The Reaction of Zinc, Cadmium, and Mercury Atoms with Methane: Infrared Spectra of the Matrix-Isolated Methylmetal Hydrides

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Abstract: The methylmetal hydride compounds of zinc, cadmium, and mercury have been formed by the insertion of the excited metal atom into methane and trapped in an argon matrix. The excitation of the zinc, cadmium, or mercury atom required to promote insertion can be effected through the use of a heated microwave discharge source of the metal by the action of its resonance radiation or by irradiation into the $^3P_1$ metal excited state. The methylmetal hydride compounds have been characterized by infrared spectroscopy and their identities authenticated by ^2H and ^{13}C enrichment. The mechanism of insertion has been investigated by selective photolysis studies of the matrix-isolated reactants. The insertion product formed by the reaction of excited mercury atoms with ethane has also been studied.

Introduction

The role of mercury photosensitization in the area of alkane functionalization catalysis is one that has received recent attention.[1,2] The primary process involves the homolytic cleavage of an alkane C–H bond by a mercury atom in the $^3P_1$ excited state, with the resultant formation of alkyl radicals and hydrogen atoms.[3,4] Studies of a range of alkane hydrocarbons toward Hg in the $^3P_1$ excited state[5] have shown the collisional quenching behavior to be consistent with an activation barrier in the order of 1000–1500 cm^{-1} (12–18 kJ mol^{-1}) for the chemical reaction of Hg($^3P_1$) with the C–H bond in methane. The reaction of excited zinc[6–7] and cadmium[8–10] atoms with alkane hydrocarbons has also been studied in the gas phase. In these cases, the reactions give alkyl radicals along with the metal hydride. The activation energy barrier for the reaction of Cd($^3P_1$) with methane has been estimated as 114 kJ mol^{-1}.[11]

We recently reported[12] the trapping and characterization of the dihydride ZnH_2, suggested by gas phase studies,[13] to be the intermediate formed in the reaction of excited zinc atoms with dihydrogen. A relatively long-lived insertion complex has been suggested as an intermediate in the reaction of Zn($^1P_1$) with methane by a very recent gas phase study,[7] and it was hoped therefore that a matrix study would make it possible to detect and identify this species. It was also hoped that, through experiments employing selective photolysis of the matrix-isolated reagents, information could be obtained concerning the nature of the excited state required for the insertion reaction to take place and comparisons drawn with the information available from studies carried out in the gas phase.

The technique of matrix isolation is ideally suited to such a study, having previously been employed to investigate the insertion products formed by reaction of the late 3d transition metals with methane.[14–18] These earlier studies included one reference[14] to the isolation of CH_3ZnH, formed by photolysis of zinc atoms trapped in a solid methane matrix, and a second reference[18] to the formation of CH_3HgH by 249-nm KrF laser irradiation of mercury atoms trapped in a methane-doped argon matrix. Matrix-isolation studies of CH_3MgH and CH_3AlH have also been reported.[19–22]

The vibrational spectra of the dimethylmetal compounds have been considered in detail,[23,24] and with the recent report of the infrared spectra of the matrix-isolated dihydrides of zinc, cadmium, and mercury,[12,25,26] it was of interest to explore the bonding in the monomethylmetal hydrides, as reflected in

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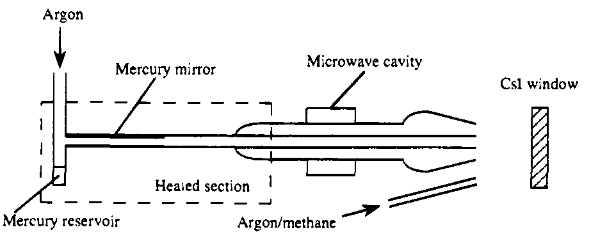

Figure 1. Schematic diagram of the mercury atom and argon/methane deposition apparatus.

comparisons involving the vibrational spectra of the species MH_2, CH_3MH, and $(CH_3)_2M$.

The compound CH_3HgH is also of current interest following recent reports of its preparation by the reduction of aqueous solutions of CH_3HgCl by sodium tetrahydroborate.[27-30] The compound has been characterized in solution at low temperature by its NMR spectrum, as well as by its mass spectrum and infrared spectrum recorded in the range 3200−600 cm^{-1}.

Experimental Section

The use of the microwave-powered reactive resonance lamp as a source of excited zinc or cadmium atoms has been described previously,[12] and the lamp is shown schematically in Figure 1. Excited mercury atoms were obtained in an analogous fashion by heating a mercury reservoir (Aldrich, 99.9995%) to a temperature of 40−50 °C. The excited atoms with argon carrier gas (BOC, Research Grade) were codeposited with a 2% methane (BOC, Research Grade) in argon mixture on a CsI window cooled to *ca.* 12 K. Typical deposition rates were 1.0−1.5 mmol/h for each gas sample, continued over a period of 2−3 h. Following deposition, the samples were subjected to broad-band photolysis using the output from an Oriel 500-W medium-pressure mercury arc in conjunction with a water filter for periods of between 2 and 4 h. The effects of selective photolysis were investigated using a Pyrex filter ($\lambda > 290$ nm), a soda filter ($\lambda > 310$ nm), a high-energy band pass filter (Oriel, $\lambda > 400$ nm); and interference filters (Oriel) at 313 nm (fwhh 16 nm) and 254 nm (fwhh 10 nm). Infrared spectra were recorded in the range 4000−400 cm^{-1} with a Mattson Galaxy FTIR spectrometer with 0.5-cm^{-1} resolution and an accuracy of ±0.2 cm^{-1}. The region 400−200 cm^{-1} was investigated using a Perkin-Elmer 580B dispersive spectrophotometer with 1.4-cm^{-1} resolution. UV−vis spectra of the matrix deposit were obtained by replacing the two outer CsI windows of the matrix shroud by quartz to increase the transmission of light of short wavelength. The central window was kept as CsI because of its superior thermal conductivity at low temperatures. The UV−vis spectra were recorded on a Perkin-Elmer-Hitachi Model 330 spectrophotometer. Isotopically enriched samples of methane ($^{12}CD_4$ and $^{13}CH_4$: CDN Isotopes, 99 atom % in each case) were used as supplied. Ethane (BOC, 99.0%) was purified by fractional condensation *in vacuo*.

