chase of the Varian A-60 nmr instrument was provided by the National Science Foundation under Grant No. GP-3674. We are also indebted to Tulane University for use of the Beckman IR-11 provided partially by funds from National Science Foundation Grant No. 28709.

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Spectroscopic Investigations of Dimethylberyllium Vapors

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Received November 7, 1968

Variable-temperature infrared spectra of saturated and unsaturated vapors of dimethylberyllium have been recorded. Band assignments have been made in comparison with published spectra for $M(CH_3)_2$ compounds (M = zinc, cadmium, or mercury). The spectrum of the unsaturated vapor is consistent with a monomer with a linear C–Be–C skeleton. Band assignments are confirmed from analysis of the infrared spectrum of the deuterated analog. Mass spectral measurements confirm the presence of monomers only. Hyperconjugation effects are employed to explain the large beryllium–carbon bond strength and the unexpected stability of the monomer.

Introduction

Vapor pressure and vapor density measurements[1] of saturated vapors of dimethylberyllium have indicated an equilibrium mixture of monomers, dimers, and trimers. It was calculated that the vapor consists of 41% monomer, 44% dimer, and 14% trimer at 180° with corresponding percentages of 27, 50, and 23 at 160°.

Infrared spectra of both saturated and unsaturated vapors have been reported[2] and interpreted in comparison with the vapor density results. For the monomer (unsaturated vapor) $\delta(CH_3)$ was assigned at 1262 cm^{-1} and methyl rocking modes were at 1086, 1032, and 816 cm^{-1}. The spectrum of the saturated vapor was more complex, consistent with the presence of polymeric structures in addition to the monomer. When the saturated vapor was heated, however, the spectra revealed unpredictable changes. Numerous new bands appeared which, in contrast to the vapor density results, implies that some new species is formed. The spectra were not fully discussed or interpreted.

We decided to measure the variable-temperature gas-phase infrared spectra of both saturated and unsaturated vapors of deuterated and undeuterated dimethylberyllium. We intended to characterize the vapors of dimethylberyllium better by making assignments of bands in the infrared spectra for each species present in the vapor.

Experimental Section

All sample preparations were carried out in an inert-atmosphere enclosure equipped with an air circulation system for removal of trace amounts of water and oxygen.[3]

Synthesis of Compounds.—Dimethylberyllium was synthesized by the reaction of beryllium metal (200 mesh powder obtained from Alfa Inorganics, Inc.) and dimethylmercury (obtained from Eastman Organic Chemicals and used without further purification). The beryllium powder was heated to 400° under vacuum to remove traces of adsorbed moisture. An equimolar quantity of dimethylmercury was combined with the activated beryllium metal in an ampoule which was sealed and subsequently heated to 120° in an oil bath. After 3 days, the ampoule was opened in the inert-atmosphere enclosure. Samples were sublimed at 100° immediately prior to use.

A Grignard method was utilized for the synthesis of $(CD_3)_2Be$. Because of the difficulty of removing trace amounts of diethyl ether from dimethylberyllium, dimethyl sulfide was utilized as the solvent.[4] The Grignard reagent was synthesized by dropwise addition of methyl-d_3 iodide (obtained as 98% d_3 from Stohler Isotope Chemical Corp. and used without further purification) dissolved in dimethyl sulfide to magnesium metal in dimethyl sulfide. The resultant exothermic reaction proceeded smoothly until all of the iodide had been added. Solid beryllium chloride (obtained from Alfa Inorganics, Inc., and used without further purification) was added to the flask containing the Grignard reagent and brought to reflux. After 4 hr excess solvent was removed under vacuum. The resultant solid was transferred to the inert-atmosphere enclosure and sublimed several times to ensure complete removal of coordinated dimethyl sulfide.[5]

For purposes of characterizing the symmetrical methyl deformation of a terminal methyl group bonded to beryllium, the trimethylamine adducts were synthesized. Excess, dry trimethylamine was vacuum transferred directly into the infrared cell containing either dimethylberyllium or dimethyl-d_6-beryllium and excess amine removed under vacuum while the cell was cooled to approximately 0°. The melting point of the undeuterated adduct was 36° compared to the reported melting point of 36°.[6] Gas-phase spectra of the adducts were recorded at room temperature.

