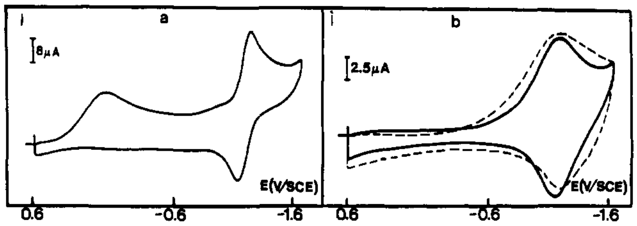

Figure 1. Cyclic voltammetry in ACN + 0.1 M NBu_4BF_4 on a GC electrode (v = 0.2 V s^{-1}, T = 22 °C) of **1** (a) (c = 0.7 mM) and of a derivatized electrode (b) after grafting (—) and after 6 months (---).

currents in electrochemical applications. It would therefore be desirable to develop alternative strategies for modifying carbon surfaces.[18]

For this purpose we have investigated a reductive, rather than an oxidative, strategy. It is based on the electrochemical reduction of diazonium salts, which leads to a very solid and noncorrosive covalent attachment of aryl groups onto the carbon surface.[19] The versatility of the method is founded on the possibility of grafting a large variety of functionalized aryl groups, hence allowing the attachment of a broad spectrum of substances.

(4-Nitrophenyl)diazonium tetrafluoroborate **1** in acetonitrile (ACN + 0.1 M NBu_4BF_4) gives rise on a (clean, carefully polished with 1 μm diamond paste) glassy carbon (GC) electrode to a broad (peak width: 180 mV), irreversible wave located at -0.04 V/SCE. This first wave is followed by the reversible wave of nitrobenzene ($E°$ = -1.18 V/SCE) that is formed upon reductive cleavage of **1** (Figure 1). At concentrations higher than 0.5 mM, the first wave of **1** shows the characteristics of an adsorption wave. On a second scan the first wave of **1** vanishes. Upon electrolysis at a GC cathode of a 1 mM solution of **1** for about 10 min and successive transfer to a pure supporting electrolyte solution, a single broad symmetrical signal is observed at the same potential as that of nitrobenzene (Figure 1). The signal is also very persistent with time: no change could be detected with electrodes left on a laboratory bench for several months (Figure 1) or with electrodes exposed to vigorous ultrasonic cleaning in ethanol, dimethylformamide, benzene, benzonitrile, and trichloroethane. The same observations were made with carbon fibers, carbon powder, or highly oriented pyrolytic graphite (HOPG) (basal plane or edge) electrodes. These experiments point to a strong covalent bonding of the 4-nitrophenyl group on the carbon surface rather than to mere adsorption. The grafting of the 4-nitrophenyl group was also investigated by XPS of GC plates. In agreement with cyclic voltammetry, these measurements indicate that the diazonium salt is adsorbed on the glassy carbon surface: after the GC plate is dipped in the solution and rinsed, signals are observed at 402 and 406 eV corresponding to the diazonium and nitro groups on the surface, respectively, and amounting to 1% of the overall signal. The intensity of the 406 eV signal increases to 7.3% after electrolysis and ultrasonic cleaning while the signal at 402 eV disappears.

The surface coverage of the modifying layer could be estimated through the integration of the voltammetric signal of the 4-nitrophenyl group. The effective surface area of the GC electrode was measured by adsorption of methylene blue and comparison with a mercury electrode of known surface. From these measurements, it appears that the surface coverage can be controlled through the concentration of the substrate and the electrolysis time. At a diazonium concentration of 1 mM and electrolysis times shorter than about 4 min, the surface coverage is a function of the time, with a limiting coverage being obtained for longer times. A very compact layer can be obtained for a 5 mM concentration of the diazonium salt: the surface is nearly completely covered by a close-packed monolayer of 4-nitrophenyl groups ($\Gamma = 14 \times 10^{-10}$ mol/cm^2).

The grafting of many other diazonium salts bearing different functionalities (for example, 4-cyano, 4-carboxy, 4-benzoyl, 4-bromo, 4-(carboxymethyl), 4-acetamidobenzene, and 4-nitronaphthalene) could also be achieved and observed by cyclic voltammetry and/or XPS.

