for H + DH where the SCTSAG and LAG rate constants are essentially the same.

Note that the ICVT/LAG results are better than ‡/W for all four reactions R4-R7 over the temperatures considered. This is consistent with studies of the collinear $O + H_2$ reaction for five potential energy surfaces,[8] on which basis, it was concluded that the LAG transmission coefficient provides an accurate method for describing tunnelling in this case.

Table IV shows that the ICVT/LAG isotope effects are in good agreement with the CSDW ones for all four ratios; the worst difference is 38%. The ICVT/SCTSAG method also does well except for HD/DH where the direction of the error is opposite that of the ICVT/LAG results. Considering the ‡/W isotope ratios, we see that the ‡/W approximation does much better in predicting isotope ratios than absolute rate constants. For (HD + DH)/D_2, the cancellation of errors in the ‡/W ratios is usually better than for the ICVT/SCTSAG or ICVT/LAG ratios, but for the other ratios it is not.

As stated in the introduction, the goal of this study has been to compare approximate rate constants and kinetic isotope effects to accurate dynamical ones for the same potential energy surface rather than to experiment. We have found that the approximate VTST/G rate constants are indeed quite reliable, and we conclude that comparisons of calculations based on more accurate potential energy surfaces to experiment for these systems[5,8,13,33,38,39] may be interpreted in terms of the accuracy of the potential energy surfaces and the experiments, with relatively much less possible error attributable to the dynamical treatment. Since the potential surfaces employed for this study are typical medium-barrier-height surfaces, the conclusion is assumed to be generalizable.

VI. Conclusions

For six of the seven independent reactions considered in this study, the ICVT/LAG rate constants agree with accurate quantum rate constants at all the temperatures considered to within the estimated (35%) uncertainty of the quantum rate constants. The only exception is the $D + H_2 \leftarrow H + HD$ reaction, for which the ICVT/LAG rate constants differ from the numerical quantal dynamical ones by 43% at 200 K. Kinetic isotope effects are also accurately predicted by the ICVT/LAG approximation, with the worst results occurring for intramolecular (X + HD) isotope ratios. The ICVT/SCTSAG rate constants are generally less accurate than the ICVT/LAG ones, with the worst error being 73%. Considering all seven reactions at all temperatures studied, the average errors for the ICVT/LAG and ICVT/SCTSAG rate constants are only 15% and 31%, respectively. Since all of these reactions have tunnelling factors larger than about 5 at the temperatures studied, these comparisons demonstrate the remarkable accuracy of the LAG and SCTSAG methods for determining tunnelling factors. Simple theories like conventional TST, with or without a Wigner tunnelling correction, are found to be grossly in error for predicting the rate constants of these reactions and usually less accurate in predicting isotope ratios.

We can summarize the overall accuracy of the ICVT/LAG method for all nine reactions for which comparisons to accurate quantal results are available by combining the present results with those of ref 11, 13, 14, and 35. The only temperature for which comparisons are possible for all nine cases is 300 K. At this temperature, the average discrepancy between the ICVT/LAG results and the accurate quantal ones is only 12%. Furthermore, in only one case is the discrepancy larger than 26%. For the reactions involved in the comparison, the error is expected to decrease as the temperature is increased because most of the error at 300 K is probably caused by inaccuracies in the semiclassical transmission probabilities for energies below the effective barrier, and these become less important as the temperature is increased. Thus the accuracy attained is very encouraging, especially since variational transition state theory with semiclassical ground-state transmission coefficients is a practical theory for a wide range of systems, including reactions of polyatomics for which more accurate methods are impractical.

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Registry No. H, 12385-13-6; H_2, 1333-74-0; D, 16873-17-9; HD, 13983-20-5; O, 17778-80-2; D_2, 7782-39-0.

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(38) Blais, N. C.; Truhlar, D. G.; Garrett, B. C. *J. Phys. Chem.* **1981**, *85*, 1094; *J. Chem. Phys.* **1982**, *76*, 2768; **1983**, *78*, 2363.

(39) Garrett, B. C.; Truhlar, D. G. *Int. J. Quantum Chem.*, in press.

