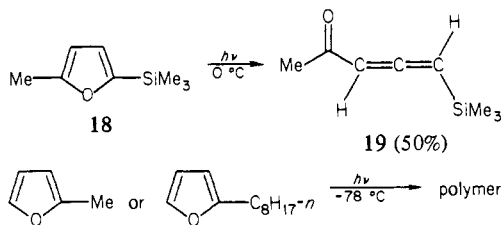
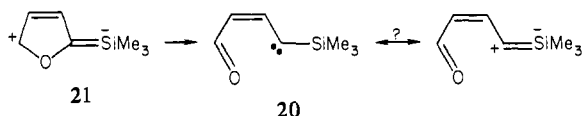


Further evidence of silicon control of furan photochemistry is found in the observation that irradiation of 5-methyl-2-(trimethylsilyl)furan (**18**) (*n*-pentane solution, 0 °C, 2 h, 45% completion) afforded a 50% yield of allenyl ketone **19** [ $^1\text{H}$  MR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.21 (s, 9 H), 2.15 (s, 3 H), 5.15 (d, 1 H,  $J = 6$  Hz), 5.45 (d, 1 H,  $J = 6$  Hz); IR  $\nu_{\text{C}=\text{C}}$  1945,  $\nu_{\text{C}=\text{O}}$  1680  $\text{cm}^{-1}$ ; calcd for  $\text{C}_8\text{H}_{14}\text{OSi}$   $m/e$  154.0814, measured  $m/e$  154.0815], while under similar (except lower temperature) conditions 2-methylfuran and 2-*n*-octylfuran afford mainly polymers and no major volatile products.



A possible explanation for the facility and cleanness of the photochemistry of silylfurans as opposed to alkylfurans may be found in the ability of silicon to stabilize a polar excited state (and ground state) through inclusion of resonance structures such as **20** in the resonance hybrid. Alternatively, it might be argued that the role of silicon is to stabilize carbene **21**. We intend to directly generate carbene **21** and similar systems to probe this point.



**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Dow Corning Corp. for support of this work.

(16) **17**:  $^1\text{H}$  NMR (pentane)  $\delta$  0.20 (s, 9 H), 0.31 (s, 9 H), 5.05 (s, 1 H), 9.80 (s, 1 H); IR (neat) 1920 and 1670  $\text{cm}^{-1}$ ; calcd for  $\text{C}_{10}\text{H}_{20}\text{OSi}_2$   $m/e$  212.10528, measured  $m/e$  212.10581.

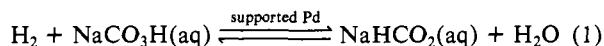
## Supported Palladium Catalysts for the Reduction of Sodium Bicarbonate to Sodium Formate in Aqueous Solution at Room Temperature and One Atmosphere of Hydrogen

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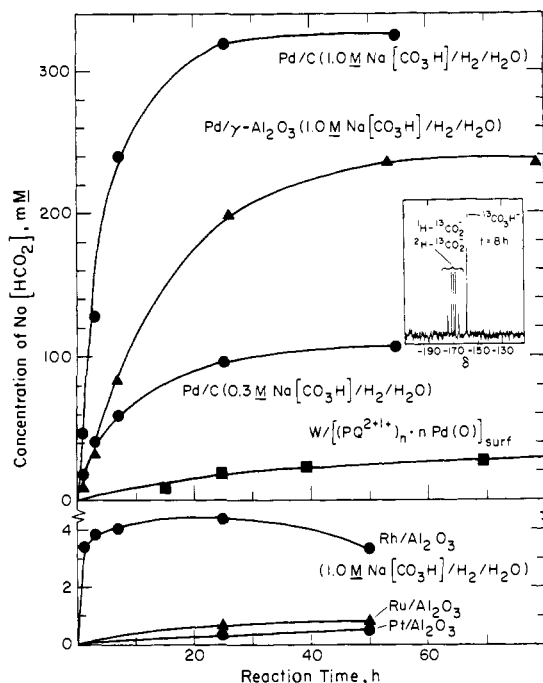
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We wish to report that the reduction of aqueous sodium bicarbonate,  $\text{NaCO}_3\text{H}$ , to aqueous sodium formate,  $\text{NaHCO}_2$ , can be effected at 298 K and 1 atm  $\text{H}_2$  using various forms of supported Pd as a catalyst for the equilibrium represented by eq 1.