Once attached to the carbon surface, the functionalized aromatic groups could be modified by classical chemical reactions. For example the 4-nitrophenyl group obtained from **1** could be reduced electrochemically (in 10/90 $EtOH/H_2O$ + 0.1 M KCl, irreversible 6e peak) to a 4-aminophenyl group (the CV and XPS signals of the nitro groups disappear and the XPS signal of the amino group appears). Such an amino group could also be obtained by hydrolysis of a 4-acetamidophenyl group. This 4-aminophenyl group could in turn be reacted with an epoxy function such as that of epichlorohydrin (the chlorine atom can be observed by XPS), demonstrating the possibility of generating covalent bonds between the carbon surface and epoxy resins. Preliminary experiments also indicated the viability of the attachment of enzymes along a similar strategy.[20]

We assign the covalent attachment of the aryl groups to the binding of the aryl radical produced upon one-electron reduction of the diazonium salt to the carbon surface. Two factors favor such a reaction: (i) the diazonium salt is adsorbed prior to its reduction, and (ii) the aryl radical is not reduced at the very positive reduction potential of the diazonium salt (opposite to what is observed, for example, with aryl halides). As concerns the carbon surface, the covalent binding seems to involve at the same time edge defects and polycyclic aromatics, as shown by the attachment of aryl groups to the basal plane of HOPG.

As a result of the reductive strategy we used and of the strong bonding between the surface and the aryl groups, low residual currents (similar to those observed at a bare electrode) were obtained over a large window of potentials, the same as for the unmodified parent GC electrode.

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Superacid-Catalyzed Protium-Deuterium Exchange in Isobutane Competing with *tert*-Butyl Cation Formation

Jean Sommer,* Jozef Bukala, Saïd Rouba, and Roland Graff

Centre de Recherches Chimie, Université Louis Pasteur
1, rue Blaise Pascal, 67008 Strasbourg, France

Per Ahlberg

Department of Organic Chemistry
University of Göteborg
S-41296 Göteborg, Sweden

Received March 3, 1992

That saturated hydrocarbons do react at room temperature and below with various superacidic media[1] has been known since the late 1960s when Hogeveen[2] and Olah and his group published their pioneering work. Both Hogeveen[4] and Olah,[5] in a HF-SbF_5-Freon

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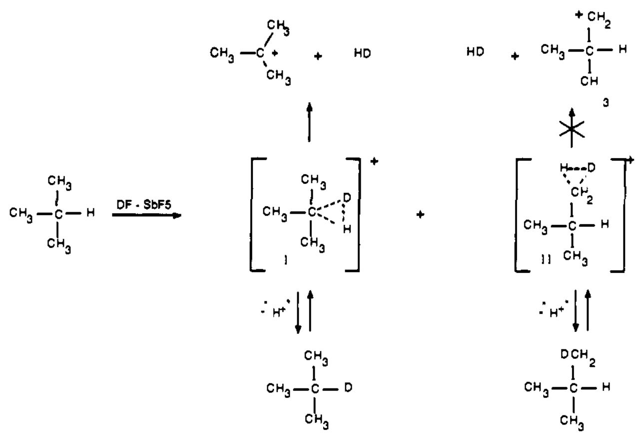
Scheme I



system and in Magic Acid at −78 °C, respectively, have observed hydrogen–deuterium exchange of the methine hydrogen during isobutane ionization, and both authors concluded that a substantial exchange of this type of hydrogen had occurred compared with the ionization. No exchange was observed in the methyl group. The recent publication of papers related to H/D exchange via pentacoordinated carbonium ions both in liquid[6] and on solid superacids[7] prompts us to present our results which show that the protonation site on isobutane is independent of the further reactivity of the pentacoordinated carbonium ion. It takes place on all C–H bonds in relation to the σ-bond basicity as defined by Olah.[8]

In the first series of experiments a mixture of isobutane and nitrogen (1:1 molar ratio) was bubbled during 1 h at a rate of 4.2 mL/min at atmospheric pressure through 1.0 mL of DF–SbF_5 solution (4:1 molar ratio; isotopic purity of DF, 93 mol % D) in a Kel-F reactor at −10 °C. The gaseous products were analyzed by GC and further condensed at −78 °C for ^1H and ^2H NMR analysis after addition of an adequate amount of a $CDCl_3/CHCl_3$ mixture used as internal standard for the H/D distribution measurement.