Results

Infrared spectra for the products of the reactions of zinc, cadmium, and mercury atoms with methane will be reported in turn.

Table 1. Infrared Absorptions (cm^{-1}) Observed following the Codeposition and Subsequent Photolysis of Excited Zinc Atoms/Argon and Methane/Argon Mixtures

$Zn/^{12}CH_4/Ar$	$Zn/^{13}CH_4/Ar$	$Zn/^{12}CD_4/Ar$	assignment
3027.5	3018.4	2262.6[a]	CH_4
2919.8	2915.7	*b*	CH_3ZnH
1955.0	1955.0	*b*	HZnOH
1870 sh	1870 sh	1357.2	ZnH_2
1866.1	1866.1	1344.7[c]	CH_3ZnH
1657.1	1657.1	*b*	Zn_2H
1623.8	1623.8	1623.8	H_2O
1607.7	1607.7	1607.7	
1589.6	1589.6	1589.6	
1493.9	1493.9	1087.5	ZnH
1467.4	1464.0	*b*	C_2H_6
1438.9	1433.1	1072.0	C_2H_4
1305.1	1297.4	993.2[a]	CH_4
1225.8	1225.8	1225.8	SiO
1179.3	1169.9	921.1	CH_3ZnH
948.1	943.3	718.6	C_2H_4
822.0	*b*	*b*	C_2H_6
736.2	*b*	542.2	C_2H_2
689.4	684.9	530.5[d]	CH_3ZnH
686.8	682.5	527.9	
630.5	630.5	454 sh	ZnH_2
617.4	612.5	452.7	CH_3
566.5	552.5	516.1	$CH_3{}^{64}ZnH$
565.1	550.8	514.7	$CH_3{}^{66}ZnH$
563.9	549.4	513.2	$CH_3{}^{68}ZnH$
442.6	442.4	317.2	CH_3ZnH

[a] Bands observed at 2997.9, 1287.1, and 1030.6 cm^{-1} are due to $^{12}CHD_3$. [b] Band too weak to be observed or obscured by other absorptions. [c] A band observed at 1865.1 cm^{-1} may be assigned to CD_3ZnH. [d] A band observed at 570.6 cm^{-1} may be assigned to CD_2HZnD.

Zinc. The infrared spectrum of the matrix formed by codeposition of Zn/Ar and CH_4/Ar samples revealed new product bands, the observed frequencies of which are listed in Table 1. Weak bands due to HZnOH, ZnH_2, Zn_2H, and ZnH appeared at 1955.0, 1870, 1657.1, 1493.9, and 630.5 cm^{-1}; these have been identified previously.[12] Simple hydrocarbon products, C_2H_2, C_2H_4, and C_2H_6, present in low concentration, were inherent in such experiments.[31-33] A weak band at 1225.8 cm^{-1} arose from SiO from the quartz discharge tube,[34] while an absorption at 617.4 cm^{-1} was due to the methyl radical.[35]

New infrared bands were observed at 1866.1, 1179.3, a doublet at 689.4/686.8, 566.5, and 442.6 cm^{-1}; all were observed to increase in intensity by a factor of approximately two following broad-band photolysis for 4.5 h. Such photolysis led, in addition, to a marked growth of the infrared features attributable to ZnH_2, but to the destruction of those due to the species Zn_2H and ZnH, as had been observed previously.[12] The region above 2000 cm^{-1} displayed bands attributable to water and methane,[36,37] along with a sharp band at 2919.8 cm^{-1} that was seen to increase on photolysis. The band centered near 566.5 cm^{-1} revealed, on closer examination, a triplet with components at 566.5, 565.1, and 563.9 cm^{-1} having relative intensities appropriate to ^{64}Zn, ^{66}Zn, and ^{68}Zn isotopes in natural abundance.

Experiments using photolysis at selected wavelengths indicated that there was no observable increase in the intensity of the new infrared bands following irradiation with light having $\lambda > 310$ nm, whereas irradiation with light of $\lambda > 290$ nm brought about an increase in their intensity.

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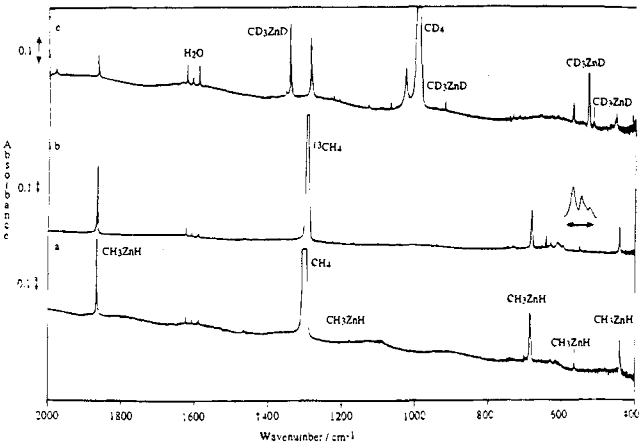

Figure 2. Infrared spectra of argon matrices following broad-band photolysis: (a) matrix containing Zn and $^{12}CH_4$; (b) matrix containing Zn and $^{13}CH_4$ (the band centered at 552.5 cm^{-1} shown expanded, the arrow represents 5 cm^{-1}); and (c) matrix containing Zn and CD_4.

The experiments were repeated using d_4-methane and ^{13}C-methane; the spectra of the matrices following photolysis are shown in Figure 2, and the corresponding frequencies for the normal and isotopically enriched species are given in Table 1. The small ^{13}C shifts observed for the bands at 689.4 and 566.5 cm^{-1} and the large deuterium shift for the feature at 1866.1 cm^{-1} are noteworthy. The low-frequency band at 442.6 cm^{-1} is seen to shift to 317.2 cm^{-1} when using CD_4 as measured with the grating spectrometer. The reaction of zinc with CHD_3 present in the CD_4 sample gave rise to new bands at 1865.1 and 570.6 cm^{-1}.

