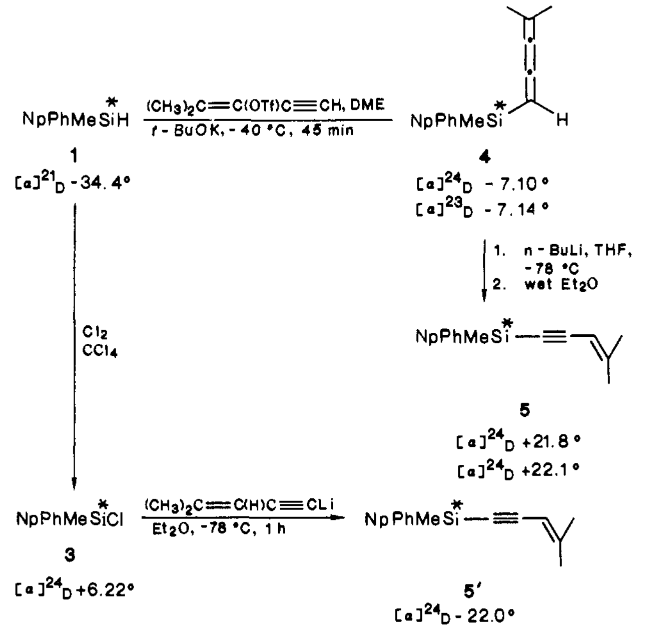
Scheme III



−4.24° (Scheme II). Conversion of the optically pure **1** to the chloride **3** is known to proceed with complete retention of configuration,[8] Interaction of chlorosilane **3** with a variety of alkyllithium compounds is known[9] to occur with complete inversion of configuration, yielding tetrasubstituted silanes, Therefore, we treated chloride **3** with $(CH_3)_2C{=}C(H)Li$ to obtain "authentic" adduct[10] **2′** of known optical purity and configuration, As seen in Scheme II, duplicate runs gave, within experimental error, an $[\alpha]_D$ of *identical magnitude but opposite sign* to the carbene insertion product. Since the anionic route involves one retention and one inversion, this establishes that the carbene insertion must proceed by complete stereospecificity with retention of configuration.

Likewise, duplicate runs of the reaction of **1** with triflate-derived $(CH_3)_2C{=}C{=}C{=}C{:}$ gave adduct **4**,[11] Unfortunately, as cumulenyl anions are unknown, we were unable to prepare authentic **4** to establish its configuration via a direct procedure. However, adduct **4** readily undergoes a base-promoted rearrangement to enynylsilane **5** (Scheme III). Since this rearrangement does not involve any bonds to the chiral silicon, neither the configuration nor the enantiomeric purity of the product should be affected. Reaction of silane-derived chloride **3** with $(CH_3)_2C{=}C(H)C{\equiv}CLi$ in duplicate runs (Scheme III) gave "authentic"[12] **5′** with an $[\alpha]_D$ of *identical magnitude but of opposite rotation* to the carbene insertion derived, rearranged, tetrasubstituted silane **5**. Since the halide displacement reaction is known[9] to involve inversion of configuration, this establishes that the $(CH_3)_2C{=}C{=}C{=}C{:}/Si{-}H$ insertion also must proceed by complete stereospecificity with retention of configuration,

Although it is conceivable, it is extremely unlikely that either the radical pairs[13] or the ion pairs in Scheme I would have a sufficiently short lifetime to undergo recombination faster than loss of chirality, Hence, we have established that alkylidenecarbenes, as well as the more extended members of the unsaturated carbene family, undergo intermolecular Si–H insertion via a concerted, three-centered transition state (albeit perhaps with some polar character) in accord with Gilbert's predictions[5] and in contrast to Newman's[15] original proposal involving ion pairs. These results are in concord with the observations of Sommer and coworkers[16] on the stereospecific insertion of $Br_2C{:}$ and $Cl_2C{:}$ into chiral NpPhMeSi*H.

Acknowledgment. We are grateful to the NSF (CHE 84-19099) for financial support and to Professor G. L. Larsen for a batch of chiral silane **1**.

