from H_5 and H_6; the remaining coupling of H_4 to H_3 gives rise to a doublet (J_{34} = 8.3 Hz). The long-lived H_5–H_6 spin states ($\alpha\alpha$ and $\beta\beta$) cause H_4 to be split into a 1:1 doublet with a separation of $J_{45} + J_{46}$ (8.0 Hz); the additional coupling to H_3 (8.3 Hz) then gives an apparent triplet. The temperature dependence of the H_4 signal is reproduced by line-shape calculations.[9] The "fractional-decoupling" effect apparently has not been previously observed.[6]

Since H_3 and H_4 give relatively sharp signals, the salicylate ion in the viscoelastic solutions must tumble much faster about an axis more or less parallel to C_1–C_4 than about perpendicular axes, as expected for an ion on the surface of a micelle. Since the H_3–H_4 and the H_4–H_5 vectors make angles of about 60° with respect to the fast rotation axis, DD relaxation is inefficient.[10,11]

Rotational diffusion rates for the salicylate ion in the various environments given in Table I were calculated by means of Woessner's equations[12] and are shown in Table II.

The present work shows that salicylate ions have very different tumbling motions in the mobile and viscoelastic micellar solutions, and therefore the suggestion[3] that the latter solutions contain linked spherical micelles is not supported by the present NMR relaxation evidence.

Acknowledgment. The 500-MHz spectrometer was purchased through funds provided in part by the National Science Foundation.

Registry No. Sodium salicylate, 54-21-7.

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(10) The 60° angle is close to the "magic angle", where $3\cos^2\theta - 1 = 0$, (Levy, G. C.; Cargioli, J. D.; Anet, F. A. L. *J. Am. Chem. Soc.* **1973**, *95*, 1527–1535). Anisotropic motions of aromatic rings in micelles have been studied by ^{13}C relaxation: Menger, F. M.; Jerkunica, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 688–691. Stark, R. E.; Storrs, R. W.; Kasakevich, M. L. *J. Phys. Chem.* **1985**, *89*, 272–277.

(11) Intermolecular DD relaxation via the CTAB protons should lead to some broadening in the salicylate protons, especially in the narrow signals of H_3 and H_4. It probably largely determines the apparent T_1's of the salicylate protons, as observed by nonselective pulse sequences.

(12) Woessner D. E. *J. Chem. Phys.* **1962**, *37*, 647–654. A slightly modified version of MOLDYN (Craik, D. J.; Kumar, A.; Levy, G. C. *J. Chem. Inf. Comput. Sci.* **1983**, *23*, 30–38) was used.

Metal Atom Reactions with Methane. Boron, Aluminum, Gallium, and Indium Atoms and Dimers

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The group 13[1] metal atoms B, Al, Ga, and In possess very high intrinsic chemical reactivity under low-temperature conditions.[2-11] Thus, recall that Al atoms react spontaneously with alkyl halides (CH_3X)[2] and water even at as low at 10 K.[9] Under the same conditions, Ga atoms also react with CH_3X but less efficiently than Al.[2] Reactions of Al atoms with CH_4 have also been reported,[10] although there is some controversy about whether photoactivation is necessary or if Al clusters are necessary.[11]

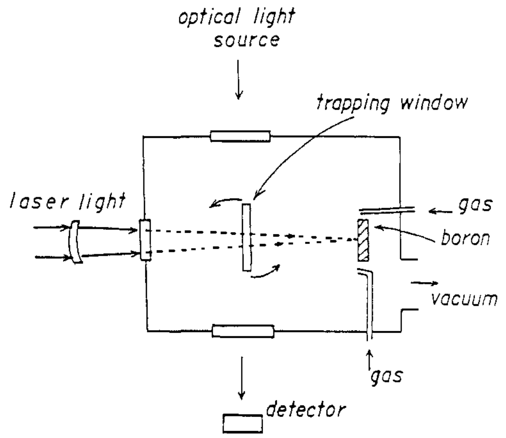

Figure 1. Schematic diagram of a matrix isolation reaction chamber with a laser evaporation source.

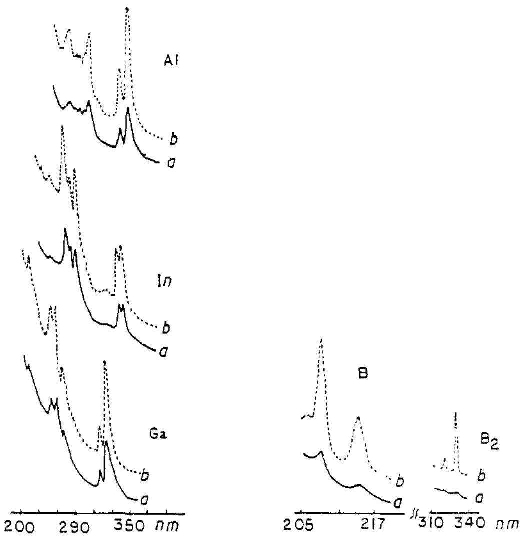

Figure 2. UV absorption spectra of B, Al, Ga, and In evaporated by XeCl excimer laser isolated in Ar matrix at 10 K: (a) in 5% CH_4/Ar matrix, evaporation time, 10 min; (b) in pure Ar matrix, evaporated an additional 10 min after (a).