We were prompted to begin this investigation by a report that a Pd/carbon catalyst would give a significant amount of formate (13 mM) from aqueous 0.3 M bicarbonate.<sup>1</sup> There has been some confusion in the literature concerning the thermodynamics for reaction 1. In particular, Pourbaix diagrams<sup>2</sup> would suggest that

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**Figure 1.** Concentration of  $\text{NaHCO}_2(\text{aq})$  vs. reaction time for various catalysts for the reduction of  $\text{NaCO}_3\text{H}(\text{aq})$  using an  $\text{H}_2$  purge. The inset is a  $^{13}\text{C}$  NMR for  $\text{H}_2$  reduction of 99%  $^{13}\text{C}$  0.3 M  $\text{NaCO}_3\text{H}$  in  $\text{D}_2\text{O}$  using 5% Pd/C at 8-h reaction time. Cf. also Figure 2b.

reaction 1 would not proceed to a significant extent. The extent to which the reaction is unfavorable cannot be very great, however, because there is evidence that the enzyme formate dehydrogenase will effect the process represented by equation 1.<sup>1,3</sup> The enzyme catalysis<sup>1,3</sup> of reaction 1 establishes that the reaction should proceed to approximately 50% conversion of  $\text{NaCO}_3\text{H}$  to  $\text{NaHCO}_2$  at 1 atm  $\text{H}_2$ . There is much interest in the mild reduction of  $\text{CO}_2$  and its aqueous equivalents, for a variety of fundamental and practical reasons. Heterogeneous Pd catalysts for the reaction represented by equation 1 have been studied previously, but the systems require elevated temperature and high pressure.<sup>4</sup> The enzyme catalysts do not work well at high ionic strength and are not durable.<sup>1</sup> There are a variety of reports claiming electrochemical reductions of  $\text{CO}_2$ , but none occur near the thermodynamic potential.<sup>5</sup> Photoelectrochemical efficiencies for the reduction of  $\text{CO}_2$  in aqueous solution are low.<sup>6</sup> The results reported herein suggest that photoreduction of  $\text{CO}_2$  in aqueous solution could be efficient, since the generation of  $\text{H}_2$  at semiconductor photocathodes has been shown to be efficient under visible light illumination.<sup>7</sup>

The reduction represented by equation 1 has been effected by using a variety of Pd-based catalysts (Table I and Figure 1). The typical procedure was to suspend 0.25 g of catalyst in 25 mL of an aqueous solution of  $\text{NaCO}_3\text{H}$  purged slowly with  $\text{H}_2$  gas or under static 1.7 atm  $\text{H}_2$ . The  $\text{NaHCO}_2$  concentration was followed

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Table I. Catalytic Reduction of Aqueous NaCO<sub>3</sub>H to NaHCO<sub>2</sub> at 298 K under H<sub>2</sub>

catalyst <sup>a</sup> (commercial source)	starting solution <sup>b</sup>	final NaHCO <sub>2</sub> concn, M (reaction time, h) <sup>c</sup>	total turnover no. <sup>d</sup>	initial turnover rate mol HCO <sub>2</sub> <sup>-</sup> /mol Pd/h
3% Pd on C (Johnson-Matthey, Type 1)	0.3 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.122 (90)	44	3.8
5% Pd on C (Johnson-Matthey, Type 2)	0.3 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.138 (90)	29	6.2
5% Pd on C (Johnson-Matthey, Type 3)	0.3 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.100 (90)	21	3.6
5% Pd on C (Johnson-Matthey, Type 2)	1.0 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.325 (54)	69	9.8
	0.3 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.106 (54)	23	3.8
	0.1 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.027 (54)	5.7	0.7
	0.03 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.011 (54)	2.3	0.3
	1.0 M Na <sup>13</sup> CO <sub>3</sub> H/H <sub>2</sub> purge <sup>e</sup>	0.285 (45)	60	
5% Pd on γ-Al <sub>2</sub> O <sub>3</sub> (Johnson-Matthey)	1.0 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.235 (53)	50	1.5
5% Pd on BaSO <sub>4</sub> (Alfa)	1.0 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.090 (50)	19	2.1
Pd black (Johnson-Matthey)	1.0 M NaCO <sub>3</sub> H/H <sub>2</sub> purge	0.198 (53)	2.1	0.02
W/(PQ <sup>2+/+/0</sup> ) <sub>n</sub> /Pd <sup>f</sup>	0.3 M Na <sup>13</sup> CO <sub>3</sub> H/H <sub>2</sub> purge <sup>g</sup>	0.048 (169)	480	5.0
5% Pd on C (Johnson-Matthey, Type 2)	1.0 M Na <sup>13</sup> CO <sub>3</sub> H/1.7 atm H <sub>2</sub>	0.53 (46) <sup>h</sup>	113	35
	1.0 M NaCO <sub>3</sub> H/1.7 atm H <sub>2</sub>	0.54 (46), 0.53 (24)	115	25

