which can be readily isolated in 75% yield by solvent removal, extraction in hexane, and crystallization. The structure of this product (III) is very likely analogous to $Fe_4N(CO)_{12}H$, but the poor quality crystals were not suitable for X-ray crystallographic analysis. We are attempting to deprotonate and/or derivatize this cluster in order to clearly establish its structure.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to Du Pont Corp. for a Young Faculty Research Grant. We also gratefully acknowledge L. H. Pignolet and M. McGuiggan for assistance in the structural analyses and the NSF for partial support of our X-ray diffraction and structure-solving equipment (NSF Grant CHE77-28505).

Supplementary Material Available: A listing of the positional and thermal parameters derived from the crystallographic analyses (7 pages). Ordering information is given on any current masthead page.

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(20) IR (ν_{CO}) 2104 w, 2071 s, 2062 s, 2043 s, 2029 s, 2000 m, 1991 m, 1968 w, 1955 w (hexane); mass spectrum, *m/z* 713 (parent) followed by peaks corresponding to stepwise loss of all the ligands. Anal. Calcd: C, 20.29; H, 0.14; N, 1.97. Found: C, 20.32; H, 0.15; N, 1.97.

Methane Activation. Photochemical Reaction of Copper Atoms in Solid Methane

Geoffrey A. Ozin,* Douglas F. McIntosh, and
Steven A. Mitchell

Lash Miller Chemical Laboratories and Erindale College
University of Toronto, Toronto M5S 1A1, Canada

J. García-Prieto

Instituto Mexicano del Petróleo
México 14 D.F., México

Received November 14, 1980

The activation of saturated hydrocarbons is of wide-ranging chemical and technological significance.[1,2] Methane chemistry, in particular, presents an important and timely challenge with ramifications for the future development of natural gas conversion processes. We report here a photosensitized reaction (320 nm) of copper atoms in methane matrices at 12 K, which produces CuH, CH_3, $CuCH_3$, and H atoms by a mechanism which appears to involve the photolytic decomposition of the intermediate $HCuCH_3$. Barrett et al.[3] have observed a reaction of methane with Fe_2 molecules but not with Fe atoms, and Hauge et al.[4a] have found that photolysis during deposition of Fe/CH_4 vapors causes iron atom insertion products to form. Billups et al. just reported the photoinsertion of several metal atoms into methane.[4b] Neither V atoms nor V_2 molecules react with saturated hydrocarbons in low-temperature matrices.[5]

The absorption spectrum of copper atoms isolated in solid methane is shown in trace A of Figure 1, and the course of the photosensitized reaction is illustrated in traces B and C. Photoexcitation of Cu[6] or Ag[7] atoms isolated in rare-gas matrices promotes diffusion and aggregation of the metal atoms, characterized by approximately second-order kinetics during the early stages of nucleation (Scheme I). In contrast, 320-nm photolysis of Cu/CH_4 matrices results in a rapid *first-order* decay of the atomic absorption bands with no apparent growth of Cu_2 or higher copper clusters but with the appearance of broad absorption features near 350, 220, and <200 nm (Figure 1C). Further evidence for photochemical reaction of copper atoms in methane matrices was obtained from fluorescence studies, which showed the characteristic $^2D \rightarrow {}^2S$ fluorescence of rare-gas matrix-isolated copper atoms[8] to be completely quenched in the case of methane matrices (Scheme I).

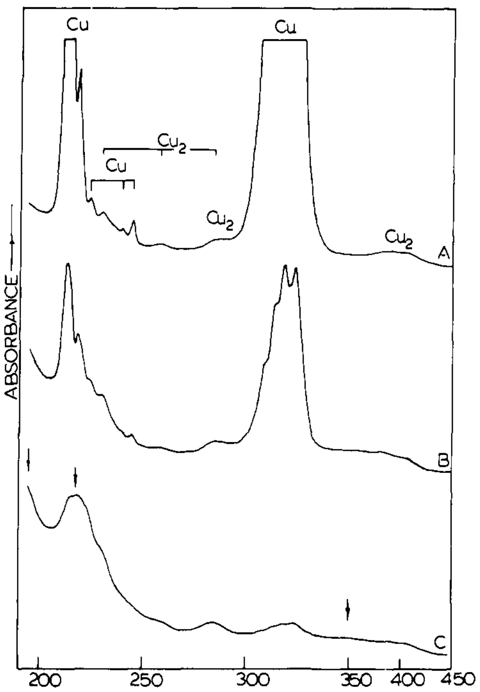

Figure 1. Absorption spectra of Cu atoms isolated in solid methane at 12 K ($Cu/CH_4 \simeq 1/10^4$), showing decay of the Cu atom bands and growth of new absorption features near 350, 220 and <200 nm as a result of 320-nm photolysis. (A) Freshly deposited matrix, (B) 1 min, 320-nm irradiation, (C) 15 min, 320-nm irradiation. Trace amounts of Cu_2 coisolated with Cu atoms are indicated. Arrows depict product absorptions (see text) which can be seen more clearly in higher density deposits.

