

pressure heads. These were constructed to allow purging with O₂, as well as sampling of the solution under reaction conditions during the course of the reactions. 2-Hexanone production was measured by GLC.

A typical catalytic reaction was run as follows: to a 250-mL Parr bottle were added 0.074 mmol of [Rh(CO)₂S'_n]₂BF₄ (prepared as earlier reported² and used immediately), 0.0171 g of Cu(NO₃)₂·2.5H₂O (0.074 mmol), 0.0219 g of NaCl (0.375 mmol—for the case in which a 5:1 mole ratio chloride/rhodium was desired), 0.41 mL of 0.36 M H₂SO₄ (0.148 mmol); as an ethanol solution prepared from aqueous concentrated H₂SO₄, 0.568 mmol of 2-heptanone, 45 mL of absolute ethanol, and 15 mL of 1-hexene (purged through alumina to remove peroxides). This mixture was purged 5 times with 60 psi of O₂, set to 40 psi of O₂, and the reaction initiated by placing in a 70 °C oil bath.

Preparation of RhCl₃(H₂O)₂·CH₃CH₂OH (II). Compound C was prepared for characterization studies most easily under 40 psi of O₂ at 70 °C by mixing 0.0514 g of [Rh(CO)₂Cl]₂ (0.132 mmol), 1.10 mL of 0.48 M HCl (in ethanol, 0.528 mmol), and 15 mL of ethanol. This produced a bright orange solution after a reaction overnight, from which C was isolated by rotovaping to dryness and drying in vacuo. *M_r* for H₄O₂Cl₃Rh calcd, 245; found, 226. Anal. Calcd for C₂H₁₀O₃Cl₃Rh: C, 8.24; H, 3.46; Cl, 36.50. Found: C, 8.41; H, 2.69; Cl, 37.17.

Determination of Acetone Production. (A) In Presence of 1-Hexene. The measurement of acetone produced in the initial stage of the Rh/Cu-catalyzed oxidation of 1-hexene with isopropyl alcohol as solvent was made by GLC as follows: To a 50-mL round-bottom flask were added to 0.159 g of RhCl₃·3H₂O (0.604 mmol), 0.137 g of Cu(NO₃)₂·2.5H₂O (0.589 mmol), and a stir bar. This was purged 20 min with O₂ at 40 °C and 30 mL of an O₂-purged, 9/1 (v/v) solution of isopropyl alcohol/1-hexene added to initiate the reaction. GLC's were recorded after 4, 8, 17, 25, and 40 min. The amount of acetone produced was determined by comparison of peak heights with standards at the same time under identical conditions. When this 1:1 Cu/Rh ratio was used, 0.5 mol of acetone was formed per mole of rhodium in the first 4-8 min. No further

production was observed. When a 2:1 Cu/Rh mole ratio was used, continuous, catalytic production of acetone was observed.

(B) In Absence of 1-Hexene. The catalytic production of acetone from the O₂ oxidation of isopropyl alcohol was observed when 1-hexene was excluded from the solutions. RhCl₃·3H₂O, Cu(NO₃)₂·2.5H₂O, and HClO₄ were all used as catalysts for this reaction. In a typical run, 0.0369 g of RhCl₃·3H₂O (0.140 mmol) and a stir bar were placed in a 15-mL round-bottom flask and purged 20 min with O₂ at 40 °C. Into this was syringed 7 mL of isopropyl alcohol, purged itself with O₂ at 40 °C, to initiate the reaction. Acetone production was measured as described above.

Titration of [Rh(CO)₂Cl]₂ with HOOH. Because the reaction of HOOH with [Rh(CO)₂Cl]₂ (A) is quite slow in ethanol, it was run at 40 °C. The visible spectrum of the intermediate, H₂[Rh(CO)Cl₂(OOH)] (B), is most clearly observed by first adding 1.0 equiv of HOOH, followed an hour later by 0.5 equiv. The first addition causes the reaction of much of the starting material A (which overlaps the band at 385 nm), so that after the second addition the band due to C at 385 nm is easily observable in the electronic absorption spectrum. Intermediate B is easily detected in the oxidation of A by HOOH by using FT IR. Since there is no overlap of the carbonyl bands of A and B, the intermediate is detected in the first addition of HOOH. HOOH was diluted in ethanol immediately before use. Aqueous dilution causes the addition of too much H₂O, which retards the reaction considerably.

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Registry No. O₂, 7782-44-7; Cu(NO₃)₂, 3251-23-8; NaCl, 7647-14-5; [Rh(CO)₂Cl]₂, 14523-22-9; [RhCl₃(H₂O)₂·CH₃CH₂OH], 85236-98-2; HOOH, 7722-84-1; 1-hexene, 592-41-6; 2-hexanone, 591-78-6; chloride, 16887-00-6.