Cadmium. Experiments analogous to those described for zinc were also performed to investigate the insertion of cadmium atoms into methane. An infrared feature at 1753.5 together with a doublet at 604.6/601.7 cm^{-1} is attributable to CdH_2;[12] these, as well as a band at 1339.4 cm^{-1} identifiable with CdH,[12] were observed on deposition, along with new features at 1760.5, 687.3/685.4, 508.6, and 433.2/430.1 cm^{-1}. The intensities of the new infrared features were observed to increase approximately 8-fold following photolysis for a period of 3.5 h, as can be seen by comparing parts a and b of Figure 3. Photolysis also caused an increase in the absorption due to the dihydride, while CdH was seen to be destroyed, in keeping with previous studies.[12] Photolysis also gave rise to an infrared feature at 1836.9 cm^{-1} due to HCdOH,[12] and to a new band in the higher frequency region, *viz.* at 2928.5 cm^{-1}.

Selective photolysis revealed that irradiation with light of wavelength near 313 nm or of $\lambda > 290$ nm caused an increase of these new infrared features, whereas no such increase was observed following irradiation with light of $\lambda > 400$ nm. We were not able to quantify the effect of photolysis intensity on product band absorbances owing to the variation in the metal atom concentration from one sample to another.

The experiments were repeated using d_4-methane and ^{13}C-methane to obtain spectroscopic information about the isotopically enriched products. The relevant spectra are illustrated in Figure 3 and the frequencies given in Table 2. Comparable photochemical growth rates were observed for the deuterium-substituted products.

A UV–vis spectrum of the condensate following deposition revealed a band at 312 nm which decreased in intensity following selective irradiation using the Pyrex filter.

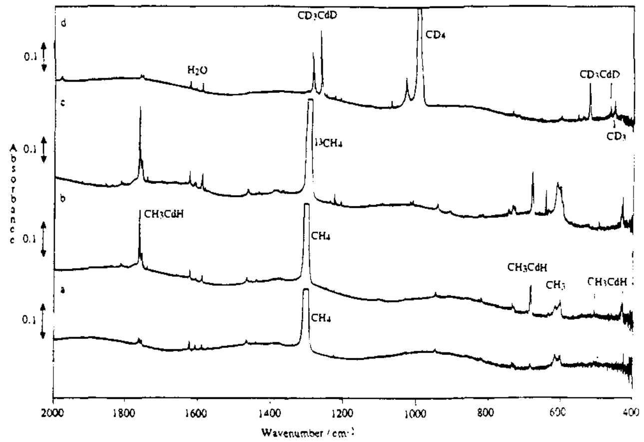

Figure 3. (a) Infrared spectrum of the deposit formed by cocondensing Cd (from a microwave discharge source) with $^{12}CH_4$ in an argon matrix. Infrared spectra of argon matrices following broad-band photolysis of (b) matrix containing Cd and $^{12}CH_4$, (c) matrix containing Cd and $^{13}CH_4$, and (d) matrix containing Cd and CD_4.

Table 2. Infrared Absorptions (cm^{-1}) Observed following the Codeposition and Subsequent Photolysis of Excited Cadmium Atoms/Argon and Methane/Argon Mixtures[a]

$Cd/^{12}CH_4/Ar$	$Cd/^{13}CH_4/Ar$	$Cd/^{12}CD_4/Ar$	assignment
2928.5	2923.6	*b*	CH_3CdH
1836.9	1836.9	*b*	HCdOH
1760.5	1760.5	1264.4[c]	CH_3CdH
1753.5	1753.5	*b*	CdH_2
1739.5	1739.5	1250.4	*d*
1339.4	1339.4	974.4	CdH
687.3	683.2	523.6[e]	CH_3CdH
685.4	681.3	521.9	
617.4	612.5	452.7	CH_3
604.6	604.6	*b*	CdH_2
601.7	601.7	*b*	
508.6	494.9	465.3	CH_3CdH
433.2	432.7	310.6	CH_3CdH
430.1	429.8		

[a] Bands due to CH_4, C_2H_2, C_2H_4, C_2H_6, H_2O, and SiO, which are given in Table 1, were also observed but are omitted here. [b] Band too weak to be observed or obscured by other absorptions. [c] A band observed at 1759.3 cm^{-1} may be assigned to CD_3CdH. [d] These weak features cannot be assigned with certainty but are probably due to a methane complex of CdH_2. [e] A band observed at 554.2 cm^{-1} may be assigned to CD_2HCdD.

A series of experiments were carried out to investigate the effect of increasing the methane concentration of the matrix, from approximately 1 to 50 mol % methane as a proportion of the total quantity of argon. This increase was observed to have little effect on the yield of the insertion species, but it did cause the infrared bands to broaden and shift in frequency, different vibrational modes being affected to different extents. As an example, the band at 1760.5 cm^{-1} for a matrix doped with 1% methane shifted to 1748.2 cm^{-1} for a matrix doped with 50% methane, while the doublet at 687.3/685.4 cm^{-1} became an unresolved, broad feature centered at 684.1 cm^{-1}.

Mercury. The infrared spectrum of the deposit formed by the codeposition of excited mercury atoms/argon and methane/argon mixtures also indicated the presence of new product bands. Infrared absorptions at 1895.3 and 773 cm^{-1} (a shoulder) may be assigned to HgH_2, based on agreement with the infrared spectrum reported previously[26] for this molecule in a matrix-isolated state and with the results of discharge experiments performed with $Hg/H_2/Ar$ mixtures in this laboratory. A new set of infrared features that grew in unison following broad-band photolysis was observed at 2921.2, 1955.3, 1424.7, 1191.8, 779.8/777.9, 534.0, and 526.5 cm^{-1}. The infrared spectra of this species and of the corresponding deuterium- and ^{13}C-enriched derivatives are shown in Figure 4; the relevant frequencies are listed in Table 3.