Construction of Infrared Cell.—During the course of this investigation it was observed that dimethylberyllium vapors react with most common gasketing materials, especially silicone rubber. For this reason a commercial variable-temperature chamber could not be used. A cell was therefore constructed from thick-walled, Pyrex tubing, 6 cm in length. A vacuum stopcock was joined to the center of the tube and the ends were ground smooth

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[1] G. E. Coates, F. Glockling, and N. D. Huck, *J. Chem. Soc.*, 4496 (1952).

[2] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 1, Methuen and Co., Ltd., London, 1967, p 106.

[3] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

[4] G. Bähr and K. H. Thiele, *Chem. Ber.*, **90**, 1578 (1957).

[5] Contrary to earlier reports we have observed complex formation between dimethylberyllium and dimethyl sulfide.

[6] G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 4501 (1952).

to accommodate potassium bromide plates. The plates were sealed to the cell using Apiezon H hydrocarbon grease. Commercial Fisher Sealit, obtained from the Fisher Scientific Co., was used to hold the plates in place. Solid dimethylberyllium was transferred into the cell by means of a specially constructed funnel which fitted through the bore of the stopcock.

Construction of Variable-Temperature Enclosure.—Nichrome wire (1.05 ohms/ft) was used as the heating element in an enclosure constructed from Transite insulation material. Opposite ends of the box were fitted with potassium bromide plates. Air within the enclosure was continuously circulated with a small electric fan to ensure the absence of temperature gradients. Transite brackets held the infrared cell in place within the enclosure permitting the passage of the infrared beam through both the enclosure and the cell. Temperature within the enclosure was controlled by varying the amount of current passing through the heating element.

Saturated and Unsaturated Vapors.—Saturated vapors were measured with excess solid present in the cell at all temperatures. Unsaturated vapors were measured by allowing most of the dimethylberyllium to sublime out of the cell at 180° into an evacuated tube attached to the vacuum stopcock. The stopcock was closed and spectra were recorded for the gas with no residual solid in the cell.

Infrared Spectral Measurements.—The infrared spectra were recorded on a Perkin-Elmer 621 infrared spectrometer over the temperature range 125–180° at 10° intervals. Polystyrene film and, when present, the CH_4 impurity were used to calibrate the spectra and all values reported are reliable to ± 2 cm^{-1}. In all cases, the room-temperature spectrum, obtained before the cell was heated, matched the background spectrum, obtained after the cell was allowed to cool, with the exception of absorptions attributable to "small" amounts of methane produced by thermal decomposition of dimethylberyllium at the higher temperatures. The vapor density studies[1] indicated that decomposition of dimethylberyllium occurred at elevated temperatures, accompanied with deposition of colorless crystals unlike dimethylberyllium in appearance and a *decrease* of pressure. A residual pressure was noted on cooling to room temperature after an experiment. *Spectroscopic* analysis of this decomposition process[7] has suggested that the involatile materials are Be_2C or polymeric $Be(CH_2)_n$ species. The purity of the compound in the infrared cell was verified at the end of each series of experiments. The infrared spectrum of the solid sublimed onto the potassium bromide windows of the cell was, with no exception, the spectrum of solid dimethylberyllium.[7]

Mass Spectral Measurement.—This experiment was run on a Bendix Time of Flight mass spectrometer at the U. S. Bureau of Mines, Petroleum Research Center, Laramie, Wyo., with the assistance of Mr. Frank Doolittle. Samples were sealed into small, glass capillary tubes with gallium metal. They were introduced directly into the mass spectrometer source and heated at 65° to cause volatilization of the compound. All spectra were recorded at 70-eV ionizing voltage.

Results

The infrared spectrum (1500–400 cm^{-1}) of saturated dimethylberyllium at 180° is shown in Figure 1. Low-intensity bands occur at 1261, 952, and 841 (sh) cm^{-1} in the spectra of both saturated and unsaturated vapors of dimethylberyllium. These were the dominant bands in the spectra obtained when silicone rubber gaskets were used in the cell. They are present in these spectra owing to the reaction between dimethylberyllium and silicone stopcock grease forming a volatile impurity which could not easily be removed by sublimation. Although this impurity has not been identified, these bands correspond to symmetrical deformation of methyl bonded to silicon, silicon–oxygen stretching, and silicon–carbon stretching, respectively.[8] Bands appearing at 3020 and 1306 cm^{-1} are assigned to methane,[9] always present as a product of thermal decomposition.