Scheme I

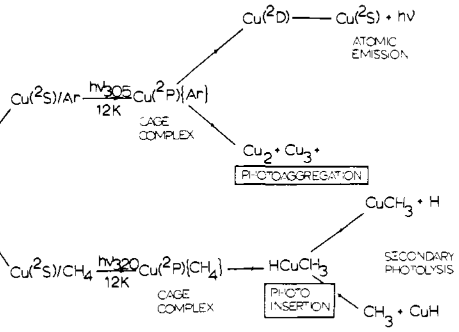

Figure 2 shows infrared spectra obtained at various stages during the Cu/CH_4 photochemical reaction, and Table I presents a summary of the major infrared bands found to grow in as a result of 320-nm copper atom photolysis. Additional bands observed below 600 cm^{-1} will be described in a separate paper. The strong bands at 1850 and 611 cm^{-1} are readily assigned to CuH[9] and CH_3[10,11] species, respectively, by comparison with known spectra.

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Table I. Cu/CH_4 Photoproducts and Infrared Frequencies (cm^{-1})

product[a,c]				
CuH	$CuCH_3$ (II)	$HCuCH_3$ (I)	CH_3	assignment[b]
			3171	$\nu(CH_3)$, (ref 11)
	2929			asym $\nu(CH_3)$
	2880			sym $\nu(CH_3)$
1850				ν(CuH); ν(CuD) 1333 cm^{-1}
		1697		ν(CuH); ν(CuD) 1229 cm^{-1}
			1396	i.p. $\delta(CH_3)$ (ref 10, 11)
	1344 1328 } [d]			asym $\delta(CH_3)$; asym $\delta(^{13}CH_3)$ 1338 and 1320 cm^{-1}
	1196			sym $\delta(CH_3)$; sym $\delta(^{13}CH_3)$ 1189 cm^{-1}
		1011		sym $\delta(CH_3)$; sym $\delta(^{13}CH_3)$ 1003 cm^{-1}; sym $\delta(^{12}CD_3)$ 786 cm^{-1}
			611	o.p. $\delta(CH_3)$ (ref 10, 11)

[a] 320-nm control photolyses of pure CH_4 at 12 K in the absence of Cu atoms showed none of the effects described in the text. [b] Band III in Figure 2 may be ascribed to a perturbed methyl radical by comparison with alkali metal-methyl halide matrix IR data (ref 15). [c] Bands associated with I and II were also observed at 433, 414, 351, and 275 cm^{-1} (see text). [d] Assigned to the asymmetric $\delta(CH_3)$ mode subject to either a site symmetry or a multiple trapping site effect.

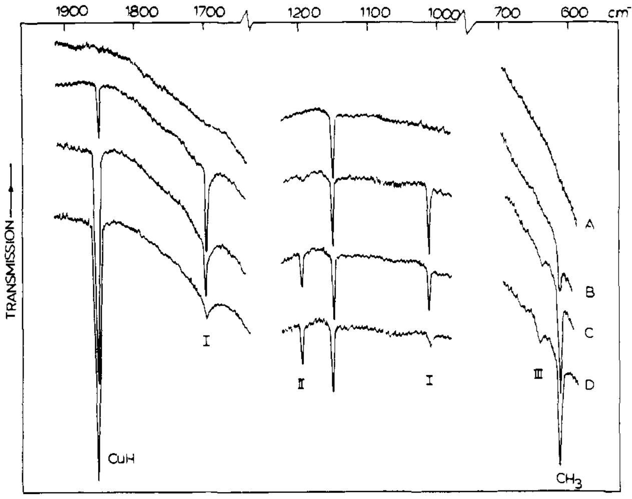

Figure 2. Infrared spectra of Cu/CH_4 $\simeq$ 1/10^4 matrices at 12 K, showing the effects of 320-nm photolysis. (A) Freshly deposited matrix, (B) 10 min, 320-nm irradiation, (C) 50 min, 320-nm irradiation, (D) 70 min, 320-nm irradiation. All regions of the IR spectrum were scanned. Only selected regions are illustrated in this figure.