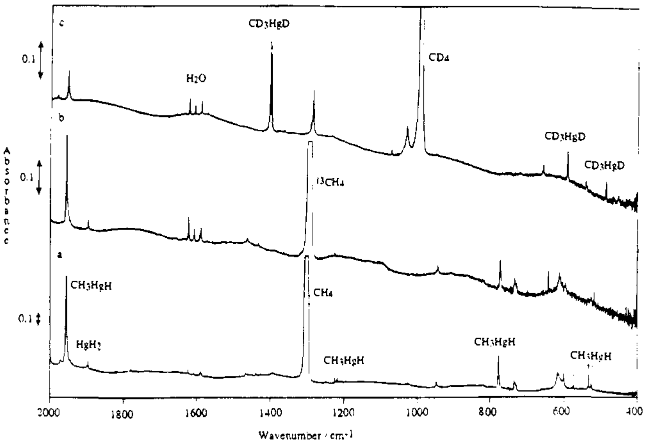

Figure 4. Infrared spectra of argon matrices following broad-band photolysis: (a) matrix containing Hg and $^{12}CH_4$; (b) matrix containing Hg and $^{13}CH_4$; and (c) matrix containing Hg and CD_4.

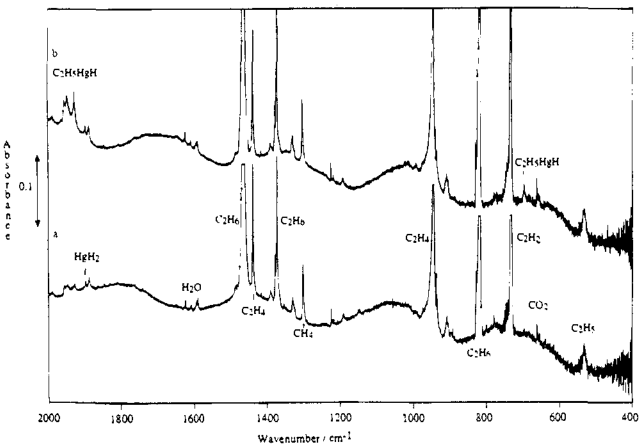

Figure 5. (a) Infrared spectrum of the deposit formed by cocondensing mercury, ethane, and argon at 12 K and (b) infrared spectrum following broad-band photolysis.

The infrared feature at 578.3 cm^{-1} assigned in Table 3 to the species HHgOH, formed by insertion of Hg* into H_2O, has been authenticated by separate experiments involving water-doped argon matrices.[38]

Experiments using selective photolysis indicated that irradiation of the deposit with light near 254 nm resulted in an increase in the intensity of the bands associated with the insertion product.

Infrared examination of the reaction between excited mercury atoms and ethane indicated, on deposition of an argon matrix, bands attributable to CH_4, C_2H_2, and C_2H_4, along with a weak, broad feature centered at 533 cm^{-1} which is due to the ethyl radical.[39] The spectrum of the matrix sample following deposition also revealed a broad absorption in the Hg−H stretching region, from which bands centered at 1954.8, 1946.8, and 1926.8 cm^{-1} were observed to develop following broad-band photolysis. A band at 698.4 cm^{-1} was seen to exhibit the same photolysis behavior. The spectra are shown in Figure 5 and the infrared frequencies are given in Table 4.

Discussion

The infrared features that have been observed on deposition and to increase following broad-band photolysis of the matrix deposit, as described in the preceding section, will be shown to arise from a monomethylmetal hydride species formed by the insertion of an excited metal atom into one of the C−H bonds of methane. The mechanism of this insertion process will be discussed. In the case of mercury, the competition between insertion into one of the C−H bonds and insertion into a C−C bond of ethane will also be examined.

Table 3. Infrared Absorptions (cm^{-1}) Observed following the Codeposition and Subsequent Photolysis of Excited Mercury Atoms/Argon and Methane/Argon Mixtures[a]

Hg/$^{12}CH_4$/Ar	Hg/$^{13}CH_4$/Ar	Hg/$^{12}CD_4$/Ar	assignment
2921.2	2917.1	2127.2	CH_3HgH
1955.3	1955.0	1404.0, 1400.4[b]	CH_3HgH
1895.3	1895.5	1363.0	HgH_2
1424.7	*c*	1041 sh	CH_3HgH
1191.8	1184.4	*c*	CH_3HgH
779.8	774.8	593.5[d]	CH_3HgH
777.9	773.6	592.1	
773 sh	*e*	*c*	HgH_2
617.4	612.5	452.7	CH_3
601.5	597.1		*f*
578.3	*c*	*c*	HHgOH
534.0	518.1	487.0	CH_3HgH
526.5	526.5	374.5	CH_3HgH

[a] Bands due to CH_4, C_2H_2, C_2H_4, C_2H_6, H_2O, and SiO, which are given in Table 1, were also observed but are omitted here. [b] A band observed at 1953.6 cm^{-1} may be assigned to CD_3HgH. [c] Band too weak to be observed or obscured by other absorptions. [d] A band observed at 658.8 cm^{-1} may be assigned to CD_2HHgD. [e] Band obscured by absorption due to CH_3HgH. [f] Unidentified infrared feature with no counterpart in the Hg/CD_4/Ar experiment.

Table 4. Infrared Absorptions (cm^{-1}) Observed following the Codeposition and Subsequent Photolysis of Excited Mercury Atoms/Argon and Ethane/Argon Mixtures[a]

Hg/C_2H_6/Ar	assignment	Hg/C_2H_6/Ar	assignments
1954.8	C_2H_5HgH	1330.9	*b*
1946.8	C_2H_5HgH	909.8	*b*
1926.8	C_2H_5HgH	698.4	C_2H_5HgH
1895.5	HgH_2	663.4	CO_2
1886.1	?	533.0	C_2H_5

[a] Bands due to CH_4, C_2H_2, C_2H_4, C_2H_6, H_2O, and SiO, which are given in Table 1, were also observed but are omitted here. [b] Bands due to unknown species which did not increase on photolysis and therefore are not associated with the mercury insertion product.

