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Registry No. Zn^{2+}, 23713-49-7; H_2TPPS_4, 35218-75-8; H_2O, 7732-18-5; glycine, 56-40-6; L-α-alanine, 56-41-7; L-valine, 72-18-4; L-phenylalanine, 63-91-2; L-tyrosine, 60-18-4; L-tryptophan, 73-22-3.

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Low-Temperature Reactions of Methane with Photoexcited Nickel Atoms

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We have been engaged recently in studies on the isolation and characterization of simple unligated alkylmetal hydrides.[1,2] These species can be prepared readily by photolysis of metal atoms in an inert-gas or neat alkane matrix and characterized by FTIR spectroscopy. In our earlier studies we were surprised to find that we were unable to characterize any species that could be attributed to an insertion product of nickel. We have now reinvestigated the reactions of nickel atoms with methane in both neat matrices and argon matrices using sensitive FTIR characterization,[3] and we find that nickel does indeed insert photolytically into a C–H bond of methane to yield CH_3NiH. Our earlier efforts to detect this species were unsuccessful because of the weak absorptions exhibited by this product.[4]

Experimental Section

A description of the multisurface matrix isolation apparatus has been reported previously.[3] Nickel atoms were obtained by vaporizing nickel metal (Mackay, 99.5%) from an alumina crucible enclosed in a resistively heated tantalum furnace over the range 1350–1500 °C. The temperature was measured with a microoptical pyrometer (Pyrometer Instrument Co.).

In a typical experiment, nickel atoms were codeposited with either methane (Matheson, 99.97%) or methane/argon (Matheson, 99.98%) onto a rhodium-plated copper surface over a period of 10 or 30 min, respectively. The copper block was maintained at 11–14 K by use of a closed-cycle helium refrigerator (Air Products, Displex Model CSW-202). Prior to deposition, the molar ratio of nickel/methane or nickel/methane/argon was measured with a quartz crystal microbalance mounted on the cold block. The molar ratios were 1/10 and 0/1/100 to 1.5/1.8/100, respectively. After deposition, the infrared spectrum of the matrix-isolated species was measured with an IBM IR-98 Fourier-transform infrared spectrometer. The frequencies were measured over the range 4000–300 cm^{-1} to an accuracy of ± 0.05 cm^{-1}.

The photolysis studies were usually carried out subsequent to deposition by exposure of the matrices to a focused 100-W medium-pressure short-arc Hg lamp. The typical exposure time was 10 min. A water filter with various Corning long-pass cutoff filters and a band filter, 280–360 nm, was used for the wavelength-dependent photolysis experiment. Carbon-13-enriched methane (Mound Facility, Monsanto, 99 atom % ^{13}C) and deuteriated methane (Icon Service, CD_4 99 atom %) were used in isotopic studies.

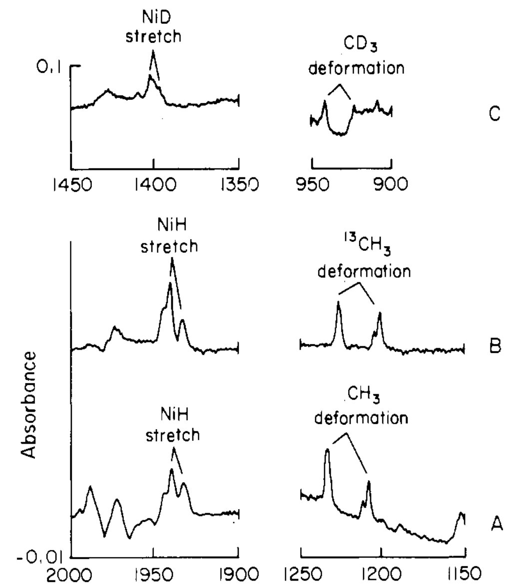

Figure 1. Isotopic study with FTIR specta of CH_3NiH (A), $^{13}CH_3NiH$ (B), and CD_3NiD (C) in methane matrices.