Activation of Methane with Metal Atoms at 10 K without Photolysis

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Abstract: Codeposition of methane with metal atoms at 10 K leads to reaction with Al atoms but not with Mg, Ca, Ti, Cr, Fe, Co, Ni, Pd, Cu, Ag, Au, Ga, In, or Sn. The unusual reactivity of Al is ascribed to its ²P radical character, coupled with comparatively high Al-H and Al-C bond strengths.

Activation of alkanes by small "naked" nickel clusters has been accomplished as low as -130 °C.¹ Clean metal surfaces of other group 8 metals have shown similar high reactivities at relatively low temperatures.² Also, it has been reported that Zr atoms react with alkanes as low as -196 °C.³

Under matrix isolation conditions of 10-50 K (-263 to -223 °C) no evidence of reaction of bare metal atoms or clusters with alkanes has been found, although many attempts have been made. Ozin and co-workers have studied V atoms in a variety of alkane media in the 10-50 K range.⁴ Likewise, we have carried out similar studies with Ni atoms and other metals.

Photolytic activation of alkanes using metal atoms is quite different, however. Gas-phase M*-alkane reactions have been

known for many years.⁵ And recently this approach has been extended to matrix-isolated metal atoms in frozen methane and ethane.^{6,7} Billups and co-workers⁶ reported photolytic activity of Mn, Fe, Co, Cu, Zn, Ag, and Au atoms with CH₄. Ozin and co-workers⁷ reported activity for Cu atoms with both CH₄ and C₂H₆ (C-H cleavage only).⁷

We have recently reported unusually high activities of certain metal atoms with CH₃Br at 10 K, especially Al and Ga, and attributed this to the low ionization potentials of these atoms coupled with their high M-Br bond strengths.⁸ Note that no photolytic activation was necessary. Likewise, Hauge, Kauffman, and Margrave have elucidated the spontaneous reaction of Al and Ga atoms with H₂O.⁹

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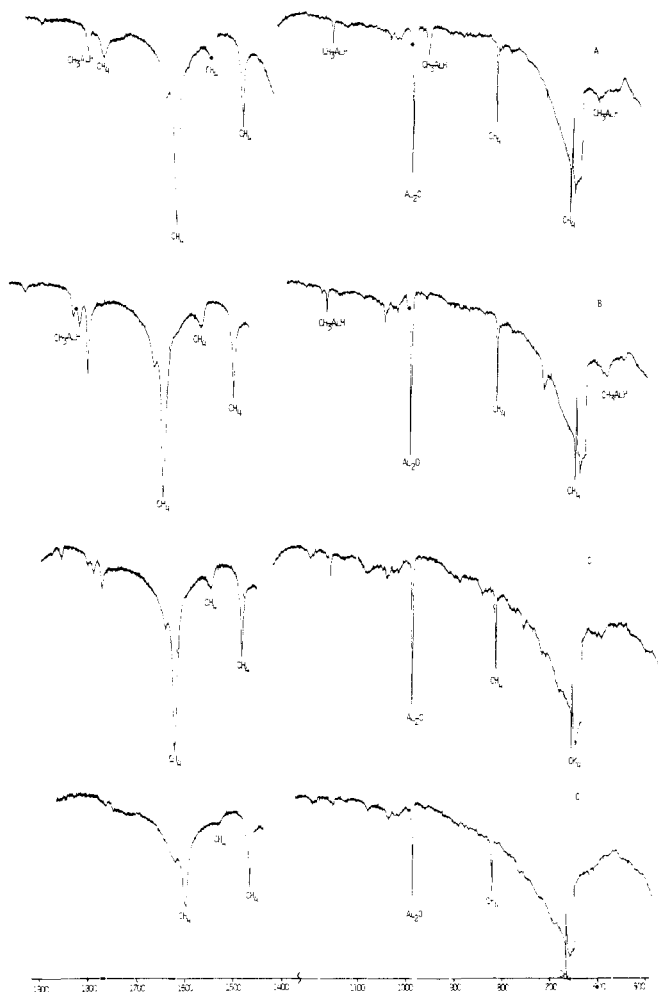


Figure 1. A. Aluminum atoms codeposited with 100-fold Excess of pure CH₄. B. After 1-h photolysis. C. After 3-h photolysis. D. After annealing at 30 K for 1 min.

This background led us to consider what properties of metal atoms may be necessary for 10 K reactions to occur with CH₄ without photolysis. We decided to survey some of the catalytically important transition-metal atoms as well as main-group atoms for activity with CH₄ (at 10 K without photolysis). Our survey led to one simple observation: Al atoms react but Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Pd, Cu, Ag, Au, Zn, Sn, Pb, Ga, and In do not. Furthermore, we have observed photolytic reactivity for one previously unstudied atom.