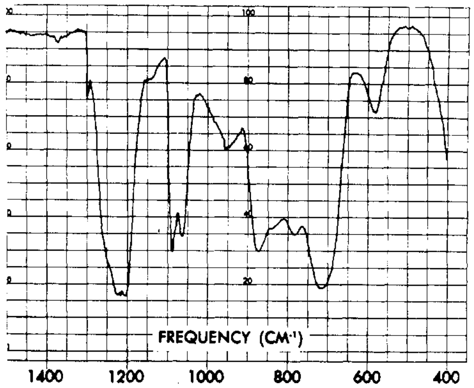

Figure 1.—Infrared spectrum of saturated $(CH_3)_2Be$ at 180° (1500-400 cm^{-1}).

The infrared spectral data are summarized in Table I. The spectra were temperature independent with the exception of an over-all increase in absorption with temperature in the saturated vapors. The bands appearing at 879, 798, and 585 cm^{-1} in the saturated vapor spectrum of $(CH_3)_2Be$ but not present in the unsaturated vapor spectrum are attributed to a polymeric species, likely only a dimer, containing both bridging and terminal methyl groups.

Table I

Infrared Spectra of Dimethylberyllium Vapor

$(CH_3)_2Be$, satd, cm^{-1}	$(CH_3)_2Be$, unsatd, cm^{-1}	$(CD_3)_2Be$, satd, cm^{-1}	ν_H/ν_D
2944 b, s[c]	2944 b, s	2193 b, s	1.35
2813 sh	2813 sh	2053 sh	1.37
1222[a] s	1222[a] s	994[a] s	1.23
1081[b] s	1081[b] s	1150[b] s	0.94
879 m	. . .	760 m	1.16
798 w	. . .	668 w	1.20
727 s	727 s	603 s	1.20
585 w	. . .	462 w	1.27

[a] P, Q, R branches. [b] P, R branches. [c] Abbreviations: s, strong; sh, shoulder; m, medium; w, weak; b, broad.

These bands are assigned, in analogy with $Al_2(CH_3)_6$,[10] to complex bridge stretching, terminal methyl rocking, and bridge methyl rocking, respectively. The analogous frequencies, which for $Al_2(CH_3)_6$ are the most interesting, occur at 772, 700, and 572 cm^{-1}. The bridge stretching mode, involving a significant amount of metal–carbon stretching, is shifted upon deuteration by 1.16 in $Be_2(CH_3)_4$ and 1.14 in $Al_2(CH_3)_6$. The low isotopic shift ratios in these two compounds are in good agreement with the high metal–carbon stretching nature of this mode. The remaining frequencies are shifted by 1.20 and 1.27 in $Be_2(CH_3)_4$ and 1.20 and 1.30 in $Al_2(CH_3)_6$, respectively. The other bands which are

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[7] J. Goubeau and K. Walter, *Z. Anorg. Allgem. Chem.*, **322**, 58 (1963).

[8] For a discussion of characteristic organosilicon infrared bands see L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, pp 334–342.

[9] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 306.

[10] A. P. Gray, *Can. J. Chem.*, **41**, 1511 (1963).

expected for $(CH_3)_4Be_2$ and are actually observed as relatively weaker absorptions in $(CH_3)_6Al_2$ are either too weak in $(CH_3)_4Be_2$ to be detected or are superimposed on the strong bands present in the remainder of the spectrum.

The remaining bands in the saturated vapor, which are the only bands present in the unsaturated vapor, are assigned to monomeric $(CH_3)_2Be$. P, Q, and R branches are clearly observed (although vibrational–rotational fine structure could not be resolved) for the 1222-cm^{-1} band which is at the expected frequency for the symmetrical methyl deformation mode ($\delta(CH_3)$) of a terminal methyl group bonded to beryllium. This mode occurs at 1209 cm^{-1} in $(CH_3)_2BeN(CH_3)_3$ and at 1033 cm^{-1} in the deuterated analog ($\nu_H/\nu_D = 1.17$). The symmetrical methyl deformation frequencies in $Al_2(CH_3)_6$ occur at 1255 cm^{-1} for bridging methyl and 1208 cm^{-1} for terminal methyl.[10] The presence of P, Q, and R branches demands that the major axis of symmetry (along the Be–C bond) be threefold or greater,[11] indicating that this is the symmetrical methyl deformation frequency of monomeric dimethylberyllium with a linear arrangement of C–Be–C atoms. A bent monomer or polymer would have at greatest a twofold axis of symmetry, precluding P, Q, and R branches for this deformation mode. The symmetric methyl deformation frequencies in $(CH_3)_2BeN(CH_3)_3$, $Al_2(CH_3)_6$,[10] and $(CH_3)_2O$[12] do not consist of P, Q, and R branches.