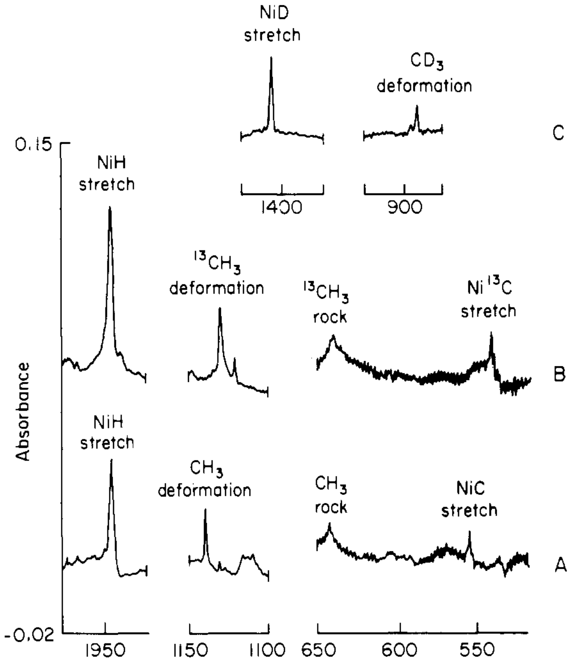

Figure 2. FTIR spectra of CH_3NiH (A), $^{13}CH_3NiH$ (B), and CD_3NiD (C) in argon matrices.

Table I. Measured Infrared Frequencies (cm^{-1}) for CH_3NiH, $^{13}CH_3NiH$, and CD_3NiD in Solid Methane and Solid Argon

	CH_3NiH		$^{13}CH_3NiH$		CD_3NiD	
vib mode	CH_4	Ar	$^{13}CH_4$	Ar	CD_4	Ar
NiC, $Ni^{13}C$ str	551.0	554.9	537.5	542.4		
CH_3, CD_3 rock		642.7		641.0		
CH_3, CD_3 def	1207.7	1120.3	1200.0	1120.4	923.0	891.9
	1233.3	1139.0	1226.4	1129.4	942.0	895.8
NiH, NiD str	1939.2	1945.1	1939.1	1945.3	1402.0	1406.8
CH_3, CD_3 str		2861.0		2855.8		
		2950.5		2940.4	2192.0	2197.5

Results and Discussion

The infrared spectrum of CH_3NiH was observed after UV irradiation of either a nickel/methane or nickel/methane/argon matrix. The stoichiometry of this insertion product and the vibrational mode assignments were confirmed by a nickel atom

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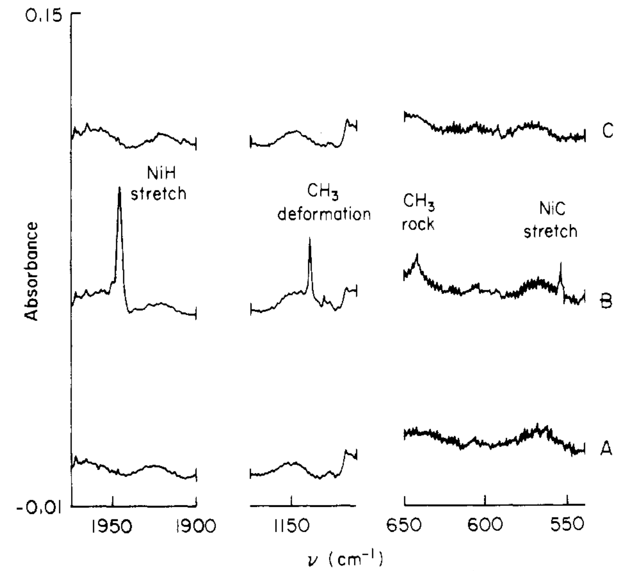

Figure 3. Photolysis study in an argon matrix (Ni/CH_4/Ar ≅ 0.7/1.8/100): (A) before photolysis; (B) after 10-min photolysis with 380 nm ≥ λ ≥ 280 nm; (C) after 10-min photolysis with λ ≥ 400 nm.

concentration study and molecular isotopic studies, respectively. Partial spectra of CH_3NiH, $^{13}CH_3NiH$, and CD_3NiD in methane and argon matrices are presented in Figures 1 and 2. In methane matrices the product absorptions are very weak and are split possibly due to matrix site effects.[5] The measured frequencies and assignments of these weak absorptions as well as those obtained in argon matrices are presented in Table I.

The observed splittings of the Ni–H stretch and methyl deformation in a methane matrix indicate a significant matrix–molecule interaction and appreciable population of two matrix sites. This may be compared to the case in an argon matrix, where the molecule is produced in essentially one site. Significant interaction of CH_3NiH with the methane matrix is also indicated by the large positive shift of the methyl deformation mode. The size of this shift from an argon matrix to a methane matrix (~95 cm^{-1}) is large when compared to similar shifts for iron and manganese (~-5 cm^{-1}) and is in the opposite direction. The magnitude of this shift suggests that methane acts as a weakly interacting ligand.