Results

Aluminum. Figure 1A illustrates the spectrum obtained when a 1000-fold excess of pure CH₄ is codeposited with Al atoms. The absorption of 1777 cm⁻¹ can be assigned to $\nu_{\text{Al-H}}$ although not diatomic Al-H which absorbs at 1593 cm⁻¹.¹⁰ The absorptions at 962, 615, and 579 cm⁻¹ can be assigned to C-H bending modes; it is possible the 615-cm⁻¹ band is due to the free methyl radical.¹¹ Photolysis of the matrix for 1 h caused additional $\nu_{\text{Al-H}}$ and δ_{CH_3} bands to appear (Figure 1B). The original bands did not change appreciably. However, prolonged photolysis (Figure 1C) caused an additional $\nu_{\text{Al-H}}$ band to appear and several other δ_{CH_3} bands to appear but with simultaneous decreases in the original bands. These results suggest that upon codeposition only a portion of the

Table I. Bands Observed in CH₄/Al and CD₄/Al Reactions (without and with Photolysis)^a

reactant/ metal	proposed species	$\nu_{\text{Al-H}}$, cm ⁻¹	$\delta_{\text{sym}}(\text{CH}_3)$, cm ⁻¹	$\delta_{\text{asym}}(\text{CH}_3)$, cm ⁻¹
CH ₄ /Al	H-Al-CH ₃	1777	579, 615 ^b	972
CD ₄ /Al		1275	575, 553, 519	960, 885
CH ₄ /Al ^c	H-Al(CH ₃) ₂	1764, 1746	732, 615 ^d	1165, 1042
	H ₂ AlCH ₃ [?]	1828	?	?
CH ₄ /Ga ^c	H-Ga-CH ₃	1723, 1710	965, 612 ^b	1269
	(no product without photolysis)			

^a All experiments were carried out at 10 K with 1000:1 excesses of methane to metal. ^b Could be free $\cdot\text{CH}_3$.¹¹ ^c After 1-h photolysis with an unfiltered 140-W medium-pressure mercury UV lamp. ^d The 615-cm⁻¹ band grew in intensity upon photolysis which supports the idea that a radical reaction is promoted by UV.

Al atoms react, and more complete reaction is forced by short photolysis.¹² Prolonged photolysis causes the destruction of the original species with the production of more new species. Likewise, annealing (Figure 1D) caused Al-H bands to almost disappear, which is probably due to association and band broadening.

Experiments with CD₄/Al and CH₄/CD₄/Al indicated that the products were mainly one methyl/one hydrido species. Thus, a 1:1 mixture of CH₄/CD₄ with Al yielded a spectrum that was very nearly a direct combination of the separate CH₄ and CD₄ spectra.

Gallium. Gallium did not insert or break the C-H bond without UV photolysis. Upon photolysis $\nu_{\text{Ga-H}}$ bands at 1723 and 1710 cm⁻¹ appeared and δ_{CH_3} bands at 1269, 965, and 612 cm⁻¹. Prolonged photolysis caused a slight increase in these absorptions. Experiments with CH₄/CD₄ indicated that only one methyl and one hydrido group were involved. This suggests that CH₃GaH is formed upon photolysis and it is stable toward photolytic decomposition.

Indium. This metal atom was unreactive during deposition and upon photolysis.

Other Metals. Metals listed previously were all unreacted upon codeposition with CH₄ at 10 K. Photolytic activity was observed with those previously reported.^{6,7}

Discussion

Strict assignment of bands is difficult, but the literature is helpful. In the absence of donor solvents $\nu_{\text{Al-H}}$ in R₂AlH compounds is in the 1750–1790-cm⁻¹ range,¹³ with [Al(CH₂H₅)₂]₃ absorbing at 1777 cm⁻¹. Other studies show that Al(CH₂H₅)₂ and Al(CH₃)₂ have $\nu_{\text{Al-H}}$ at 1780 cm⁻¹¹⁴ and $\nu_{\text{Al-D}}$ for Al(CH₂H₅)₂ at 1290 cm⁻¹.¹³ Furthermore, although diatomic Al-H absorbs at a low value of 1593 cm⁻¹,¹⁰ "free" AlH₃ is estimated to have $\nu_{\text{Al-H}}$ in the 1850–1900-cm⁻¹ range.¹⁵ Also relevant are the $\nu_{\text{Al-H}}$ and $\nu_{\text{Ga-H}}$ values observed for matrix-isolated HOAlH (1743 cm⁻¹) and HOGaH (1670 cm⁻¹).⁹

Examination of several X-Al(CH₃)₂ and X-Al(CD₃)₂ derivatives indicates that strong δ_{CH_3} bands appear at 1212, 720, and 588 cm⁻¹ and 1010, 980, 950, 680, and 595 cm⁻¹, respectively.¹⁶ Since the bands observed in our experiments with CH₄ and CD₄ do not match with these but are in a range consistent with δ_{CH_3} absorptions in general, we conclude that Al(CH₃)₂ and Al(CD₃)₂ are not the primary products even though $\nu_{\text{Al-H}}$ is consistent. Thermodynamically these compounds would not be favored since the formation of Al(CH₃)₂ from 2CH₄ and Al would be endothermic by 8 kcal/mol.¹⁷ However, the formation of

(12) Low concentrations of Al atoms still led to reaction, indicating that Al atoms rather than (Al)_x clusters are the reacting species.

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