Intrinsic Reactivity of Magnesium Surfaces toward Methyl Bromide

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Abstract: The chemisorption and subsequent decomposition of methyl bromide on a Mg(0001) single-crystal surface is found to lead cleanly to the formation of a surface bromide and gas-phase hydrocarbon products including ethane. Stable surface alkyls are not observed even at temperatures as low as −150 °C. Co-adsorbed dimethyl ether does not perturb this reactivity pattern. The formation of either a thin surface bromide or a surface oxide passivates this material to further reaction under UHV conditions. The implications of these results with respect to the mechanisms of carbon–halogen bond cleavage on magnesium and the formation of Grignard reagents are discussed.

There is perhaps no general class of organometallic reactions that rivals in importance the reductive cleavage of carbon–halogen bonds by active metals.[1] Of the many examples of this type of process that one could cite, none assumes the synthetic and historical stature of the formation of the Grignard reagent. The reactivity of these complexes has been studied extensively and, as a result, there is much known about the application of these reagents in synthesis.[1,2] Reliable information about the mech-

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(1) Coates, G. E.; Green, M. L. M.; Wade, K. *Organometallic Compounds. Volume* 1. *The Main Group Elements*, Methuen and Co.: London, 1967; and references cited therein.

(2) See, for example: Kharasch, M. S.; Reinnuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954; and references cited therein.

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anism(s) by which magnesium atoms formally insert into a carbon–halogen bond has emerged, by comparison, much more slowly. This latter fact directly reflects the enormous complexity of studying heterogeneous reactions in solution.

In a series of recent papers, Whitesides and his co-workers definitively established many of the important features characterizing the reaction of organic halides with magnesium.[3] Their studies convincingly demonstrated that the rates of reaction for all alkyl iodides and most alkyl bromides are mass transport limited. Those alkyl bromides which reacted at slower rates and most alkyl chlorides were found to exhibit reaction velocities close to, but not limited by, that of mass transport. Thus, for many organic halides, the process by which a carbon–halogen bond is cleaved by magnesium in the presence of a polar solvent is characterized by a low activation energy, $E_a \leq 2$–4 kcal/mol. Their studies also confirmed the central role which organic radicals play in the formation of Grignard reagents.[4]

To date, most insights into the mechanisms of reductive carbon–halogen bond cleavage, significant as they are, largely derive from analyses of kinetics, structure–reactivity profiles, and product distributions. For heterogeneous reactions occurring at transport limited rates, kinetics yields little information about important processes occurring *on* the surface. Even in the absence of transport limitations, the nature of the surface reactions might be such so as to conceal subtle features of the reaction mechanism(s); for example, similar products might be obtained from competing reaction channels of markedly different character. We are thus led to ask whether the mechanistic complexity characterizing electron transfer reactions in solution is mirrored in those occurring at or on a surface? How do carbon–halogen bonds cleave on a metal surface? Are radicals (neutrals or ions) formed? How does surface composition influence the rate of such reactions? What are the intrinsic barriers to such processes?

With these questions in mind, and in order to bring a full complement of modern surface spectroscopies to bear on this interesting system, we have conducted an ultra-high-vacuum (UHV) study of the interaction of an alkyl halide with a magnesium single-crystal surface. This paper, reporting our results for the chemisorption and subsequent decomposition of methyl bromide on Mg(0001) (neat and in the presence of dimethyl ether), presents, what to us was, a surprising conclusion. It is shown that the reaction of this simple, prototypical alkyl halide with atomically clean magnesium *does not result generally in the formation of a stable metal–carbon bond.* We show further that the presence of dimethyl ether proves ineffective in stabilizing this bond under our reaction conditions. The implications of our results with respect to the *mechanisms* by which magnesium cleaves a carbon–halogen bond will be detailed.

Experimental Section

Experiments were performed in two UHV chambers. The XPS experiments were run in a ion and titanium sublimation pumped system containing a modified Kratos X-SAM 800 X-ray photoelectron spectrometer. The hemispherical electron energy analyzer was operated in a fixed analyzer transmission mode with an instrumental resolution of ~1.1 eV. Both Al Kα and MgKα X-ray sources were used. All core levels have been referenced to the magnesium 2p core level (unresolved doublet, binding energy = 88.6 eV). Auger electron spectroscopy (AES) could also be performed in this system.