<sup>a</sup> Typically, 0.25 g of catalyst was suspended in 25.0 mL of the starting solution, unless noted otherwise. The catalysts were obtained from the indicated commercial source and used as received. Type 1 Pd/C has ~9–15 m<sup>2</sup> of Pd/g of catalyst; Type 2 Pd/C has ~22 m<sup>2</sup> of Pd/g of catalyst; and Type 3 Pd/C has ~50 m<sup>2</sup> of Pd/g of catalyst commercially obtained from Johnson-Matthey. <sup>b</sup> H<sub>2</sub>O solution except where noted. <sup>c</sup> NaHCO<sub>2</sub> measured by an enzyme assay at the indicated reaction time. <sup>d</sup> No. of HCO<sub>2</sub><sup>-</sup> ions produced per Pd added as catalyst. <sup>e</sup> 2.0 mL was the initial volume and contained 0.02 g of catalyst. This experiment corresponds to the <sup>13</sup>C NMR in Figure 2. <sup>f</sup> This catalyst was prepared as described in ref. 11: a coiled tungsten wire, ~13.2-cm<sup>2</sup> total surface area, was derivatized with 7 × 10<sup>-8</sup> mol/cm<sup>2</sup> of a polymer having 2+ monomer units, (PQ<sup>2+/+/0</sup>)<sub>n</sub>; PdCl<sub>4</sub><sup>2-</sup> was used as the source of Pd by reducing [(PQ<sup>2+/+/0</sup>·PdCl<sub>4</sub><sup>2-</sup>)<sub>n</sub>]. The total amount of Pd was ~5 × 10<sup>-7</sup> mol. <sup>g</sup> 5.0 mL was the initial volume, and D<sub>2</sub>O was the solvent. <sup>h</sup> 3.0 mL was the initial volume and contained 0.03 g of catalyst.

by withdrawing aliquots for HCO<sub>2</sub><sup>-</sup> determination (after filtering to remove the catalyst) using an enzyme assay<sup>8</sup> or by using <sup>13</sup>C, <sup>1</sup>H, or <sup>2</sup>H NMR.<sup>9</sup> When the mixture is purged with H<sub>2</sub> significant loss of CO<sub>2</sub> occurs, but the final ratio of HCO<sub>2</sub><sup>-</sup> to CO<sub>3</sub>H<sup>-</sup> is essentially unchanged by purging.