The assignments were confirmed by isotopic substitution experiments involving CH_nD_{4-n} (where n = 0–4) matrices. The infrared bands not associated with CuH or CH_3 can be grouped into two categories, depending on whether they persist as final products or first grow in and then decay with further irradiation. Two bands in the latter category apparently associated with the same species are denoted I in Figure 2, in which the initial growth and subsequent decay behavior is illustrated. The species I band at 1697 cm^{-1} was found to shift to 1229 cm^{-1} in the case of CD_4 matrices and was invariant to $^{12}C/^{13}C$ substitution of methane. In addition, the spectrum for a 1:1 CH_4/CD_4 matrix was found to be a simple superposition of the CH_4 and CD_4 spectra. We therefore assign species I as a monohydride with 1697 cm^{-1} corresponding to ν_{Cu-H}, shifted to lower energy from the corresponding band of CuH at 1850 cm^{-1}. The species I band at 1011 cm^{-1} was found to be sensitive to both H/D and $^{12}C/^{13}C$ substitution of methane (Table I). These results strongly suggest that I is the Cu(II) species $HCuCH_3$, with the vibrational assignments listed in Table I. The frequencies and isotopic shifts of the species II bands are closely similar to those observed for isotopically substituted $LiCH_3$ molecules isolated in rare-gas matrices.[12] We therefore identify species II as $CuCH_3$, and list tentative assignments of the observed infrared bands in Table I.[13] A more detailed analysis of the infrared spectrum of $CuCH_3$ will be presented in the full paper. It is interesting to note that all of the products described above could also be produced in ~1:10 CH_4/Ar matrices.

The preliminary results of an ESR study of the Cu/CH_4 photochemical reaction are consistent with the above assignments. In particular, the characteristic spectrum of methyl radical is readily identified, and the assignment of I as the Cu(II) species $HCuCH_3$ is strongly supported both by the overall appearance of the spectrum, which is of the form expected for a randomly oriented $^2\Sigma^+$ axial system split by a $I = {}^3/_2$ ($^{63}Cu/^{65}Cu$, natural abundance 69%/31%) nucleus,[14] and the hyperfine pattern caused by the hydride, deuteride, or carbon-13 nucleus when using $^{12}CH_4$, $^{12}CD_4$, and $^{13}CH_4$ matrices, respectively. Interestingly, the ESR spectra reveal the presence of significant amounts of H atoms as photoproducts.

We feel that the overall photochemical reaction may be best described in terms of an initial insertion of an optically excited copper atom into a C–H bond of methane, followed by secondary photolysis of $HCuCH_3$ to form mainly CuH and CH_3 but also $CuCH_3$ and H atoms as illustrated in Scheme I. Matrix kinetic experiments designed to probe the mechanistic details of this important photochemical reaction are presently underway in this laboratory.

Acknowledgment. The generous financial assistance of the Natural Science and Engineering Research Council of Canada's Strategic Energy Programme is gratefully acknowledged. S.M. also acknowledges NSERC and Noranda for graduate scholarships. J.G.P. acknowledges the Instituto Mexicano del Petróleo for financial support during his leave of absence at the Lash Miller Chemical Laboratories.

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[13] In the case of Cu/CH_4, where the reactions were induced by broad band photolysis either during or after matrix formation, Billups et al. find infrared bands at 1855.7, 1200.1, 613.8, 433.9, and 417.4 cm^{-1}, which they assign to the species $HCuCH_3$. However, we prefer the assignments listed in Table I, for reasons explained in the text. Thus the products observed by Billups etal. include CuH (1855.7 cm^{-1}), $CuCH_3$(1200.1 cm^{-1}, 433.9 cm^{-1}, 417.4 cm^{-1}), and CH_3(613.8 cm^{-1}) but not $HCuCH_3$, although this latter species was observed as an intermediate in the present study.

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Reaction of Two-Coordinate Phosphorus Compounds with Group 3A Alkyls: A Novel Double Group Shift and Concomitant Cyclization

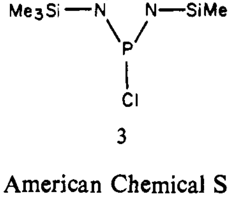
A. H. Cowley,* J. E. Kilduff, and J. C. Wilburn

*Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712*

Received November 6, 1980

The two-coordinate phosphorus compound **1** reacts with BCl_3 and Al_2Cl_6 to afford the heterocycles **3**[1] and **4**,[2] respectively. We

1,[3] R = R' = Me_3Si
2,[4] R = t-Bu; R' = Me_3Si



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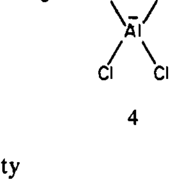

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