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[10] The two vinylsilanes **2** and **2′** prepared by the carbene insertion and the anion route were identical in all respects, IR, NMR, GC retention, etc., but for the direction of rotation. For **2**: IR (neat) 1619 (C=C), 1440, 1429, 1250, 1103, 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 12), 5.73 (s, 1), 1.97 (s, 3), 1.65 (s, 3), 0.82 (s, 3); ^{13}C NMR ($CDCl_3$) δ 155.02, 138.08, 136.84, 135.67, 135.05, 134.69, 133.31, 129.91, 128.81, 128.73, 127.71, 125.41, 125.20, 125.02, 120.76, 29.73, 23.85, −0.75; mass spectrum, EI, *m/z* (relative intensity) 302 (M^+, 92), 287 (100), 259 (20), 247 (33), 233 (23).

[11] For **4**: IR (neat) 2028 (C=C=C=C), 1428, 1250, 1210, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 12), 5.92 (sept, 1, J = 1.05 Hz), 1.92 (d, 3, J = 1.05 Hz). 1.68 (d. 3. J = 1.05 Hz), 0.84 (s, 3); ^{13}C NMR ($CDCl_3$) δ 173.64, 157.28, 136.93, 135.38, 134.66, 134.06, 133.27, 130.30, 129.14, 128.82, 128.69, 127.74, 125.56, 125.31, 124.98, 124.04, 25.61, −2.11; mass spectrum, FAB, *m/z* 327 (MH^+), 247, 169.

[12] The two enynylsilanes **5** and **5′** were identical in all respects, IR, NMR, GC retention, etc., but for the *direction* of rotation. Both **2** and **5** gave satisfactory C and H analyses. For **5**: IR (neat) 2120 (C≡C), 1428, 1250, 1106, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 12), 5.38 (sept, 1, J = 0.97 Hz), 1.94 (d, 3, J = 0.97 Hz), 1.82 (d, 3, 0.97 Hz), 0.86 (s, 3); ^{13}C NMR ($CDCl_3$) δ 151.37, 136.60, 135.94, 135.21, 134.44, 133.27, 132.88, 130.56, 129.37, 128.69, 128.62, 127.83, 125.63, 125.37, 124.96, 107.32, 105.47, 92.78, 24.95, 21.43, −0.56; mass spectrum, EI, *m/z* (relative intensity) 326 (M^+, 89), 311 (100), 284 (11), 271 (16), 247 (16), 231 (23).

[13] Although there is evidence[14] for the existence of chiral NpPhMeSi*•, in no instance has there been complete stereospecificity observed in these radical reactions. Moreover, radical traps such as galvinoxyl, O_2, and *t*-BuNO did not affect our insertion reactions.

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Kinetics of Hexafluorobenzene Decomposition on a Pt Surface

J, N. Chen, H. Kang, and J. W. Rabalais*

Department of Chemistry, University of Houston
Houston, Texas 77004

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Kinetics of gas-solid heterogeneous reactions are usually monitored by means of mass spectrometric techniques, in which the probe can be ions (secondary ion mass spectrometry—SIMS),[1] thermal energy (thermal desorption spectrometry-TDS),[2-4] and lasers (laser-induced desorption),[5-7] or by means of electron spectroscopic techniques.[8] In this communication we present a novel technique (direct recoil spectrometry—DRS)[9] for monitoring surface kinetics which provides direct time-resolved compositions of surface constituents. Application to decomposition of hexafluorobenzene (HFB) on platinum has found that carbon is deposited on the surface while fluorine is evolved, the kinetics follow a second-order rate law with a 4-kcal/mol activation energy, and a proposed mechanism involving migration of surface fluorine is the rate-limiting step.

The DRS technique, which has been described elsewhere,[9] has been used for monitoring chemisorption and for studying ion-

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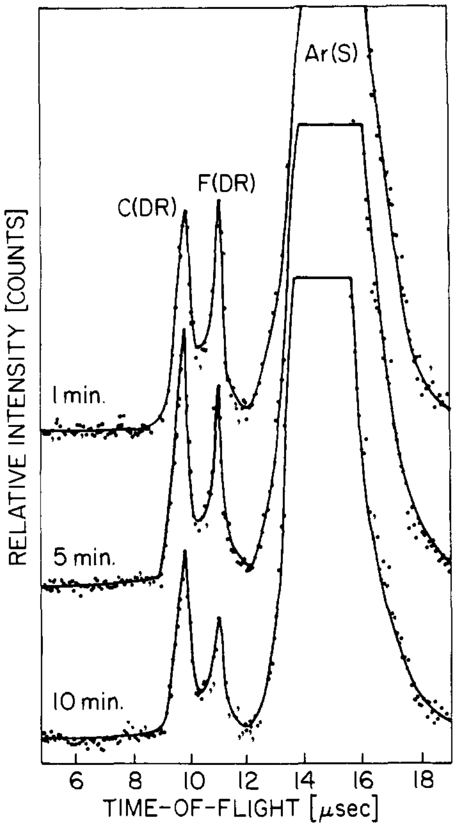