<sup>13</sup>C NMR spectroscopy has been used to unambiguously establish that HCO<sub>2</sub><sup>-</sup> is generated from reduction of the added NaCO<sub>3</sub>H. One of the key experiments is that catalyzed reduction of 99% <sup>13</sup>C-enriched NaCO<sub>3</sub>H in D<sub>2</sub>O using H<sub>2</sub> gas yields both H<sup>13</sup>CO<sub>2</sub><sup>-</sup> and D<sup>13</sup>CO<sub>2</sub><sup>-</sup>, as determined by nondecoupled <sup>13</sup>C NMR. The <sup>13</sup>C chemical shift is slightly different for H<sup>13</sup>CO<sub>2</sub><sup>-</sup> and D<sup>13</sup>CO<sub>2</sub><sup>-</sup> (Figures 1 and 2). The chemical shift for authentic H<sup>13</sup>CO<sub>2</sub><sup>-</sup> is the same as for the material made in a catalytic reduction, but the resonances and coupling constants for H<sup>13</sup>CO<sub>2</sub><sup>-</sup> are dependent on pH. Figure 2 shows the doublet for the H<sup>13</sup>CO<sub>2</sub><sup>-</sup> produced in H<sub>2</sub>O, under H<sub>2</sub> purge using 5% Pd on C. In this case, the integration of the <sup>13</sup>C resonances for the H<sup>13</sup>CO<sub>2</sub><sup>-</sup> and <sup>13</sup>CO<sub>3</sub>H<sup>-</sup> shows about a 1/1 ratio.<sup>9</sup> Further, a D<sub>2</sub>O solution of 0.3 M NaH<sup>12</sup>CO<sub>2</sub>/0.7 M Na<sup>13</sup>CO<sub>3</sub>H (99% <sup>13</sup>C-enriched bicarbonate) was exposed to catalysis conditions, 10 mg/mL of catalyst and a slow H<sub>2</sub> purge, and the <sup>13</sup>C NMR after 7 h showed the generation of significant D<sup>13</sup>CO<sub>2</sub><sup>-</sup> and H<sup>13</sup>CO<sub>2</sub><sup>-</sup> (Figure 2). The integration<sup>9</sup> showed a ratio of <sup>13</sup>C formate to <sup>13</sup>C bicarbonate of ~0.8/1.0. The NMR data establish that (1) formate is the only significant reduction product, no other <sup>13</sup>C resonances are observed, (2) the ratio of formate/bicarbonate under a slow purge of H<sub>2</sub> ultimately becomes ~1/1 by using the Pd-based catalysts, and (3) a mixture of formate and bicarbonate near the equilibrium composition rapidly scrambles a <sup>13</sup>C label and incorporates deuterium from D<sub>2</sub>O into the formate under catalysis conditions.

The reduction of NaCO<sub>3</sub>H by H<sub>2</sub> can be rapid; an initial rate of reduction from the data available at 1-h reaction time gives a turnover rate of at least ~35 HCO<sub>2</sub><sup>-</sup> ions produced per Pd atom per hour. This represents a lower limit on the activity, considering

that a fraction of the Pd is not accessible. Comparisons between the various catalysts are not easily made, since the accessibility to active Pd cannot be determined. Further, the experimental procedure used has not allowed accurate acquisition of initial rate data. The experimental error is estimated to be ±50%. The total turnover number has been shown to exceed 400. This, too, is a lower limit, since recovered catalysts have been demonstrated to be active. The activity of recovered catalysts is being investigated and will be reported in the full paper. All forms of Pd seem to be active; the Pd powder is not as active as the supported material presumably owing to the lower ratio of surface to bulk Pd. Under conditions where the Pd is active, similar catalysts based on Pt, Ru, or Ni fail to yield significant NaHCO<sub>2</sub> concentrations (Figure 1). Of the other catalysts tried, only Rh showed significant activity, but this was still well below the activity of Pd-based catalysts.

The most active Pd-based catalysts are able to raise the NaHCO<sub>2</sub> concentration to a value that increases with increased starting NaCO<sub>3</sub>H concentration. In the situations where the starting system is 1.0 M NaCO<sub>3</sub>H/1.7 atm H<sub>2</sub>, the HCO<sub>2</sub><sup>-</sup> concentration appears to go to ~0.54 M. The reaction as written in eq 1 does not proceed to completion. Indeed, a solution containing initially 0.7 M NaHCO<sub>2</sub> and 0.3 M NaCO<sub>3</sub>H exposed to catalysis conditions ultimately decays to a ~1/1 HCO<sub>2</sub><sup>-</sup>/CO<sub>3</sub>H<sup>-</sup> ratio with a slow H<sub>2</sub> purge. The decline in HCO<sub>2</sub><sup>-</sup> concentration accords well with the fact that Pd is a known catalyst for the decomposition of formate.<sup>10</sup> Solutions of 1.0 M Na<sup>13</sup>CO<sub>3</sub>H, 0.5 M H<sup>13</sup>CO<sub>2</sub><sup>-</sup>/0.5 M <sup>13</sup>CO<sub>3</sub>H<sup>-</sup>, or 0.3 M HCO<sub>2</sub><sup>-</sup>/0.7 M <sup>13</sup>CO<sub>3</sub>H<sup>-</sup> under 1.7 atm H<sub>2</sub> each yields an ~1.5/1 H<sup>13</sup>CO<sub>2</sub><sup>-</sup>/<sup>13</sup>CO<sub>3</sub>H<sup>-</sup> ratio (±20%) by <sup>13</sup>C NMR integration. Our data show that Pd-based catalysts equilibrate the H<sub>2</sub>/NaCO<sub>3</sub>H(aq)/NaHCO<sub>2</sub>(aq) system at 298 K to a formate/bicarbonate ratio of ~1/1 to ~1.5/1 under 1–1.7 atm H<sub>2</sub>. This accords well with results using enzymes<sup>1,3</sup> to catalyze the reaction given in eq 1.

