoproducts. (4) To explore the surface reactions of the primary photoproducts. And (5) to examine the correlation between the degree of softening and photo-reactivity.

Firstly, the photochemistry of cyclohexane was examined on a Cu(111) surface. This adsorption system is very suitable for elucidating the excitation mechanism, since cyclohexane does not decompose on this surface. Temperature-programmed desorption (TPD) results taken as a function of the number of photons irradiated (N_{ph}) at 6.4 eV reveal that the intensity of the cyclohexane molecular desorption peak at 180 K decreases with N_{ph} . In addition, the associative hydrogen desorption peak at 350 K grows. These results clearly indicate that the dehydrogenation of cyclohexane is induced by the irradiation of 6.4-eV photons.

We observed another desorption species in the post-irradiation TPD measurements. After photoirradiation, the desorption peak of cyclohexene (C_6H_{10}) at 230 K was detected. The cyclohexene desorption was caused by the thermal dehydrogenation of a primary photoproduct,

because cyclohexene adsorbed on Cu(111) desorbs at 185 K, much lower temperature compared with the post-irradiation TPD result. Therefore, the primary photoproduct was assigned to be cyclohexyl (C_6H_{11}). Thermal reactions do not proceed after cyclohexene desorbs molecularly, which was evidenced by the fact that the intensity of the C1s spectrum observed by X-ray photoelectron spectroscopy (XPS) was completely lost after heating.

Photoreaction cross sections were used for the measure of photoreactivity. The intensity of C1s in post-irradiation XPS was measured as a function of N_{ph} . The fittings of the changes in C1s intensities with the first-order kinetic rate equations result in a photo-dehydrogenation cross section, $\sigma_{dis}=4.7\times 10^{-21}$ cm², and a photodesorption cross section, $\sigma_{des}=0.7\times 10^{-21}$ cm². No detectable photoproducts were observed by the irradiation of 5.0-eV photons.

The ultraviolet absorption spectrum of cyclohexane in the gas phase was referenced to examine whether or not isolated cyclohexane can absorb 6.4-eV photons. The absorption of cyclohexane in the gas phase starts at 7.0 eV and shows the absorption cross section of 2×10^{-22} cm² and the absorption cross section at 6.4 eV is much less than this. Thus, the observed photochemical cross section of cyclohexane at 6.4 eV is significantly larger than the absorption cross section at the energy. This is very similar to the photochemistry of methane on metal surfaces. The photoyields of cyclohexyl obtained from multilayer of cyclohexane on Cu(111) were found to be same as one for monolayer. This result indicates that only cyclohexane in the first layer, directly interacting with the metal substrate, is photo-active. The interaction with the Cu(111) substrate is a key for lowering the excitation energy in the photochemistry.

There are two excitation mechanisms on metal and semiconductor surfaces. One is direct excitation of electronic states of adsorbate itself. Thus, the photochemical cross section is proportional to $|\mu \cdot E|^2$, where μ is a transition dipole moment of adsorbate and E is the electric field vector of incident light at the surface. Another one is indirect excitation where the substrate absorbs photons, so that hot electrons created are attached to the adsorbate. In this case, the photochemical cross section is proportional to absorbance of substrate. Since the electric field particularly along the surface normal shows a very different dependence on polarization and incident angle of the incoming light from that of the substrate photon absorbance, the excitation mechanism can be identified by the measurements of the polarization and incident angle dependence of photochemical cross sections if the adsorption system has a transition dipole along the surface normal. As a result, the cross sections observed with p-polarized light clearly show deviation from the absorbance of the substrate. This indicates that the electronic transition in adsorbate plays a central role in the photochemistry.