The remaining assignments are made in analogy with monomeric gaseous dimethylzinc,[13] -cadmium,[14,15] and -mercury.[13,15] Infrared and Raman spectra for these compounds indicate that the molecular point group is D_{3h}', indicating that the methyl groups are freely rotating.

Table II lists for comparison the infrared-active fundamentals of D_{3h}' symmetry for the $(CH_3)_2M$ system (M = zinc, cadmium, or mercury) together with the assigned frequencies of monomeric $(CH_3)_2Be$. The frequency designations are those of ref 13. The asymmetric metal–carbon interaction (ν_7) in the beryllium compound occurs predictably at higher frequency owing to the significantly lighter mass of beryllium. The shape of this band, however, is conspicuously similar in all of these compounds. The asymmetric metal–carbon stretching frequency consists of P and R branches only. A parallel band which has no Q branch results if for a linear polyatomic molecule the changing dipole moment for a given vibrational mode is parallel to the molecular axis.[16] The asymmetric C–O stretching frequency in CO_2, for example, is a parallel band with no Q branch. An unanticipated result, however, is that the deuterium shift ratio of ν_7 is 0.94, the fundamental moving to higher frequency upon deuteration. Significantly, the 1081-cm^{-1} frequency in $(CH_3)_2Be$ is the only band which does not shift to lower frequency upon deuteration. (All other deuterium shift ratios range from 1.20 to 1.37.) This fact, coupled with the preceding band shape discussion, is verification of the assignment of 1081 cm^{-1} in $(CH_3)_2Be$ and 1150 cm^{-1} in $(CD_3)_2Be$ to ν_7. The band appearing at 727 cm^{-1} in the spectrum of $(CH_3)_2Be$ is best assigned to ν_{10}. This frequency is predictably in close proximity to the analogous modes in dimethylzinc, -cadmium, and -mercury. The deuterium shift of 1.20 observed for this frequency is consistent with the similar ratio in $Al_2(CH_3)_6$ where deuterium shift ratios ranging from 1.20 to 1.27 imply that the frequencies are either methyl rocking or deformation modes.[10] The deuterium shift of 1.23 observed for ν_6 is likewise in good agreement with this observation.

TABLE II

INFRARED-ACTIVE FUNDAMENTALS OF SYMMETRY D_{3h}' FOR DIMETHYLZINC, -CADMIUM, -MERCURY, AND -BERYLLIUM

	Freq, cm^{-1}			
	$(CH_3)_2Zn$	$(CH_3)_2Cd$	$(CH_3)_2Hg$	$(CH_3)_2Be$
ν_5 C–H sym str	2870	2920	2880	2813
ν_6 CH_3 sym def	1185	1140	1205	1222
ν_7 C–M–C asym str	615	538	550	1081
ν_8 C–H asym str	2935	2885	2970	2944
ν_9 CH_3 asym def	1448	1441	1475	. . .
ν_{10} CH_3 ⊥ rock	707	705	788	727
ν_{11} C–M–C def	146	150	156	. . .

The asymmetric methyl deformation frequency (ν_9) and the C–M–C deformation frequency (ν_{11}) have not been observed in this work. This is not surprising, however, since the methyl deformation frequency in $Al_2(CH_3)_6$ is very weak[10] and is weak or missing in methylgallium complexes.[17] Potassium bromide optics precluded the detection of ν_{11} which is expected at low (less than 400 cm^{-1}) frequency.