The second UHV chamber was a diffusion and titanium sublimation pumped system equipped with 4-grid low-energy electron diffraction (LEED) optics (Varian), a single pass cylindrical mirror analyzer (Phi) for Auger electron spectroscopy (AES), a quadrupole residual gas analyzer (Inficon) for temperature-programmed desorption (TPD), and a high-resolution electron energy loss spectrometer (EELS). Typical EELS beam currents were 1–2×10^{-10} amps (at ~4.5 eV) and electrons were collected only in the specular direction. The elastic scattering peak from a clean magnesium surface was 1–2×10^5 counts s^{-1}, with a full width at half maximum (fwhm) between 50 and 70 cm^{-1}. Both UHV chambers contained ion sputtering guns for sample cleaning and simple effusive molecular beam sources for gas dosing.

A Mg(0001) single crystal (>99.98% pure) was oriented (±1/2°), cut, and polished by standard metallographic techniques. The sample was cleaned of trace carbon, oxygen, and sulfur impurities by repeated cycles of neon, argon, or xenon ion bombardment (500–1000 eV, 10 μA/cm^2) at both 25 and 150 °C followed by annealing under vacuum at 150 °C to remove implanted gases and restore surface order (LEED showed a sharp (1X1) pattern with negligible background intensity). Sample cleanliness was carefully monitored by using both AES and XPS. The sample could be cooled to −150 °C with lN$_2$ for low-temperature adsorption studies.

Methyl bromide and dimethyl ether were obtained from Matheson Gas Inc. and were of ≥99.5% and 99.9% purity, respectively. The methyl bromide was further purified by removing the head gas from the cylinder several times by venting the cylinder into a stainless steel manifold which had been evacuated previously to ~5×10^{-7} Torr. In situ mass spectroscopic analysis of the gas stream from the doser showed methyl bromide with no water or methane present above background levels. In a separate control experiment, appearance potential, Fourier transform-mass spectroscopy established that hydrogen bromide (HBr) and bromine (Br$_2$) were insignificant contaminants (<300 ppm). The dimethyl ether cylinder was prepared in a manner similar to that described above for methyl bromide. Methyl-d_3 bromide (99.5% isotopic purity) was obtained from Merck Isotopes and was used as received.

Results

Photoemission Data. Due to the limited sensitivity of X-ray photoelectron spectroscopy, much of the data which follows correspond to surfaces which have been exposed to greater than monolayer quantities of methyl bromide (low exposure data obtained by EELS are described below). Even with this restriction, it is found that the nature of the materials formed upon dosing a clean, cold ($T = -150$ °C) Mg(0001) surface with methyl bromide depends strongly on the magnitude of the gas exposure. At exposures of the order of 20 L (1 L = 1 langmuir = 1×10^{-6} Torr s), core level spectra are observed which are consistent with the formation of a physisorbed multilayer. Subsequent analyses by both EELS and temperature-programmed desorption confirms that the majority of this spectral intensity does, in fact, originate from such a mulilayer (see below). At lower exposures (of the order of several langmuirs), an examination of the core level spectra provided evidence for both the physisorption and dissociative chemisorption of methyl bromide. Careful analysis of these same spectra proved inconclusive as regards the fate of the methyl moiety associated with the dissociated bromide which was observed.

Slowly warming the sample to temperatures greater than −130 °C results in the desorption of the multilayer (and, as will be shown, a hydrocarbon product as well). Figure 1a shows the 3p core level spectrum of the residual, strongly chemisorbed bromine. The spin–orbit splitting of 6.4 eV and the binding energy of 184.1 eV are consistent with the assignment of a surface magnesium bromide. As shown in Figure 2, there are no observable shifts in the metal core levels as demonstrated here for the Mg 2s line.[5] Careful inspection of this same data reveals that the plasmon structure associated with the above is only slightly modified in that the intensity and definition of the surface plasmon is reduced after reaction with methyl bromide. This result suggests that the reaction of this surface with the alkyl halide under UHV conditions

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(3) (a) Roger, H. R.; Hill, C. L.; Fujiwara, Y.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 217–226. (b) Rogers, H. R.; Deutch, J.; Whitesides, G. M., *J. Am. Chem. Soc.* **1980**, *102*, 226–231. (c) Rogers, H. R.; Rogers, R. J.; Mitchell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 231–238. (d) Barber, J. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 239–243. (e) Root, K. S.; Deutch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 5475–5479.