Recent results of near-edge X-ray absorption fine structure (NEXAFS) provide a useful clue for an understanding of the excitation mechanism. The NEXAFS spectra taken from cyclohexane on Cu(111) shows that the Rydberg/CH anti-bonding-state resonance located at 287.7

eV is strongly quenched and a distinct new peak denoted as M^* resonance at 285.1 eV appears. The M^* resonance was attributed to the transition from the C1s inner core state to the band caused by hybridization between the electronic states of cyclohexane and the metal substrate. Furthermore, the occurrence of the M^* resonance correlates with the degree of CH vibrational mode softening. Since the broad M^* band is located close to the Fermi level, a part of M^* band is occupied, i.e., back-donation from metal filled states to the band with the CH anti-bonding character of cyclohexane. Ultraviolet photoelectron spectroscopy shows that the highest occupied molecular orbital (HOMO) band is located at 5 eV. Thus, the electronic excitation from the HOMO band to the unoccupied M^* band just above the Fermi level is possible by 6.4-eV photons. Consequently, the CH vibrational mode softening and the photochemistry of cyclohexane on metal surfaces have the origin in common.

Secondly, the photochemistry of cyclohexane on Pt(111) was investigated. Here the main focus is on the post-irradiation thermal chemistry. Photochemistry was investigated with TPD, XPS and infrared reflection absorption spectroscopy (IRAS). From TPD results, photo-dehydrogenation was confirmed on Pt(111) as well. IRAS spectra after photo-irradiation indicate that the primary photoproduct is cyclohexyl.

We measured the photoreaction cross sections of cyclohexane on Pt(111) at 6.4 and 5.0 eV. The obtained photo-dehydrogenation cross sections are $(3.1 \pm 0.2) \times 10^{-21}$ and $(1.1 \pm 0.6) \times 10^{-21}$ cm² at 6.4 and 5.0 eV, respectively. The appreciable cross section at 5.0 eV suggests the larger adsorbate interactions on Pt(111) compared with those on Cu(111). The excitation mechanism was investigated by the same procedure for Cu(111). The cross sections with p-polarized light again deviate from the absorbance of the substrate. This indicates clearly that the excitation mechanism is the same on Cu(111).

On Pt(111), it has been known that cyclohexane is thermally dehydrogenated to benzene (C₆H₆) via C₆H₉. Benzene converted from the monolayer of cyclohexane does not desorb molecularly because benzene is further dehydrogenated to atomic C. In contrast, after photo-irradiation at 6.4 eV, the desorption of benzene in post-irradiation TPD was clearly observed. Then the thermal reactions of the primary photoproduct, cyclohexyl, were investigated by IRAS. Absorption bands attributable to cyclohexene (C₆H₁₀) appeared at 200 K. This species has not been identified in the studies on thermal reactions of cyclohexane on Pt(111). UV photons can produce a larger amount of cyclohexyl than that induced thermally. In this case, the adsorption sites are largely occupied by produced cyclohexyl and hydrogen, which may increase the activation barriers for dehydrogenation of cyclohexene and benzene in the post-irradiation thermal chemistry.

Thirdly, the photochemistry of cyclohexane was also investigated on Ni(111) and the photoreactivity of the various surfaces were compared. It was found that on the Ni(111) surface cyclohexane is not dehydrogenated thermally but photodissociated to cyclohexyl and hydrogen by

the irradiation of 6.4-eV photons as on Cu(111) and Pt(111) surfaces. Post-irradiation TPD results show that benzene is desorbed from the surface. The photodehydrogenation cross section was determined to be $(4.5 \pm 0.4) \times 10^{-21} \text{ cm}^2$ at 6.4 eV.

The amount of redshift of the softening mode shows a linear correlation with the adsorption energy estimated from the temperature of the desorption peak, i.e., Pt(111) > Ni(111) > Cu(111). Furthermore, thermal dehydrogenation takes place only on Pt(111) among the metal substrates studied in this work. Thus, as the redshift of the softening increases, the activation barrier for dehydrogenation is lowered. On the other hand, the photo-dehydrogenation cross section is not correlated well with the redshift of the softening band and the adsorption energy, i.e., it decreases in the order of Ni(111), Cu(111), and Pt(111). There are two factors influencing the photo-reactivity of the metal surface: the interaction strength and the quenching rate of the excited state. The former helps to lower the energy of the excited state, so that it increases the density of the M^* state near the Fermi level. Thus, it enhances the photo-reactivity. In contrast, the latter factor discourages the photo-reactivity, since faster quenching (a shorter lifetime of the excited state) reduces a fraction of adsorbate which has excess energy enough to surmount the dissociation barrier when it is quenched back to the ground state. The two factors are mutually related. Namely, the larger the adsorption energy, the faster (shorter) the quenching (lifetime) would be. Therefore, the photo-reactivity of metal is determined by the subtle balance between the two factors. Among three metal substrates studied in this work, it seems that the interactions between cyclohexane and Ni(111) are best suited for the photochemical C-H activation of cyclohexane.