Assignment of the Infrared Spectra. The monomethylmetal hydride molecule may adopt two geometries, namely linear at the metal (C_{3v}) or bent (C_s). For such a molecule with C_{3v} symmetry, eight infrared-active vibrational fundamentals are to be expected, four non-degenerate (a_1) and four doubly degenerate (e). A lowering of symmetry to C_s lifts the degeneracy of the e modes and results in two components for each such mode which should, in principle, give rise to separate infrared absorptions. Although some of the bands which are assigned to the monomethylmetal hydride in Tables 1−3 are indeed split, this splitting is in the order of 2−3 cm^{-1} which is more likely to arise from matrix-site splitting[40] than from a nonlinear C−M−H skeleton. The splitting of the δ(M−C−H) modes associated with the species CH_3MnH and CH_3FeH isolated in solid methane was reported to be 9 and 7 cm^{-1}, respectively, and led to the conclusion that these molecules have a bent C−M−H skeleton.[15] That the molecule CH_3MH (M = Zn or Cd) has a linear C−M−H skeleton with C_{3v} symmetry overall is supported by *ab initio* calculations.[41,42]

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With the geometry of the molecule thus established, the vibrational fundamentals observed in infrared absorption may be assigned by reference to the effects of isotopic substitution, and through comparisons with the vibrational spectra of the corresponding $(CH_3)_2M$ and MH_2 molecules (M = Zn, Cd, Hg), as well as with the infrared spectra of other methylmetal hydride species.[12,14,18,19,23-26]

For experiments involving the insertion of a zinc or cadmium atom into a molecule of either $^{12}CH_4$ or $^{13}CH_4$, the high-frequency region associated with the C−H stretching modes shows one weak band which grows on photolysis. The relative weakness of the band compared with other associated features is expected and in keeping with the behavior of similar species, such as CH_3MgH.[19] The band may be assigned to the symmetric (a_1) ν(C−H) mode by virtue of the small shift observed on isotopic substitution of ^{13}C for ^{12}C. The corresponding antisymmetric mode (e), along with both modes for the deuteriated species, is presumably masked by other stronger absorptions. Billups *et al.*,[14] in the study of CH_3ZnH isolated in solid methane, did not observe any ν(C−H) absorption in the infrared spectrum, presumably because of masking by broad methane absorptions. In the experiments involving mercury we observe very good agreement with the previously determined values for the symmetric (a_1) ν(C−H) mode for the molecules CH_3HgH and CD_3HgD,[18] and in addition, the value of 2921.2 cm^{-1} we find for CH_3HgH is close to that (2929 cm^{-1}) obtained from the GC/FTIR spectrum.[27] However, the band observed at 2990 cm^{-1} in our experiments did not grow with the CH_3HgH bands on photolysis and its assignment[18] is open to question.

The bands observed at 1866.1 (Zn), 1760.5 (Cd), and 1955.3 cm^{-1} (Hg) for the products of the reactions involving CH_4 may be assigned to the ν(M−H) mode of the monomethylmetal hydride species. As expected, the band is perturbed little or not at all by ^{13}C substitution but is shifted 1−2 cm^{-1} by replacement of CH_3 by the CD_3 group. The frequency of the corresponding ν(M−D) mode gives H/D ratios of 1.3877, 1.3924, and 1.3927/1.3962 for M = Zn, Cd, and Hg, respectively, as expected for a vibration involving primarily motion of the hydrogen atom. The frequency of 1866.1 cm^{-1} for ν(Zn−H) is to be compared with the value of 1845.8 cm^{-1} quoted by Billups *et al.*[14] Such a perturbation is not unexpected with the change from the less polarizable (Ar) to the more polarizable (CH_4) matrix medium. As noted earlier, a shift of 12.3 cm^{-1} is observed for ν(Cd−H) with the switch from a matrix consisting of 1% methane to one consisting of 50% methane. The frequencies of the metal−hydrogen and −deuterium stretching modes of CH_3HgH and CD_3HgD are again in very close agreement with the previously reported values,[18] while the GC/FTIR frequency[27] of 1969/1943 cm^{-1} is also in accord with the value of 1955.3 cm^{-1} we obtain. The observed trend in the value of the ν(M−H) stretching mode—notably the marked increase in the ν(Hg−H) frequency—is due to the lanthanide contraction and relativistic effects which also give rise to short Hg−H bonds, as discussed by Pyykkö.[43]

In the infrared region 1100−1400 cm^{-1} associated with both the symmetric and antisymmetric deformation modes of the methyl group, only the $\delta_{sym}(CH_3)$ mode of CH_3ZnH could be detected, and this at 1179.3 cm^{-1}. The observed H/D ratio of 1.2803 compares with the value of 1.287 found for CH_3MgH.[19] The $^{12}C-^{13}C$ shift for the $\delta_{sym}(CH_3)$ mode, expected to lie in the approximate range 8−12 cm^{-1},[44] is observed in fact to be 9.4 cm^{-1}, thereby endorsing the assignment. Billups *et al.*[14] assign a feature at 1069.5 cm^{-1} to a methyl motion of CH_3ZnH isolated in a solid methane matrix; in the light of our results, this must now be questionable. In close agreement with previous workers,[18] we observe the $\delta_{sym}(CH_3)$ mode of CH_3HgH at 1191.8 cm^{-1} with the ^{13}C counterpart appearing at 1184.4 cm^{-1}, a reasonable shift of 7.4 cm^{-1}. The corresponding band for CD_3HgD is quoted at 1024.5 cm^{-1} in the previous study;[18] although we do observe such a band in our experiments, its intensity did not increase on photolysis and it was also to be found in experiments involving zinc or cadmium. A band in this position would, furthermore, give a H/D ratio of 1.163 which is very low for such a motion. Unfortunately, we were unable to observe any deuterio analogue for the $\delta_{sym}(CH_3)$ mode, our attempts presumably being thwarted by the inherent weakness of the band. As regards the antisymmetric deformational mode, we were able to observe only that of the methylmercury hydride molecule. A very weak, broad feature at 1424.7 cm^{-1} was observed to grow on photolysis, thereby confirming the tentative assignment of Legay-Sommaire *et al.*[18] The corresponding band for CD_3HgD is observed as a shoulder at *ca.* 1041 cm^{-1}, giving an H/D ratio of approximately 1.369.