The superacid phase containing the stable long-living *tert*-butyl ion was also analyzed by 400-MHz ^1H and ^2H NMR after addition of a mixture of acetone/acetone-d_6 as an internal standard.

In accord with our previous results, the analysis of the gaseous reaction products showed the formation of a stoichiometric amount of hydrogen corresponding to 20% conversion of isobutane into the *tert*-butyl ion. Small amounts of methane, ethane, and propane could also be detected, in agreement with less than 1.5% competitive protolytic C–C bond cleavage.

The ^1H, ^2H, and ^{13}C NMR spectra of the recovered isobutane, however, showed a deuterium distribution which to our surprise is at variance with the previously published results.[4,5]

Whereas of the methine hydrons 8 atom % was deuterium, of all hydrons in the methyl groups 18% were found to be deuteriums. The deuterium appeared as CH_2D, CHD_2, and CD_3 groups.

The NMR analysis of the acid phase showed approximately 5 mol % D in the *tert*-butyl ion. In a separate experiment the *tert*-butyl cation was generated under the same reaction conditions from *tert*-butyl chloride in DF–SbF_5 and analyzed immediately for H/D exchange and again after 1 h at −10 °C. The D content was less than 1.5 mol % initially and did not increase with time. Thus the observed exchange must have occurred before ionization. The exchange mechanism is here clearly different from the one taking place in less acidic media such as H_2SO_4, in which case only the methyl protons exchange for deuterium.[9]

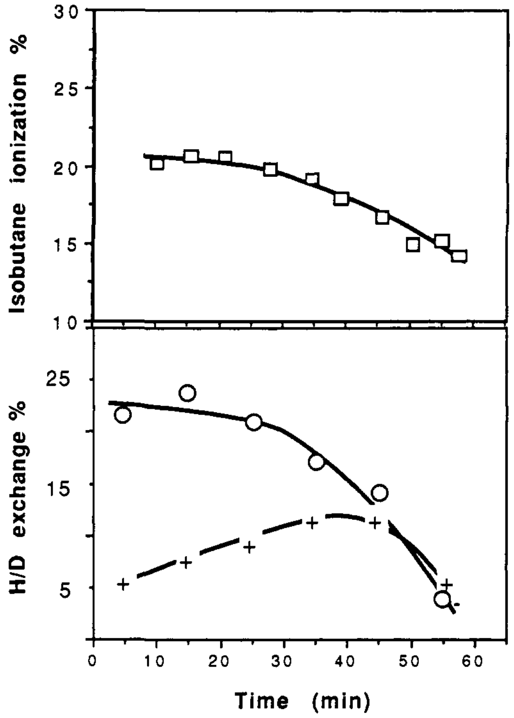


Figure 1. Time dependence of the ionization and exchange processes (methyl H, ○; methine H, +).

Our results demonstrate that the H/D exchange rates are approximately twice as fast for primary as for tertiary hydrogens. The main difference lies in the fate of the protonated alkane: methine-protonated isobutane I may ionize easily and form the *tert*-butyl cation whereas such a process for methyl-protonated isobutane II would lead to an unstable primary ion (Scheme I).

In order to check the time dependence of the exchange and ionization processes, we have run a second series of experiments under the same conditions as above, but isobutane was trapped every 10 min and analyzed for H/D exchange by NMR. The ionization reaction was monitored by hydrogen evolution which was followed by GC. The results plotted in Figure 1 show that ionization of isobutane starting above 20% slows down to 12% after 1 h. H/D exchange of the methyl hydrogen follows the same trend whereas the H/D exchange of the methine hydrogen increases. These results are consistent with a progressive decrease of the acidity of the superacid solution.

The apparently slower initial H/D exchange in the methine proton and its increase with time can be rationalized by the competition of two acidity-dependent pathways yielding isobutane: (1) ionization followed by hydride transfer from isobutane (no exchange on the methine hydrogen); (2) exchange without ionization. The importance of the first pathway diminishes with decrease in acidity.