Figure 1. Time-of-flight spectra of scattered (S) and directly recoiled (DR) particles for a polycrystalline Pt foil exposed to 100 L (1 L = 10^{-6} Torr·s) of C_6F_6. The times between initial chemisorption and spectral measurement are shown on the figure. The conditions were as follows: primary beam, 3 keV Ar^+; angle of incidence to surface, 11°; scattering and recoiling angle, 22°.

surface charge-exchange processes. Briefly, a pulsed mass-selected keV ion beam impinges on a surface at a glancing angle, and both the atoms and ions which are scattered or directly recoiled (DR) into a forward scattering angle are monitored by means of time-of-flight (TOF) methods. The DR flux consists of surface atoms with high discrete energies and predictable trajectories originating from quasi-single collisions of primary ions. The energies (and hence velocities) of these DR species can be predicted from the classical binary collision model. Both DR ions as well as neutrals are detected directly by a channeltron electron multiplier (CEM), i.e., without the need for postionization techniques. This is possible because CEM's are sensitive to the high energy (>1 keV) neutral DR atoms. The technique is sensitive to the outermost atomic layer, since it is predominantly these atoms that can escape from the surface without suffering several intermediate collisions. The low primary ion flux (<0.1 nA/cm^2) results in a nondestructive method which detects all surface atoms, including hydrogen, and the rapid spectral acquisition (<2 s) allows kinetic studies in real time. The DR technique has advantages over secondary ion mass spectrometry (SIMS), which monitors the low-energy cascade-sputtered distribution, in that it does not require postionization techniques for detection of neutrals, it is free of the "matrix effects" that alter SIMS ion and cluster size distributions, it is sensitive to the outermost atomic layer, and it uses multichannel detection techniques.

Figure 1 shows representative DR spectra for different times after exposure of polycrystalline Pt foil at 85 °C to 100 L (1 L = 10^{-6} Torr·s) of HFB. Peak assignments are made by using the binary collision model to calculate TOF and by electrostatic sector analysis.[10] It is observed that the C(DR)/F(DR) peak intensity ratio increases with time and that the F(DR) peak is eventually not detectable. It has been asserted that the C(DR) peak intensity remains constant by referencing to the intensity of the scattered Ar peak. This constancy of the C(DR) peak intensity is not obvious from Figure 1, where the spectra are not normalized to a constant scattering intensity. Control experiments in which the sample was not exposed to the pulsed ion beam until 20–30 min after chemisorption verified that desorption of fluorine was spontaneous and not ion beam induced. Auger electron spectroscopy verified that fluorine is depleted from the surface, and the Auger line shape identified the deposit as a carbidelike structure. Despite the high HFB dose used, the chemisorption coverage was <10% of a monolayer, as determined by calibration to DR intensities of adsorbates on surfaces with known coverages.[9] Spectra were acquired at various Pt temperatures between ambient and 130 °C, the total integrated counts in the F(DR) peak (which is proportional to fluorine concentration [F]) as a function of time were measured for each temperature. The results did not fit a first-order rate expression, i.e., ln [F] vs. t; however, they did fit a second-order expression plotted as 1/[F] vs. t as shown in Figure 2. The slopes of these lines, obtained from linear least-square fits to the data, are proportional to the rate constants; they are 0.0127 (35°), 0.0250 (85°), and 0.0700 (130°) in units of [(rel·counts)·min]$^{-1}$. The resulting activation energy is 4 ± 1 kcal/mol over the temperature range covered.