(論文審査結果)

出願された博士論文は、典型的な環状飽和炭化水素であるシクロヘキサンの表面光化学についての実験的な研究成果をまとめたものである。シクロヘキサンは金属表面に吸着するとブロードで大きく低波数側にシフトした CH 伸縮振動モードに基づく吸収バンドを示し、このシフト量(吸着エネルギー)と熱反応の間には相関があることがわかっている。そこで、これらの表面に吸着したシクロヘキサンの吸着状態、光反応、および、光反応生成物の熱反応機構について詳細な実験的研究を行った。本研究での最も重要な発見は、シクロヘキサンが Cu(111)、Pt(111)、Ni(111)などの金属表面上に吸着すると気相や液相などの均一系では吸収しない 6.4 eV 以下の光により解離反応を起こすことである。この事実を中心に本論文では次の3つの主題について詳しく述べられている。

(1) Cu(111)面を用いて光反応における励起機構を明らかにした。この表面は上記の表面のうちではシクロヘキサンの吸着エネルギーがもっとも小さく、熱反応はまったく起きないので、光反応だけの効果を調べられ、この目的には好都合である。6.4eV の光ではシクロヘキサンはシクロヘキシルと水素に解離し、生成されたシクロヘキシルは昇温によりシクロヘキセンに脱水素化されることを見出した。また、直線偏光した光を用い、光反応に関する有効断面積の偏光・入射角依存性を測定することにより、表面による光吸収ではなく、シクロヘキサンの最高占有準位からシクロヘキサンと金属の軌道間での混成により生じる非占有状態への遷移により光反応が誘起されることを提案した。

(2) Pt(111)表面では、シクロヘキサンは熱反応し、ベンゼンを生成することがわかっている。しかし、水素原子が共吸着する場合には熱反応が完全に抑制されることを見出した。この結果を利用することにより、同表面上では 5.0、6.4eV の光によってシクロヘキサンが Cu(111)表面上と同じ励起メカニズムによりシクロヘキシルへと解離することを明確にした。これを昇温すると熱反応に比べて多量のベンゼンが生成される。従来の熱反応研究では、ベンゼン生成にいたる中間体としては C_6H_9 のみが同定されていた。しかし、本論文では、光反応によりより低温で多量のシクロヘキサンを解離させることにより、 C_6H_{11} 、 C_6H_{10} 、 C_6H_9 と逐次的に安定な中間体が存在することを初めて明らかにし、従来の反応機構モデルをより拡張した形で構築することに成功した。

(3) 光反応性と吸着エネルギーとの関連を明らかにするために Ni(111)表面上でも測定を行い、3つの表面での光反応断面積を比較した。その結果、6.4eV の光エネルギーでの反応断面積のみに着目すると単純な相関はみられないが、もっとも吸着エネルギーの大きな Pt(111)面上でのみ 5.0eV で光反応が起きるなど熱反応と同様な相関を示唆する実験事実も明らかとなった。この点については吸着エネルギーと励起寿命との関連から考察を行った。

本論文は、金属に吸着したシクロヘキサンが気相では吸収のない波長で解離することを含め、新規性の高いいくつかの発見を行っており、その現象の解析についても詳しい議論がなされ、その成果の一部はすでに Phys.Chem.Chem.Phys.誌に発表されている。以上のことを勘案し、本論文の内容は博士論文として十分な質を備えたものと判断した。