The strong infrared absorption associated with the degenerate CH_3 rocking mode is easily identified for all three monomethylmetal hydride species, *viz.* at 689.4/686.8 (Zn), 687.3/685.4 (Cd), and 779.8/777.9 (Hg). The shift in frequency following ^{13}C substitution is in good agreement with that of 4 cm^{-1} reported for CH_3MgH.[19] The frequency of the $\varrho(CH_3)$ mode of CH_3ZnH compares with the value of 689.1 cm^{-1} obtained by Billups *et al.*,[14] and the frequency of the corresponding mode of CH_3HgH is also in agreement with the previously reported values.[18,27] The higher frequency found for $\varrho(CH_3)$ in the case of CH_3HgH may be predicted by reference to the infrared spectra of the dimethylmetal compounds.[24] The average frequencies of the two vibrations associated with the $\varrho(CH_3)$ modes ν_{10} (e_{1d}) and ν_{14} (e_{2d}) are 655.5, 665, and 739.5 cm^{-1} for the molecules $(CH_3)_2Zn$, $(CH_3)_2Cd$, and $(CH_3)_2Hg$, respectively.

The assignment of the metal−carbon stretching mode is also assisted by recourse to the vibrational spectra of the dimethylmetal compounds. The average frequency of the symmetric and antisymmetric metal−carbon stretching modes is 564.9, 505.4, and 533.9 cm^{-1} for the zinc, cadmium, and mercury compounds, respectively. We observe bands at 566.5 cm^{-1} for CH_3ZnH, 508.6 cm^{-1} for CH_3CdH, and 534.0 cm^{-1} for CH_3HgH. The excellent agreement with the values foretold by the dimethylmetal compounds, the isotopic shifts, which are wholly consistent with such a vibrational mode, and the observation of splitting associated with naturally occurring zinc isotopes, in sum, leave little doubt that these bands originate in the metal−carbon stretching mode. Billups *et al.*[14] have assigned a band at 447.1 cm^{-1} to the ν(Zn−C) fundamental of CH_3ZnH, which is shown here, in fact, to be due to the hydrogen bending mode (*vide infra*). The authors of the previous study of CH_3HgH also reported a band at 534.1 cm^{-1}, but because they did not obtain a ^{13}C isotopic shift, nor were they able to observe the corresponding feature for CD_3HgD (the band lying outside their spectrometer range), they were unable to determine whether it should be assigned to the metal−carbon stretching or to the hydrogen bending mode. The assignment to the former may now be made with certainty.

The hydrogen bending mode, δ(C−M−H), remains the only vibration still to be assigned. The infrared spectrum displayed by the product formed from the reaction of zinc atoms with methane has a band at 442.6 cm^{-1} which displays the appropri-

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Table 5. Observed Infrared Absorptions (cm^{-1}) for the Monomethylmetal Hydrides, CH_3MH (M = Zn, Cd, or Hg)

CH_3ZnH	CH_3CdH	CH_3HgH	assignment	description of vibrational mode
2919.8	2928.5	2921.2	$\nu_1(a_1)$	$\nu_{sym}(C-H)$
1866.1	1760.5	1955.3	$\nu_2(a_1)$	$\nu(M-H)$
1179.3	*a*	1191.8	$\nu_3(a_1)$	$\delta_{sym}(CH_3)$
566.5 565.1 563.9	508.6	534.0	$\nu_4(a_1)$	$\nu(M-C)$
a	*a*	*a*	$\nu_5(e)$	$\nu_{asym}(C-H)$
a	*a*	1424.7	$\nu_6(e)$	$\delta_{asym}(CH_3)$
689.4 686.8	687.3 685.4	779.8 777.9	$\nu_7(e)$	$\varrho(CH_3)$
442.6	433.2 430.1	526.5	$\nu_8(e)$	$\delta(C-M-H)$

[a] Not observed.

ate photolysis behavior. If this is the δ(C−M−H) mode, however, its frequency is well removed from the value of 630.5 cm^{-1} associated with the corresponding bending mode, ν_2, of ZnH_2.[12] That such a shift is reasonable and arises predominantly through the greater mass of the methyl group compared with hydrogen may be shown by calculation. Using the calculated structure and the full infrared data available for the different isotopomers of ZnH_2, and predicting the frequencies of the infrared-silent modes using the calculated shifts $\nu_1-\nu_3$,[12] it is possible to generate an harmonic force field for the ZnH_2 molecule.[45] The C−Zn−H fragment of monomethylzinc hydride may then be modeled using a Zn−C distance of 1.93 Å, based on the structure determined for the gaseous $(CH_3)_2Zn$ molecule by electron diffraction,[46] and the calculated harmonic force field for ZnH_2. The results of this calculation predict for CH_3ZnH a ν(Zn−C) mode at 587 cm^{-1} and a δ(C−Zn−H) mode at 463 cm^{-1}. The reasonable agreement of the calculated with the observed Zn−C stretching frequency indicates that the transfer of the force field and the neglect of the internal motions of the methyl group are reasonable approximations, and so shows that the frequency of the skeletal bending mode should be in the vicinity of 450 cm^{-1}.

For the mercury insertion product, the intensity of the δ(C−M−H) band was seen to be much weaker in comparison with the other spectral features, so that, for example, it is less intense than the ν(Hg−C) absorption, this being the reverse of the situation for CH_3ZnH and CH_3CdH. Such behavior is not unexpected, however, when it is noted that the bending mode, ν_2, of the HgH_2 molecule is much weaker in infrared absorption than is the antisymmetric stretching mode, ν_3,[26] a pattern quite different from that exhibited by the corresponding zinc and cadmium compounds.[12] The band observed at 526 cm^{-1} by Legay-Sommaire *et al.*[18] may now be assigned to this vibrational mode.

The infrared spectrum arising from the product formed through the reaction of an excited atom of zinc, cadmium, or mercury with methane has thus been shown to be entirely consistent with a linear monomethylmetal hydride molecule derived from insertion of the excited metal atom into one of the C−H bonds of methane. The observed infrared frequencies of the methylmetal hydride species are gathered together in Table 5.