(4) See ref 3, especially 3c and 3d, and references cited therein.

(5) It might be expected, as a first-order analysis, that the observation of a strongly chemisorbed bromide would require a concommitant finding of strong perturbations of the magnesium core levels. This need not be so for several reasons. First, the kinetic energy of the photoelectrons yielding the data in Figure 2 are large (i.e. > 1000 eV). We are thus sampling a significant volume of the substrate and, as such, any spectral contributions from a submonolayer bromide are likely to be lost in the much larger, bulk-derived intensity. Second, the precise binding energy of a sub- to monolayer bromide is expected to be extremely sensitive to such complex issues as Madhelung potentials and other final state effects.

(6) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume I*; NSRD-NBS 39; U.S. Government Printing Office: Washington D.C.; 1972.

(7) Ault, B. S. *J. Am. Chem. Soc.* **1980**, *102*, 3480–3484.

(8) Huber, K. P.; Herzberg, G. "*Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979; p 394.

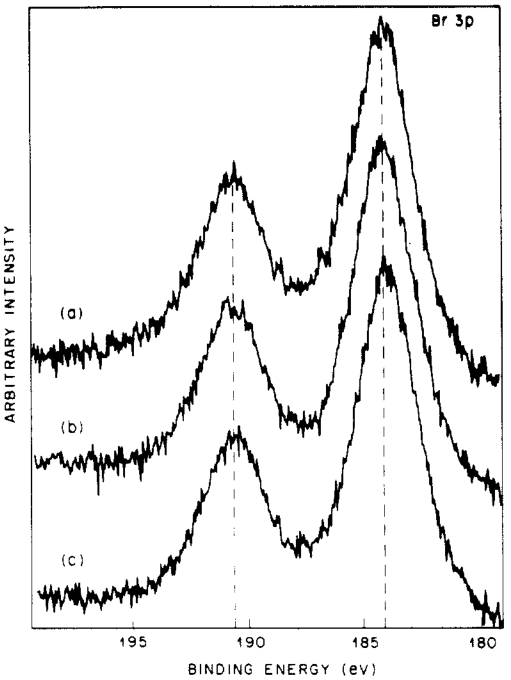

Figure 1. Bromine 3p core level spectra for a Mg(0001) surface reacted with methyl bromide under varying conditions: (a) 300 L of neat MeBr at −150 °C then warmed to −20 °C; (b) 300 L of 2:1 dimethyl ether: methyl bromide at −20 °C; (c) as in spectrum b except a 5:1 mixture of dimethyl ether and methyl bromide was used. All spectra are normalized to the spectral intensity in spectrum a.

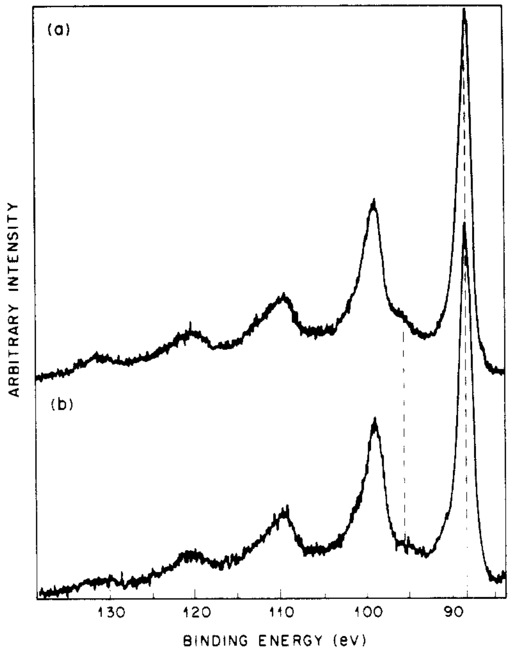

Figure 2. XPS data showing the Mg 2p core level (unresolved doublet at 88.6 eV) and associated plasmon loss features. The spectra are for the (a) clean and (b) the reacted surfaces, respectively. The exposure in spectrum b was 20 L of neat MeBr at −150 °C followed by warming to ambient temperature. The dashed lines denote the positions of the 2p core level and the principal surface plasmon.