It will be interesting to study the relative rates of these two processes by trapping the intermediate *tert*-butyl ion with carbon monoxide. We have used successfully this technique for mechanistic studies in superacid-catalyzed propane carbonylation.[10]

Previous investigations in comparable superacid systems but under various experimental conditions have already shown that substantial exchange accompanies ionization. However, no quantitative results have been presented and in isobutane the exchange process was supposed to take place on the methine proton exclusively. Our results are consistent with pentacoordinated carbocations as intermediates in both the exchange and ionization reactions.

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Further studies, especially on the temperature and acidity dependence of this exchange process in small alkanes, are in progress.

Acknowledgment. Support by EXXON (European Science and Engineering Program) to J.B. and by the Swedish Natural Science Research Council is kindly acknowledged.

Registry No. Isobutane, 75-28-5.

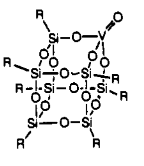
Olefin Polymerization by Vanadium-Containing Silsesquioxanes: Synthesis of a Dialkyl–Oxo–Vanadium(V) Complex That Initiates Ethylene Polymerization

Frank J. Feher* and Rusty L. Blanski

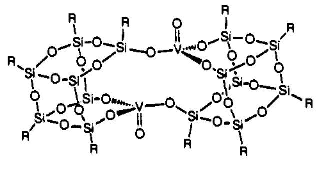
Department of Chemistry, University of California
Irvine, California 92717

Received December 6, 1991

Silica-supported vanadium[1-6] catalysts have attracted attention as olefin polymerization catalysts because their excellent hydrogen response and high comonomer incorporation potentially allow greater control over the properties of the polymer.[3] Low-valent vanadium surface species have been implicated as active sites for polymerization in many of these systems,[4-6] but to the best of our knowledge, there is no direct evidence to objectively support any of the surface species which have been implicated in these systems. In this paper we report our preliminary efforts to elucidate the identity of the olefin polymerization catalyst formed by the reaction of **1**[7] with small amounts (2–5 equiv) of trialkylaluminum reagents.[8]



1 (R = c-C_6H_{11})



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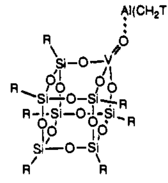

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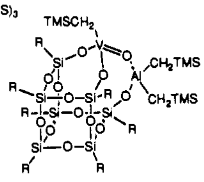

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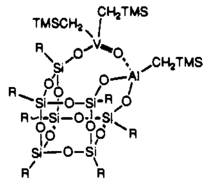

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As reported previously,[7] vanadate **1** can be prepared by the reaction of $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$[9] with $(n\text{-}PrO)_3VO$. The dimerization of **1** to **2** is enthalpically favored ($\Delta H° = -6.02 \pm 0.27$ kcal/mol), but the large negative entropy for dimerization ($\Delta S° = -17.1 \pm 0.2$ eu) can be exploited to prepare solutions containing predominantly (>95%) **1**. At 25 °C, a 0.1 M solution of **1** and **2** in toluene-d_8 contains ~75% of monomer **1** (by ^{51}V NMR spectroscopy), but the proportion of **1** can be increased to >96:4 by first heating the solution to 110 °C and then rapidly cooling it in a dry ice/acetone bath (−78 °C). Addition of $Al(CH_2SiMe_3)_3$[10] (1 equiv) to this toluene-d_8 solution at −78 °C produces a deep red solution, which at −50 °C exhibits ^1H, ^{13}C, ^{29}Si, ^{51}V, and ^{17}O NMR spectra[11] consistent with Lewis adduct **3**. Of particular relevance were a ^{51}V resonance at δ −705, a ^{17}O resonance at δ 934, and three silsesquioxane ^{29}Si resonances with relative integrated intensities of 3:1:3, one of which was broadened ($w_{1/2} = 40$ Hz) due to unresolved two-bond coupling between ^{51}V ($I = {}^7/_2$) and the ^{29}Si nuclei closest to the vanadium center.