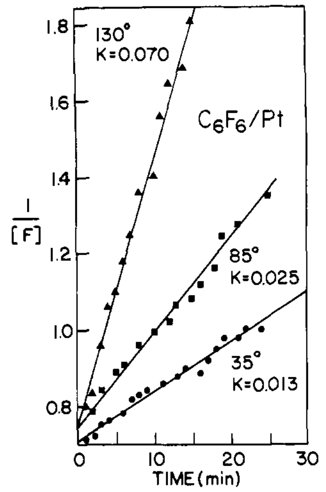

Figure 2. Plots of 1/[F] vs. t at various substrate temperatures, where [F] is determined by integrating the area under the F(DR) Peak.

Constant carbon concentration during the reaction indicates that the evolving species do not include fluorocarbons and are, therefore, most likely either F_2 or PtF_x, $x = 2$ or 4. The latter products have been observed[2] in thermal desorption studies from a Pt surface upon which elemental fluorine was chemisorbed. Due to the low HFB adsorbate coverage, the amount of F_2 or PtF_x evolved is small and dispersed over a long time period, rendering difficulties in mass spectrometric detection. In accordance with the above results, a mechanism in which HFB is dissociatively chemisorbed to form carbides and surface fluorine atoms may be postulated as

$$C_6F_6(g) + Pt(s) \xrightarrow{\text{fast}} 6PtC(s) + 6F(ad) \quad (1)$$

$$Pt(s) + 2F(ad) \xrightarrow{\text{slow}} F_2(ad) \text{ or } PtF_x(ad) \quad (2)$$

$$F_2(ad) \text{ or } PtF_x(ad) \xrightarrow{\text{fast}} F_2(g) \text{ or } PtF_x(g) \quad (3)$$

where g, s, and a denote gas, surface, and adsorbed species. Fluorine atoms migrate on the surface until they recombine to form F_2 or PtF_x. The second-order kinetics agree with the conjecture that fluorine diffusion on the surface is the rate-limiting step. The activation energy measured for the decomposition is also in the same range as diffusion barriers determined for H on Pt (7–12 kcal/M),[7,11] H on Ni (4 kcal/M),[5] CO on Cu (2–3

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kcal/M),[6] and CO on Ni (3.3–4.2 kcal/M)[12] by using other desorption techniques.

The selectivity and reactivity of molecular rearrangements on Pt surfaces have been found to be strongly dependent on the surface structure.[8] We have also observed this phenomenon: the Pt foil used in the above experiments was annealed to 800 °C before each measurement. Surfaces that were roughened by ion sputtering exhibited a different behavior. Details of the decomposition of both C_6F_6 and C_2F_4 on Pt surfaces are presently under investigation by DRS and Auger, X-ray, and UV electron spectroscopy.

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Electroreduction of CO to CH_4 and C_2H_4 at a Copper Electrode in Aqueous Solutions at Ambient Temperature and Pressure

Yoshio Hori,* Akira Murata, Ryutaro Takahashi, and Shin Suzuki

Department of Synthetic Chemistry
Faculty of Engineering, Chiba University
Yayoi-cho, Chiba 260, Japan

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Carbon monoxide is a substance of primary importance from the viewpoint of utilization of carbon resources. Hydrogenation of CO in the gas phase has been widely studied, but only a small number of papers has been published about electrochemical reduction. Electroreduction of CO did not proceed effectively according to the previous papers;[1] the cathodic partial currents for electroreduction of CO were very small, not exceeding 5×10^{-5} A cm^{-2}. We briefly describe here an electroreduction of CO at a Cu cathode in aqueous solutions. This procedure allows an effective cathodic reduction of CO to form hydrocarbons and alcohols with appreciable current densities.

An electrodeposited copper sheet (purity 99.999%), donated by Sumitomo Metal Mining Co. Ltd., was cut into an electrode (20 × 20 × 1 mm) with a copper lead strip attached. We did not mount the electrode in resin in order to avoid possible contamination of the boundary interface of electrode/resin. The electrode was polished with fine emery paper (no. 1500), electrolytically polished in 85% phosphoric acid for ca. 2 min at ambient temperature, and then rinsed with doubly distilled deionized water. Electrochemical measurements were conducted at 18 °C with a three-compartment cell in which two anode compartments faced each side of the Cu electrode. The cathode compartment (36-mm inner diameter) was separated from the two anodes with sheets of cation exchange membrane (Selemion). The potential of the cathode was measured with respect to an Ag/AgCl reference electrode. The electrode potential was corrected for the IR drop between the Luggin capillary tip and the cathode. The catholyte (60 mL) was prepared from doubly distilled deionized water and reagent grade chemicals. The catholyte was purified by preelectrolysis with a 30 × 20 mm Pt black cathode at 2.5×10^{-5} A cm^{-2} under purified N_2 atmosphere for more than 15 h. The Pt black cathode was regenerated by anodic polarization in 0.5 mol dm^{-3} H_2SO_4 before use. Carbon monoxide (high purity grade, >99.95%, hydrocarbon content <0.5 ppm, dew point below −65 °C), purchased from Nihon Sanso Co. Ltd., was introduced to the catholyte after passing through a KOH solution.