Mechanism of Insertion. The reaction between methane and the metal atoms of Group 12 has been extensively studied in the gas phase, as outlined in the Introduction.[3−10] A theoretical study of the reactions of methane with both zinc and cadmium atoms in their ^1S, ^3P, or ^1P electronic states has also been reported.[41,42] For the reaction involving zinc atoms, Castillo *et al.* calculate that, in its ^1S ground electronic state, the atom is not capable of activating the methane molecule, a result in accord with the results of Billups *et al.*[14] relating to the cocondensation of thermal zinc atoms with methane, and which disclosed no new features in the infrared spectrum of the deposit. Castillo *et al.* further stated that, for insertion into a C−H bond of methane to take place, the zinc atom requires energy. Excitation to the ^1P state allows for spontaneous insertion into the methane molecule to form the CH_3ZnH complex. This product may then dissociate, without activation barriers, to the products CH_3 + ZnH or CH_3Zn + H if energized by at least 267 or 290 kJ mol^{-1}, respectively. By contrast, excitation to the ^3P state presents an interaction between the metal and the methane molecule which is initially repulsive and, only after a barrier of 75 kJ mol^{-1} has been surmounted, is it possible to achieve a stable configuration of the $^3A'$ excited state of the CH_3ZnH complex (with a bent C−Zn−H skeleton). The authors find, in conclusion, that Zn(^3P) cannot activate the C−H bond of methane in matrix-isolation experiments, a result which, they state, accords with the experimental experience of Billups *et al.*[14] The calculations relating to the reaction of cadmium atoms with methane lead to similar findings. In this case, however, the metal atom in the ^1P state is unable spontaneously to break a C−H bond of methane, being opposed by a 72.4 kJ mol^{-1} barrier. An endothermic process then leads, without activation barriers, to the formation of CH_3 + CdH or CH_3Cd + H. A cadmium atom in the ^3P state has been calculated to undergo reaction with methane by initially forming a C_{3v} face-on Cd(^3P)−H_3CH van der Waals exciplex;[47] it then faces a barrier (113 kJ mol^{-1}) to insertion into a C−H bond of the methane molecule to give a stable, bent CH_3CdH intermediate in an electronically excited (3A′) state. The van der Waals exciplex has been characterized by gas phase studies,[48] while a study of the reaction between Cd(^3P_J) and methane over a range of temperatures has estimated the activation energy barrier at 114 kJ mol^{-1}.[11]

The gas phase reaction between methane and zinc[49] or cadmium[50] in the $^3P_1$ excited state contrasts sharply with the reaction between dihydrogen and these metals, even though the exothermicities of the reactions are essentially the same, the C−H bond strength in methane being virtually identical with the H−H bond strength in dihydrogen. A suggested reason for this difference in activation energy barrier[51] is that side-on attack of the C−H bond by the excited metal atom cannot be accomplished without overcoming repulsive forces due to steric hindrance from the other C−H bonds. Furthermore, the overlap of the metal p orbital with the lowest lying σ^* antibonding orbital of CH_4 may be much less favorable than in the case of H_2; this has been shown for transition metal d-orbitals with regard to their interaction with the σ^* antibonding orbitals of methane and dihydrogen.[52]

The findings of these calculations and of gas phase studies appear to be at odds with the results of the matrix-isolation

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experiments we obtain for zinc and cadmium. The relevant electronic transitions have been recorded for the atoms isolated in argon matrices.[53] For zinc, the $^1P_1 \leftarrow {}^1S_0$ transition occurs at 207 nm, and the $^3P_1 \leftarrow {}^1S_0$ transition appears as a weak doublet at 295/298 nm; for cadmium, the two transitions are observed as a strong band at 220 nm and a much weaker, asymmetric doublet at 311/313 nm, which we observed as a single band at 312 nm in the UV−vis spectrum of the deposit.

Although the microwave discharge used in the present matrix experiments both populates the $^1P_0$ and $^3P_1$ excited states of the atoms and provides resonance radiation which can excite another atom and so facilitate insertion into a C−H bond of methane, the subsequent accretion of monomethylmetal hydride following selective UV photolysis in the region associated with the $^3P_1 \leftarrow {}^1S_0$ transition of the respective metals makes it clear that, in the matrix at least, it is excitation to the $^3P_1$ state that causes insertion. The previous account[14] by Billups *et al.* includes no mention of selective photolysis for the reaction of zinc atoms with methane, and thus does not support the proposition made by Castillo *et al.* that insertion demands atoms in the ^1P rather than the ^3P excited state. The wavelengths for the $^3P_1 \leftarrow {}^1S_0$ transition in gaseous zinc and cadmium atoms are 307.7 and 326.2 nm, respectively,[54] indicating that the matrix causes a blue shift of approximately 1225 cm^{-1} for Zn and 1395 cm^{-1} for Cd. This blue shift places an upper limit on the activation energy barrier of approximately 14.7 kJ mol^{-1} for Zn and 16.7 kJ mol^{-1} for cadmium, considerably less than the values suggested by the calculations and gas phase studies discussed above.

The gas phase reaction of mercury and methane has also been investigated.[3−5] Such studies[5] have shown that, whereas the collisional quenching of $Hg(^3P_1)$ by H_2 occurs at essentially every collision ($\sigma_Q \approx 30$ Å^2), with chemical products (HgH + H, Hg + 2H) generated in nearly 100% yield, the quenching of $Hg(^3P_1)$ by methane is very inefficient ($\sigma_Q \approx 0.3$ Å^2). Duval *et al.*[5] have estimated the activation energy for the reaction to be in the order of 1000−1500 cm^{-1} (12−18 kJ mol^{-1}). Mercury atoms isolated in an argon matrix have a strong absorption at 245 nm, attributable to the $^3P_1 \leftarrow {}^1S_0$ transition, and a weaker band at 224 nm, due to the $^3P_2 \leftarrow {}^1S_0$ transition.[53] The $^1P_1 \leftarrow {}^1S_0$ transition of mercury atoms isolated in a krypton matrix[55] has been recorded at 183 nm and, as such, is well beyond the atmospheric "cutoff". The wavelength for the $^3P_1 \leftarrow {}^1S_0$ transition in gaseous Hg atoms is 253.7 nm, giving a matrix blue shift of approximately 1404 cm^{-1} and setting an upper limit on the activation energy barrier of 16.8 kJ mol^{-1}. This lies within the range of values for the activation energy estimated by Duval *et al.*,[5] and so no conflict arises between the results derived from the gas phase studies and those from the current matrix-isolation investigation for Hg.