To substantiate our infrared results the mass spectrum of unsaturated vapor was measured. Absence of mass peaks greater than 39 and mass peaks occurring at 39, 24, 23, 10, and 9 (with relative abundances of 15, 100, 60, 5, and 15%, respectively) due to $(CH_3)_2Be^+$, $(CH_3)Be^+$, CH_2Be^+, BeH^+, and Be^+, respectively, are confirmation that monomer is the major constituent in the vapor phase under *unsaturated* conditions. Mass spectral analysis of dimethylberyllium vapors allowed to equilibrate in a chamber showed, in addition to a *predominance* of the mass peaks cited above, *very low-intensity* peaks assigned to octameric, heptameric, hexameric, and pentameric dimethylberyllium.[18]

Discussion

From this study it is concluded that the unsaturated vapor of $(CH_3)_2Be$ contains only monomers with a linear C–Be–C skeleton. Some other polymeric species is also present in *small* amounts under saturated conditions.

It is difficult for us to rationalize the vapor density determination[1] or the previous infrared study.[2] We

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[11] For detailed description of the band envelopes expected see ref 9, p 414.

[12] See ref 9, p 353.

[13] H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949).

[14] H. S. Gutowsky, *J. Am. Chem. Soc.*, **71**, 3194 (1949).

[15] M. G. Miles, J. H. Patterson, C. W. Hobbs, M. J. Hopper, J. Overend, and R. S. Tobias, *Inorg. Chem.*, **7**, 1721 (1968).

[16] R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, p 224.

[17] G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1295 (1964).

[18] G. E. Coates unpublished results.

suggest that the previously reported infrared spectra included data for products of reaction between $(CH_3)_2Be$ and a silicone compound used as gasketing material or as grease on cell stopcocks.[19] These results agree well with preliminary observations made by us when silicone materials were exposed to $(CH_3)_2Be$. The symmetric methyl deformation frequency of a methyl group bonded to silicon occurs at 1261 cm^{-1} in the volatile decomposition product. The value reported earlier for the symmetrical deformation frequency of terminal methyl bonded to beryllium is 1262 cm^{-1}.

The unexpected shift of ν_7 to higher frequency upon deuteration ($\nu_H/\nu_D = 0.94$) requires explanation. It has been determined that the asymmetric B–C stretching frequency in $(CH_3)_3B$ shifts from 1156 to 1206 cm^{-1} in the deuterated analog ($\nu_H/\nu_D = 0.96$).[20] The shift was explained in $(CH_3)_3B$ by vibronic interactions and resonance effects which can be applied to the present case. The symmetric methyl deformation frequency, ν_6, would "normally" be expected to shift to about 924 cm^{-1} (1222 cm^{-1}/1.32) upon deuteration. The asymmetric Be–C stretching frequency, ν_7, would correspondingly "normally" be expected to decrease toward 1050 cm^{-1} (1081 cm^{-1}/1.03). ν_6 and ν_7 are both of symmetry class A_{2u}, however, thus placing such shifts in violation of the noncrossing rule.[21] The ν_6 frequency will accordingly assume the character of the Be–C stretching mode while the ν_7 frequency assumes the character of the methyl deformation mode. Comparison of the line shapes and intensity ratios of ν_6 and ν_7 in $(CH_3)_2Be$ and $(CD_3)_2Be$ lends validity to the preceding discussion. The P and R branches of the 1081-cm^{-1} line in $(CH_3)_2Be$ appear as broadened P and R branches of the 1150-cm^{-1} line in $(CD_3)_2Be$, indicating interaction with ν_6. The P, Q, and R branches of the 994-cm^{-1} line in $(CD_3)_2Be$ are likewise broadened indicating interaction with ν_7. In the spectra of $(CH_3)_2Be$ and $(CD_3)_2Be$, ν_6 and ν_7 are the strongest bands. In $(CH_3)_2Be$, ν_6 is more intense than ν_7 while in $(CD_3)_2Be$, ν_7 is the most intense band indicating, again, interaction between these frequencies.