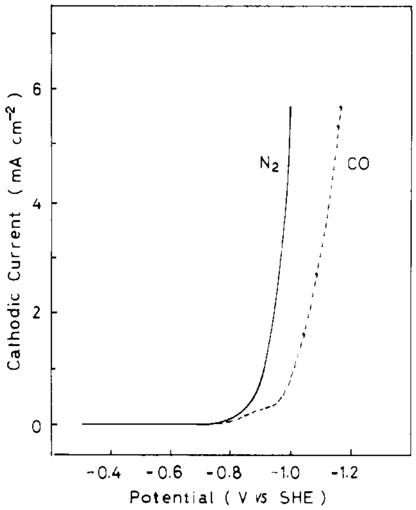

Figure 1. Voltammograms obtained in a phosphate buffer solution (0.17 M KH_2PO_4/0.03 M K_2HPO_4, pH 6.1) saturated with N_2 or CO. Scan rate 50 mV s^{-1}.

Voltammetric measurements were conducted with electrolytes saturated with purified CO or N_2. Coulometric measurements at constant currents were conducted in $KHCO_3$, KOH, and a phosphate buffer aqueous solution with CO bubbled into the catholyte (flow rate: ca. 70 mL min^{-1}) for 30 min; the catholyte was stirred vigorously with a magnetic stirrer.

CH_4 and C_2H_4 in the effluent gas from the cell were analyzed at 5-min intervals by a gas chromatograph equipped with an FID detector (Shimadzu 3BF). H_2 was analyzed by a gas chromatograph equipped with a TCD detector (Shimadzu 3AH). The volume of the gas sampling tube was 3 mL. The analytical data were averaged over 30 min of electrolysis. The limit of quantitative analysis was 0.6 ppm for CH_4 and 0.3 ppm for C_2H_4; these values correspond to a faradaic yield of 0.1% in a constant current (2.5 mA cm^{-2}) electrolysis. C_2H_5OH and *n*-C_3H_7OH in the solution were also analyzed after electrolysis by a gas chromatograph (Shimadzu 3BF). Formaldehyde in the solutions was determined by the chromotropic acid colorimetric method. The limit of quantitative analysis for the soluble products was 3×10^{-6} mol dm^{-3} for C_2H_5OH and *n*-C_3H_7OH and 0.1×10^{-6} mol dm^{-3} for HCHO. The faradaic yields for these limits are 0.3% for C_2H_5OH and *n*-C_3H_7OH and 0.002% for HCHO. The following analytical columns were employed for the identification of the products by the gas chromatograph; molecular sieve 5Å and 13X, Porapak N + Porapak Q, activated alumina TR, and silica gel for CH_4; Porapak N + Porapak Q, activated alumina TR, and silica gel for C_2H_4; Porapak Q, PEG 400/Chromosorb, Unisole 30T (alkylene glycol phthalate)/Chromosorb, and PEG 20M/Shimalite for C_2H_5OH; PEG 400/Chromosorb, Unisole 30T/Chromosorb, and PEG 20M/Shimalite for *n*-C_3H_7OH. The formation of CH_4 and C_2H_4 was also confirmed by a gas chromatograph mass spectrometer.

Figure 1 shows voltammograms obtained for N_2 and CO saturated phosphate buffer solutions (pH 6.1). The cathodic current is greatly suppressed in the presence of CO. Anodic oxidation of CH_3OH, as is well known, is markedly interfered with by some intermediate species formed in the reaction, e.g., by CO adsorbed on the electrode or some other related species.[2] Adsorption of

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