A photoreversible oxidative-addition/reductive-elimination reaction[6] was also observed in this study as depicted in Figure 3. Thus, in an argon matrix (Figure 3A) the insertion product CH_3NiH was formed after UV irradiation (Figure 3B) but λ ≥ 400 nm photolysis caused the complete disappearance of this species (Figure 3C):

$$CH_4 + Ni \underset{\lambda \geq 400\ \mathrm{nm}}{\overset{\mathrm{UV}}{\rightleftharpoons}} CH_3NiH$$

The observation of photoinsertion of atomic nickel into methane shows then that all of the metal atoms from manganese to zinc undergo photoinsertion into methane. The lack of photoinsertion for the first half of the 3d-transition-metal series[1] suggests that the photoinsertion product for these metals is not physically stable and reverts readily to methane and the respective metal atom.

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Registry No. CH_4, 74-82-8; Ni, 7440-02-0; CH_3NiH, 86392-32-7; $^{13}CH_3NiH$, 110638-26-1; CD_3NiD, 110638-27-2.

Supplementary Material Available: Figure showing the FTIR spectrum from 500 to 3500 cm^{-1} of a Ni/CH_4 reaction and photochemistry in an Ar matrix at 12 K (1 page). Ordering information is given on any current masthead page.

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Metal-Exchange Reactions between the Uranyl-18-Crown-6 Complex and Na^+ Ion in Propylene Carbonate

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In this paper we report a new aspect of crown ether kinetics: a metal-exchange reaction between the uranyl ion and sodium ion in the 18-crown-6 ether (L) complex

$$UO_2L^{2+} + Na^+ \rightleftharpoons UO_2^{2+} + NaL^+ \qquad (1)$$

in propylene carbonate (PC) medium ($[(C_2H_5)_4NClO_4]$ = 0.1 M).

Actually, kinetic studies on crown ether complexes have been quite sparse. The main results concern principally alkali-metal- and alkaline-earth-cation complexation (complex formation or decomplexation). These reactions have been the subject of great interest because of their suitability as models for biochemical processes. Only very few kinetic studies on crown ethers have focused on other metals or polyatomic units. For example Eyring et al.[1,2] have determined the complexation rate constant of Tl^+, Ag^+, and NH_4^+ cations with the 18-crown-6 ligand. The rates of all these complexation reactions are very fast. In particular, the rate of complexation of the Na^+ ion with 18-crown-6[1,3-7] in water or in various solvents is almost diffusion controlled. Our recent study[8] on the complexation of the 18-crown-6 ether with the uranyl ion has shown a formation rate constant several orders of magnitude lower than those normally encountered for alkali-metal or alkaline-earth cations complexed by the same ligand. Then kinetic measurements could be carried out by stopped-flow spectrophotometry.

It appears in all these kinetic studies that the short-range interactions are very important. In particular, the macrocycle ligand and the solvent molecules are competitors for the first coordination sphere of the cations.

Experimental Section

All chemicals were analytical reagent grade. The crown ether 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctane) and sodium perchlorate were purchased from Merck. Tetraethylammonium perchlorate and propylene carbonate were obtained from Fluka, and uranium perchlorate was purchased from Ventron GmbH. The perchlorate salts were dried under vacuum. PC was purified according to the method of Gosse;[9] all the solutions in PC contained after purification less than 100 ppm of H_2O. The concentration of the uranyl ion was determined by polarography.[10] The ionic strength was maintained constant at 0.1 M by addition of $(C_2H_5)_4NClO_4$.

The rates of the metal-exchange reaction were determined by means of a spectrophotometric technique. The stopped-flow spectrophotometer, a Durrum Gibson type equipped with a Datalab DL 905 transient recorder, was interfaced to an Apple II microcomputer. This system and the computer programs used have been previously described.[11] Reaction rates were followed at 290 nm and at 25.0 ± 0.1 °C. At this wavelength the greatest change in absorption between reagents and products was found. Kinetic runs were performed by mixing a UO_2L^{2+} solution ($[UO_2L^{2+}]_0 = 1.375 \times 10^{-4}$ M with an excess of L, 2×10^{-4} or 5×10^{-4} M, to ensure the complexation of the uranyl ion) with sodium perchlorate solutions in concentrations of 5×10^{-3}–5×10^{-2} M (after mixing). For

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