The asymmetric Be–C stretching frequency in monomeric, gaseous $(CH_3)_2Be$ is high in comparison with the other beryllium alkyls listed in Table III. The data seem to indicate an unusually strong Be–C bond in monomeric $(CH_3)_2Be$. This enhanced bond strength (and stability of the monomer) is likely due to hyperconjugation, the attached alkyl groups releasing electrons into the vacant 2p orbitals of the metal. Diagrammatically, the situation can be represented by the valence bond structures

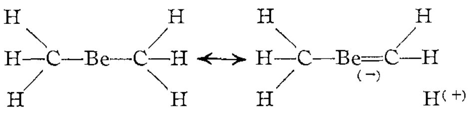

Table III

Asymmetric Be–C Stretching Frequencies in Selected Beryllium Alkyls

Beryllium alkyl	Be–C asym str, cm^{-1}
$(CH_3)_2Be$, monomeric vapor	1081[22]
$(CD_3)_2Be$, monomeric vapor	1150[22]
$(t\text{-}C_4H_9)_2Be$, monomeric vapor	450[23]
$(CH_3)_2BeN(CH_3)_3$, monomeric vapor	790[22]
$(CH_3)_2BeN(CH_3)_3$, cyclohexane soln	794[24]
$(CH_3)_2Be(N(CH_3)_2CH_2)_2$, cyclohexane soln	874[24]

The hyperconjugative effect has been employed to explain the stability of monomeric $(CH_3)_3B$.[25]

The metal–carbon asymmetric stretching frequency occurs at 450 cm^{-1} in gaseous, monomeric $(t\text{-}C_4H_9)_2Be$.[23] The low value here is indicative of a very weak Be–C bond and may be initially thought to be caused by steric interaction of the *t*-butyl groups. Steric factors are invoked to explain the decrease, from 615 to 308 cm^{-1}, in the M–C asymmetric stretching frequencies of $(CH_3)_2Zn$[13] and $(t\text{-}C_4H_9)_2Zn$,[23] respectively. These data suggest that decrease of steric interactions, when *t*-butyl is replaced by methyl, increases the M–C asymmetric stretching frequency approximately twofold. The existence of the rather crowded $(t\text{-}C_4H_9)_3B$,[26] $(n\text{-}C_5H_{11})_3B$, $(i\text{-}C_5H_{11})_3B$, $(i\text{-}C_4H_9)_3B$ compounds with relatively high B–C stretching frequencies at 1123, 1127, 1133, and 1138 cm^{-1}, respectively,[27] is contrary to this interpretation, however.

Since methyl groups are known to be involved in hyperconjugative effects while *t*-butyl groups probably have a zero or negligible hyperconjugative effect and since the beryllium atom is geometrically well disposed to *receive* electron density by such a mechanism, we feel that hyperconjugation is indeed the dominant factor in explaining these frequency anomalies. If this be true,[28] this system represents the most profound examples of hyperconjugation with stabilization energies on the order of 10 kcal/mol rather than the 1–2 kcal/mol usually attributed to hyperconjugation.[29] The value of 10 kcal/mol is predicted by the following arguments. (1) The predominance of monomer in the vapors of dimethylberyllium suggests that *hyperconjugation* is able to compete successfully with *polymerization* as a stabilization process. (2) Polymerization energies are large; for example, the heat of reaction accompanying formation of 1 mol of dimer from 2 mol of monomer as in the reaction $2Al(CH_3) = Al_2(CH_3)_6$ is on the order of 10 kcal/mol of monomer.[30]

The amine adducts of $(CH_3)_2Be$ exhibit asymmetric M–C stretching in the 790–880-cm^{-1} region, intermediate between the 1081- and 450-cm^{-1} extremes. These

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(19) We understand that silicone materials were used: G. E. Coates, personal communication.

(20) W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **31**, 1071 (1959).

(21) See ref 9, p 200.

(22) This work.

(23) G. E. Coates, P. D. Roberts, and A. J. Downs, *J. Chem. Soc., A*, 1085 (1967).

(24) N. A. Bell, G. E. Coates, and J. W. Emsley, *ibid.*, 49 (1966).

(25) P. G. Perkins and D. H. Wall, *ibid.*, 1207 (1966).

(26) Doubt concerning the existence of $(t\text{-}C_4H_9)_3B$ has appeared in the literature: G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **79**, 5190 (1957).

(27) W. J. Lehmann and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).

(28) We shall measure the Be–C bond length by electron diffraction to test this argument.

(29) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 69.