The mechanism by which excitation of Zn and Cd atoms to the $^3P_1$ state in the matrix cage with CH_4 leads to the photoproduct, CH_3MH (M = Zn or Cd), is not clear. Although the matrix cage does slightly blue shift the $^3P_1$ excited state and hold the reagents together for many collisions, these may still not be able to account for the reaction which we observe. The possibility of absorption of a second photon by the long-lived $M(^3P_1){\cdot}CH_4$ complex into higher excited states which possess more than enough energy to overcome the ^3P or ^1S barrier to insertion cannot be ruled out. Similar matrix-isolation experiments have provided evidence for high-pressure mercury arc two-photon ionization of naphthalene, biphenyl, and phenylpropyne in solid argon.[56] Finally, Cartland and Pimentel have shown that excitation into the $^3P_1$ excited state of zinc, cadmium, and mercury atoms initiates insertion into carbon−halogen bonds.[55]

As mentioned previously, the monomethylmetal hydride species is suggested by calculations to be the intermediate in the reaction between the metal atom and methane occurring in the gas phase, and which results in the formation of methyl radicals and metal hydride in the case of cadmium and zinc and in the formation of methyl radicals and hydrogen atoms in the case of mercury.[11] The infrared spectra of the condensates formed immediately after deposition do indeed contain bands attributable to the monohydrides of zinc and cadmium, whereas no band attributable to HgH is found to be present in the spectrum of the $Hg/CH_4/Ar$ matrix. The monohydride HgH has been observed to give an absorption at 1209 cm^{-1} in matrix studies of the reaction between Hg atoms and dihydrogen,[26] and emission studies have given a fundamental transition at 1203.24 cm^{-1} for the gaseous HgH molecule.[57] The presence of methyl radicals may indeed result from the reaction of the metal atom with methane, but it is certain also to derive from vacuum-ultraviolet photolysis of methane, a method which has been used to generate the radicals in earlier matrix-isolation experiments.[35] The dihydrides of the metals observed in the present matrix experiments result presumably from the reaction of the metal atom or the metal monohydride with dihydrogen or with hydrogen atoms formed *via* the windowless photolysis of methane molecules.

The monomethylmetal hydrides of zinc, cadmium, and mercury seem to be photostable, at least with respect to radiation from our photolysis source; this contrasts with the reported behavior of CH_3CuH which undergoes dissociation on selective photolysis, giving CH_3, CuH, CH_3Cu, and H and Cu atoms.[58] No infrared bands attributable to CH_3M (M = Zn, Cd, or Hg)[59,60] were observed on prolonged broad-band photolysis; any monohydride of zinc or cadmium would be destroyed under these conditions.[12]

Mercury and Ethane. The reaction of excited mercury atoms with ethane offers two alternatives for insertion, resulting in the formation of either dimethylmercury or monoethylmercury hydride. The bands we observed at 1954.8, 1946.8, and 1926.8 cm^{-1} in the infrared spectrum of a matrix formed by co-condensing Hg*/Ar and C_2H_6/Ar mixtures may be assigned to the ν(Hg−H) stretching mode of an ethylmercury hydride species. The broadness and splitting of the absorption are presumed to reflect the occupation of very different sites of the matrix or the coexistence of different configurations of the C_2H_5HgH molecule. A band at 698.4 cm^{-1} may be assigned to a CH_2 rocking mode, which is responsible for one of the strongest bands in the infrared spectrum of ethylmercury chloride (coming at 696.2 cm^{-1}).[55] The failure to observe any other bands associated with the insertion product can be explained by its small yield and by the broadness of its infrared features.

No infrared features associated with the alternative insertion product, $(CH_3)_2Hg$, were observed; the strongest infrared bands of this molecule in the region below 2000 cm^{-1} occur at 787 [ν_{10}, $\varrho(CH_3)$] and 548.3 cm^{-1} [ν_7, ν(C−Hg)].[24] There is no hint either of the radicals $CH_3^{\bullet}$ or $CH_3Hg^{\bullet}$.[35,60]

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These findings argue that insertion is confined to the C−H bond of ethane and does not extend to the C−C bond. Similar conclusions have been reached from a study of the interaction of copper atoms with ethane,[61] and from analysis of the products formed in the gas phase.[51] That the stronger C−H bond is more susceptible to attack than is the weaker C−C bond may be due, it has been suggested, to the presence of a significant steric barrier opposing attack of the excited metal atom on the C−C bond. As in the reaction with methane, the insertion into the C−H bond proceeds *via* excitation of the mercury atom to the $^3P_1$ excited state. The activation energy for the reaction of Hg($^3P_1$) with a range of alkane hydrocarbons has been shown to decrease with decreasing C−H bond strength and therefore the excess energy we are able to donate to the matrix-isolated reagents is in excess of that measured for the activation energy barrier.

Conclusions

A study of the reaction between excited zinc, cadmium, or mercury atoms and methane molecules has been carried out using the technique of matrix isolation to trap the intermediates which may be present in the gas phase. These intermediates have been identified and characterized by their infrared spectra. By reference to the spectra of different isotopomers and comparison with the spectra of known species, the results have been shown clearly to indicate the formation of the monomethylmetal hydride species, CH_3MH (M = Zn, Cd, or Hg), through insertion of the metal atom into one of the C−H bonds of methane. The mechanism of the insertion process has been investigated using filtered photolysis, and it has been shown that excitation to the $^3P_1$ metal atom state initiates insertion into a methane molecule when the reagents are confined together in a solid matrix at low temperatures. A further study of the reaction between excited mercury atoms and ethane indicates that the only detectable metal-containing product arises from the insertion of the metal atom into a C−H bond to give ethylmercury hydride, CH_3CH_2HgH; no trace of dimethylmercury was detected.

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