Theoretical support for the low activation barrier for $CH_4 + M \rightarrow CH_3MH$ has been found, especially for B and Al atoms and for the B anion.[12] A partially filled p-shell appears to be very important so that an empty p-lobe can interact with the C–H σ^* orbital.[12]

To gain further understanding of the C–H bond-breaking process on single atoms, we have extended our studies to B atoms and have compared these with Al, Ga, and In atoms. In order to study all of these systems under similar conditions we have designed a matrix-isolation unit that utilizes an excimer laser as a heat source for evaporation of bulk B, Al, Ga, and In. The basic matrix unit is similar to what we have described earlier. However, the laser beam (75 mJ/pulse and about 5 pulses/s) is directed through the center of the cold window (a hole in the window) onto the target, which is vaporized (Figure 1), and as the laser beam bores a hole in the target the exiting vapor is directed back along the laser beam path and onto the window.[13,14] This design allows

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(1) Numbered according to the recent American Chemical Society scheme (groups 1–18). IUPAC is also considering approval of this scheme.

(2) Tanaka, Y.; Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 1013–1016.

(3) Timms, P. L. *Chem. Commun.* **1968**, 258–259.

(4) Owens, P., work described in: McGlinchey, M. J.; Skell, P. S. In *Cryochemistry*; Moskovits, M., Ozin, G. A., Eds.; Wiley Interscience: New York, 1976; p 153.

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(11) Parnis, J. M.; Ozin, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1699–1700.

(12) Lebrilla, C. B.; Maier, W. F. *Chem. Phys. Lett.* **1984**, *105*, 183–188.

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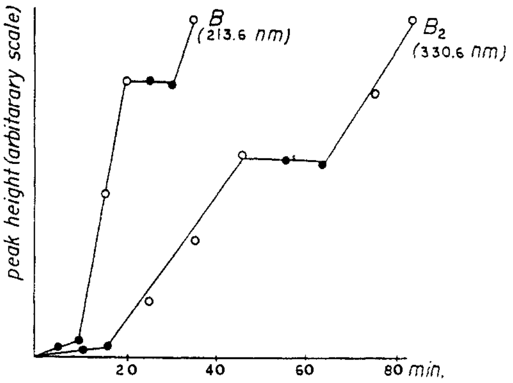

Figure 3. Absorption areas vs. time of atomic and dimer species in argon vs. CH_4/Ar: (○) in pure Ar matrix; (●) in 10% CH_4/Ar matrix.

evaporation of almost any material and the vapor is deposited immediately after each laser pulse (so the sequence is pulse–deposit–pulse–deposit etc., and the light should not perturb the gaseous species traveling to the window).

Using this laser evaporation method combined with UV–vis and IR spectroscopy, we have monitored the behavior of B, B_2, Al, Al_2, Ga, and In atoms and dimers in the presence of argon (Ar) and CH_4. Figure 2 illustrates a spectrum of B and B_2 in pure argon.[15] Note that the growth of the B and B_2 is almost negligible in the presence of 5% CH_4/Ar. However, in pure Ar for the same period of time and evaporation rate B and B_2 grows rapidly. The Al system is intermediate; that is, growth is moderately more rapid in Ar than in 5% CH_4/Ar. With In and Ga the growth rates are about the same. Figure 3 illustrates this in another way for B and B_2. We have used such monitoring techniques successfully before[16,17] and believe in this case they show that B and B_2 are efficiently consumed by CH_4 while Al species are less so, and Ga and In species are not at all. Thus, taking ratio's of peak areas such as [(area b − a)/area a], we find the values B atom 3.5, B_2 8.0, Al atoms 1.3, Ga atoms 0.8, and In atoms 0.8. A value near 1.0 would indicate no reaction.

Infrared studies of B–CH_4 systems were also carried out (Figure 4). New bands at 823, 894, 909, and 971 cm^{-1} (δ_{BH} or δ_{CH}) and 2007, 2027, 2051, 2118, 2134, and 2500 cm^{-1} (δ_{BH} bridged and terminal) were observed, clearly showing that reaction products are formed upon deposition of B and B_2 with CH_4 at 10 K. The IR data suggest that both terminal and bridged B–H species are formed. Also, bands in the 820–971-cm^{-1} region suggest the presence of H_3C–B species.[2]

These results demonstrate that ground-state B and B_2 react spontaneously with CH_4 under matrix conditions. Our earlier results combined with these indicate that ground-state Al atoms react with CH_4, albeit less efficiently, but Ga and In do not. Our preliminary results indicate that C_2, Si, and Si_2 do not react with CH_4. We have not been able to monitor C atoms as yet.

We are continuing our studies of B and B_2 reactions with other substrates and plan to utilize our laser-evaporation–matrix-isolation apparatus for studies of many other species including metal oxide molecules and heavy metal atoms.

Figure 4. Infrared spectrum of B/B_2 reaction with CH_4 (cm^{-1}).

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(13) Friichtenicht (Friichtenicht, J. F. *Rev. Sic. Instrum.* **1974**, *45*, 51–56) first demonstrated that metal atom beams can be produced in this manner. A high-power laser pulse can instantaneously increase the temperature of the target surface within the focused area well above its boiling point. An important advantage of laser evaporation is that heating is localized to a small area and the remainder of the sample and apparatus remain at ambient temperature.

(14) Kang et al. (Kang, H.; Beauchamp, J. L. *J. Phys. Chem.* **1985**, *89*, 3364–3367) have demonstrated that the vapor preferentially exists directly back along the laser beam path. This is due to the hole that is bored acting like a rifle barrel directing the beam. Another advantage is that very little surface oxide is encountered by the beam, so metal oxide vapor as a containment is minimized.

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Bonding in the First-Row Transition-Metal Monocarbonyl Molecules

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The molecules MCO, where M is a first-row transition metal, have been of considerable interest as prototypes for CO chemisorption on the metal surfaces. There are now a surprisingly large number of theoretical papers concerning the electronic and bonding properties of these species,[1] particularly NiCO. Much less experimental data have been obtained, mostly from rare-gas matrix

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