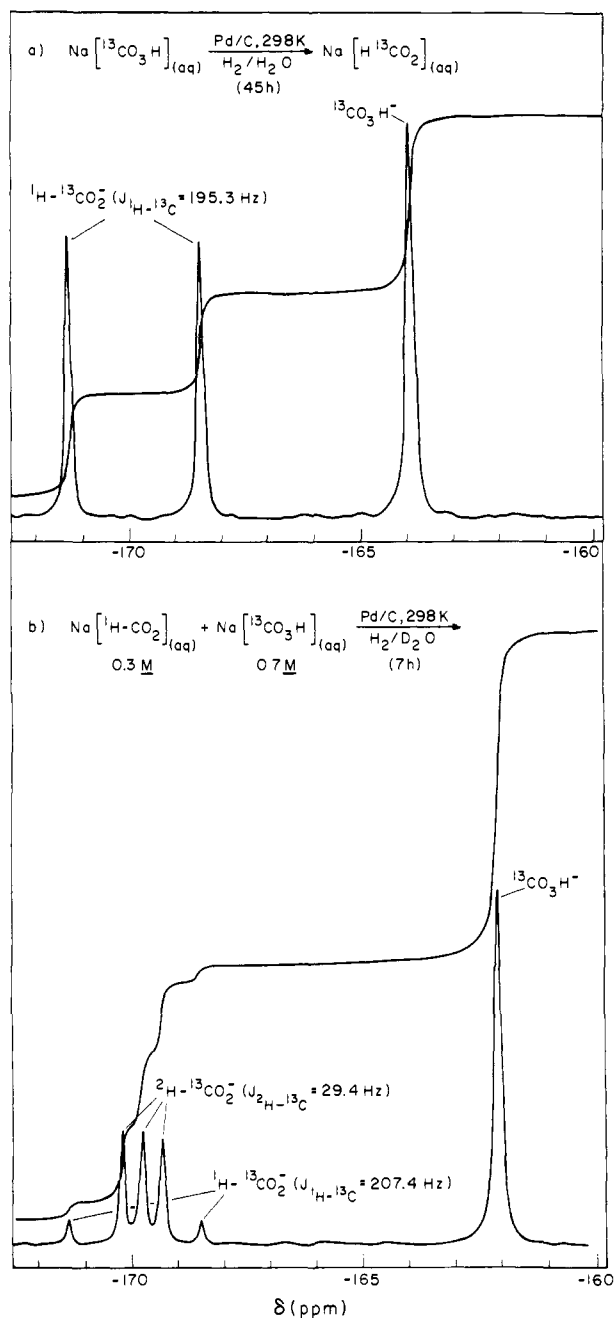
Our data are consistent with the conclusion that it is possible to reduce CO<sub>2</sub> at room temperature near the thermodynamic potential. Among the catalysts employed was Pd supported in a redox polymer, (PQ<sup>2+/+/0</sup>)<sub>n</sub>, confined to a W-electrode surface (Table I and Figure 1). This polymer has been shown<sup>11</sup> to be photoelectrochemically reduced in aqueous solution with good efficiency, and thus when impregnated with Pd, the polymer may be an electrode catalyst for the reduction of NaCO<sub>3</sub>H to NaHCO<sub>2</sub> near the thermodynamic potential. The initial rate of bicarbonate reduction in the experiments summarized by Table I indicates that the current density would be 1–35 μA/cm<sup>2</sup> at ~50 mV more negative than E<sup>0</sup>(NaCO<sub>3</sub>H/NaHCO<sub>2</sub>). Hopefully, the overall