(30) A. W. Laubengayer and W. F. Gillman, *J. Am. Chem. Soc.*, **63**, 477 (1941).

can be explained by at least three factors which cannot be separated. (1) Hyperconjugation effects in the amine adducts should be smaller. There are two vacant p orbitals in monomeric $(CH_3)_2Be$, only one in monomeric $(CH_3)_2BeN(CH_3)_3$, and none in $(CH_3)_2Be(N(CH_3)_2CH_2)_2$. (2) There is a change in hybridization from sp in $(CH_3)_2Be$ and sp^2 in $(CH_3)_2BeN(CH_3)_3$ to sp^3 in $(CH_3)_2Be(N(CH_3)_2CH_2)_2$. (3) There is also an inductive effect due to coordinated nitrogen which will affect the Be–C bond strength.

Acknowledgment.—We are indebted to the National Science Foundation for support of this work under Grant GP-8595.

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The Infrared Spectrum and Vibrational Assignments for Pentacarbonylmanganese Hydride[1]

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Received August 2, 1968

The infrared spectrum of pure $HMn(CO)_5$ in the region 4000–300 cm^{-1} has been obtained in the vapor phase. The observed spectrum has been analyzed to distinguish the fundamental frequencies, the rotational–vibrational band structure, and overtone and combination frequencies. An assignment of the observed vapor-phase frequencies to the fundamental modes of vibration has been made based on C_{4v} symmetry, which the $-Mn(CO)_5$ moiety is known to possess in the solid state. The positions of middle-frequency bands of $DMn(CO)_5$ are reported and used to test the C_{4v} assignment with the Teller–Redlich isotope product rule. It is shown that it is not necessary to assume lower than C_{4v} symmetry for $HMn(CO)_5$, as has been done in all previous considerations of the entire infrared spectrum of $HMn(CO)_5$.

Introduction

Since the initial report[4] of its preparation, the nature of the compound $HMn(CO)_5$ has been the subject of a number of studies. Investigation of the vapor-phase infrared spectrum led Cotton, Down, and Wilkinson[5] and Wilson[6] to the conclusion that the molecular symmetry is definitely lower than C_{4v}, although no vibrational assignments were made. Subsequently, however, La Placa, Hamilton, and Ibers[7] showed that $HMn(CO)_5$ crystallizes such that the $Mn(CO)_5$ moiety does have C_{4v} local symmetry in the solid state and suggested that it is unlikely that it would assume lower symmetry in the vapor phase. This structure determination prompted Huggins and Kaesz[8] to report a prior interpretation[8b] of the C–O stretching region (1900–2200 cm^{-1}) of the solution spectrum of $HMn(CO)_5$ based upon C_{4v} symmetry. Kaesz and coworkers[9] subsequently reported the study of several isotopic analogs of $HMn(CO)_5$ in the same spectral region (1900–2200 cm^{-1}). In addition, Davison and Faller[10] have reported the observation of the 1700–2200-cm^{-1} region of the Raman spectrum of $HMn(CO)_5$ and one band outside of this region.

However, these studies do not solve the problem of the apparent disparity between the X-ray results[7] and previous infrared data,[5,6] which include measurements at frequencies lower than those of the 5-μ region (1900–2200 cm^{-1}). This problem arises only partly from the spectral complexity of the 5-μ region. Its more difficult aspect concerns understanding the middle- and low-frequency modes which compose eleven ($4\ A_1 + 7\ E$) of the fifteen ($7\ A_1 + 8\ E$) infrared-active vibrational frequencies. Since the spectra of both $HMn(CO)_5$ and its deuterated analog, $DMn(CO)_5$, are identical in the 5-μ region, it is only with the remainder of the spectrum that a C_{4v} assignment can be tested by the Teller–Redlich isotope product rule.

In order to resolve this disparity, we have reinvestigated the infrared spectrum of gaseous samples of $HMn(CO)_5$ which are known to be pure, so that no bands due to impurities are taken as indications that it has lower than its true symmetry.

We report here the high-resolution spectrum of highly pure, gaseous $HMn(CO)_5$ in the region 4000–300 cm^{-1}, we propose a vibrational assignment of the infrared-active modes of $HMn(CO)_5$, based upon C_{4v} symmetry, and we test this assignment by the isotope product rule using the reinvestigated high-resolution spectrum, in the middle-frequency region (800–300 cm^{-1}), of the deuterated analog $DMn(CO)_5$.

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[1] Abstracted from the Ph.D. Thesis of W. M. Risen, Jr., Purdue University, 1967.

[2] Monsanto Predoctoral fellow, 1965–1966.

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