Lewis adduct **3** is stable below −50 °C, but upon warming to −20 °C, it reacts rapidly to produce a new vanadium complex in quantitative NMR yield. This complex, which is only stable below −10 °C (vide infra), was identified as **4** on the basis of multinuclear NMR spectra (obtained at −50 °C):[12] (i) the ^{29}Si NMR spectrum exhibits five resonances for the $c\text{-}C_6H_{11}Si$ groups (2:1:1:1:2), indicating that the metallasilsesquioxane framework of **4** is bisected by a mirror plane of symmetry; (ii) the ^{51}V resonance (δ 54.5) appears more than 700 ppm downfield from the starting vanadate,[13] and only one ^{29}Si resonance (for two Si) is broadened ($w_{1/2}$ = 35 Hz) by coupling to ^{51}V, consistent with alkyl transfer from

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(11) For **3**: ^1H NMR (500.1 MHz, C_7D_8, −50 °C) δ 2.00 (br m, 13 H), 1.55 (br m, 38 H), 1.10 (br m, 26 H), 0.44 (s, 27 H, $CH_2Si(CH_3)_3$), −0.36 (s, 6 H, $CH_2Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, C_7D_8, −50 °C) δ 27.50, 27.35, 27.21, 26.95, 26.85, 26.77 (CH_2), 23.25, 22.88, 22.78 (CH, 1:3:3), 3.48 ($CH_2Si(CH_3)_3$), 1.50 ($CH_2Si(CH_3)_3$); $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_7D_8, −50 °C) δ 0.662 ($CH_2Si(CH_3)_3$), −61.96 ($w_{1/2} = 40$ Hz), −68.18, −68.72 (3:1:3); ^{51}V NMR (131.54 MHz, C_7D_8, −50 °C) δ −705 ($w_{1/2} = 1800$ Hz); ^{17}O NMR (67.79 MHz, C_7D_8, −50 °C) δ +934 ($w_{1/2} = 800$ Hz).

(12) For **4**: ^1H NMR (500.1 MHz, C_7D_8, −50 °C) δ 3.82 (br s, 2 H, $VCH_2Si(CH_3)_3$), 2.11 (br m, 14 H), 1.60 (br m, 35 H), 1.21 (br m, 28 H), 0.46 (s, 18 H, $AlCH_2Si(CH_3)_3$), 0.08 (s, 9 H, $VCH_2Si(CH_3)_3$), −0.45 (d, J = 13 Hz, 2 H, $AlCH_2Si(CH_3)_3$), −0.51 (d, 2 H, J = 13 Hz, $AlCH_2Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, C_7D_8, −50 °C) δ 116 (br s, $w_{1/2} = 400$ Hz, $VCH_2Si(CH_3)_3$), 28.40, 28.13, 27.95, 27.65, 27.54, 27.32, 27.23, 27.09 (CH_2), 25.75, 24.39, 23.69, 23.40 (CH, 1:2:2:2), 3.32 ($AlCH_2Si(CH_3)_3$), 0.291 ($VCH_2Si(CH_3)_3$), −1.43 ($AlCH_2Si(CH_3)_3$); $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_7D_8, −50 °C) δ 7.24 ($VCH_2Si(CH_3)_3$), 0.85 ($AlCH_2Si(CH_3)_3$), −63.54 ($w_{1/2} = 35$ Hz), −67.74, −68.56, −68.65, −69.58 (2:1:1:1:2); ^{51}V NMR (131.54 MHz, C_7D_8, −50 °C) δ +54.5 ($w_{1/2} = 1800$ Hz); ^{17}O NMR (67.79 MHz, C_7D_8, −50 °C) δ +825 ($w_{1/2} = 850$ Hz).

(13) (a) ^{51}V resonances for **1** and $(Me_3SiCH_2)_3VO$ appear at δ −676 and +1205, respectively. Similar trends are seen for ^{51}V NMR data from other $R_n(OR)_{3-n}VZ$ (Z = NR or O) systems.[13b-d] (b) Preuss, F.; Ogger, L. *Z. Naturforsch.* **1982**, *37b*, 957–964. (c) Lachowicz, A.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1977**, *431*, 88–94. (d) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408–16.

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