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**Figure 2.**  $^{13}\text{C}$  NMR spectrum of reaction mixtures: (a) solution was initially 99%  $^{13}\text{C}$  1.0 M  $\text{NaCO}_3\text{H}$ , spectrum of reaction mixture at 20-h reaction time in the presence of 1 atm  $\text{H}_2$  at 298 K with 5% Pd/C as the catalyst; (b) initial solution was 0.3 M  $\text{NaHCO}_2$  and 0.7 M  $\text{Na}^{13}\text{CO}_3\text{H}$  in  $\text{D}_2\text{O}$ , spectrum is shown after 7-h exposure to catalysis conditions, 1 atm  $\text{H}_2$ , 298 K, 5% Pd/C catalyst. Chemical shifts are in ppm vs.  $\text{Si}(\text{CH}_3)_4$  using a  $\text{CH}_3\text{CN}$  external standard.

kinetics can be improved to achieve useful electrochemical rates.

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**Registry No.** Sodium bicarbonate, 144-55-8; sodium formate, 141-53-7; palladium, 7440-05-3.

## Gas-Phase Reactions of Group 8 Metal Hydride Ions ( $\text{FeD}^+$ , $\text{CoD}^+$ , and $\text{NiD}^+$ ) with Hydrocarbons

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Understanding the activation of C-H and C-C bonds by transition metals continues to be one of the most challenging problems in the field of catalysis.<sup>1</sup> Recent gas-phase studies of the reactions of atomic metal ions with hydrocarbons represent an approach to access the inherent reactivity of these ions in the absence of solvent or ligand interferences.<sup>2-12</sup> A logical extension of this research is to study the effects that small ligands bound to the metal center have on the gas-phase metal ion reactivity.<sup>2</sup> In this paper, we report the gas phase reactions of the first-row, group 8 transition-metal hydrides with various hydrocarbons.

Metal hydrides were formed in a complex experiment<sup>8</sup> using a Fourier transform mass spectrometer (FTMS) equipped with a pulsed inlet valve.<sup>9</sup> Reaction of laser-desorbed<sup>4-9</sup>  $\text{Fe}^+$  and  $\text{Co}^+$  with nitromethane or methylnitrite and  $\text{Ni}^+$  with methylnitrite yields a methoxy-metal moiety which decomposes by loss of formaldehyde under collisional activation<sup>6,7</sup> to form the corresponding metal hydride (reaction 1) in good yield.



The major primary reactions (>5%) of  $\text{FeD}^+$ ,  $\text{CoD}^+$ , and  $\text{NiD}^+$  with  $\text{H}_2$  and a variety of simple hydrocarbons are listed in Table I. Previously, H/D exchange reactions have been employed to indicate metal hydride character.<sup>5</sup> It is clear that not all hydride species will exchange, since  $\text{FeD}^+$  does not exchange with hydrogen despite its obvious hydride character.

Only  $\text{NiD}^+$  is observed to react with methane. Oxidative addition to the C-H bond is followed by loss of HD or  $\text{CH}_3\text{D}$  forming  $\text{NiCH}_3^+$  or  $\text{NiH}^+$ , respectively. This represents a surprising change in reactivity since  $D(\text{M}^+-\text{CH}_3)$  and  $D(\text{M}^+-\text{H})$  are considerably stronger for  $\text{Fe}^+$  and  $\text{Co}^+$  than for  $\text{Ni}^+$ ;<sup>3e</sup> yet both of these hydrides are unreactive with methane. With ethane, which has a slightly weaker C-H bond,  $\text{NiD}^+$  and  $\text{CoD}^+$  both react losing HD to form a  $\text{MC}_2\text{H}_5^+$  product in contrast to the bare metal ions which do not react with ethane.  $\text{NiD}^+$  and  $\text{CoD}^+$  react with propane to form metal-allyl products.  $\text{FeD}^+$ , however, reacts with propane forming only  $\text{FeC}_3\text{H}_7^+$  by a single HD loss. All three of the metal hydrides react with *n*-butane and 2-methylpropane but with differing product distributions. None of the ions show

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