is not corrosive, terminating at or near monolayer quantities of deposited bromide (see below). Careful inspection of the C 1s region surprisingly revealed that little or no carbon was present on the reacted metal surface. This is clearly shown in Figure 3a. In this spectrum, the vertical axis was scaled so as to present equal intensity as that observed for the Br $3p_{3/2}$ (Figure 1a) core level if a 1:1 atomic ratio were present (a relative cross section of 3.3 was assumed for Br $3p_{3/2}$ to C 1s). Only noise is apparent, a result suggesting that the cleavage of methyl bromide on Mg(0001) results in the loss of carbon from the surface. This result was

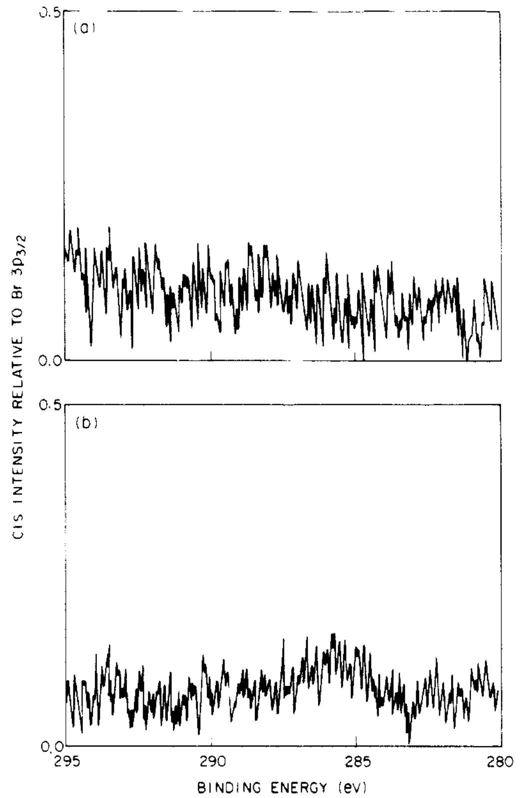

Figure 3. XPS data showing the C 1s core level region. The spectra in parts a and b correspond to the exposures described in parts a and b of Figure 1, respectively. The spectra have been normalized to the observed intensity of the Br $3p_{3/2}$ core level spectra a and b in Figure 1 assuming a relative cross section of 3.3. These spectra thus reflect the atomic ratio of carbon to bromine present on the surface.

independently confirmed with use of Auger electron spectroscopy.

A series of experiments in which the temperature of the substrate was varied over a wide range (−100 to 180 °C) did not yield results substantively different from that described above. It was also found that doses of MeBr as high as 300 L ($T \leq 20$ °C) deposited only slightly more of the stable bromide on the surface as that obtained at the lower exposure described above. We have also examined the materials that result from dosing the surface with mixtures of dimethyl ether and methyl bromide. Three different stoichiometries were examined: 1:1, 2:1, and 5:1. With use of the Br 3p core level spectra as a diagnostic probe of reactivity, the influence of dimethyl ether is readily discerned as shown by the representative data given in Figure 1. The spectra shown in parts b and c of the figure arise from a 300-L exposure of the clean surface to 2:1 and 5:1 mixtures (by pressure) of dimethyl ether and methyl bromide, respectively, at ca. −20 °C. These spectra have been normalized to the spectrum in part a which was obtained from a sample given to 300-L exposure to neat MeBr at −150 °C followed by warming to −20 °C. Both the quantity and identity of the stable surface bromide produced are unaltered by the presence of the ether. Gas exposures and substrate temperatures were again varied in a manner comparable to that described above. Except for the quantity of bromide chemisorbed (smaller quantites than that described above were noted at lower exposures), the results obtained were identical. As was the case for neat MeBr, little or no carbon was found on this surface. This is clearly shown in Figure 3b where a 300-L exposure to a 5:1 mixture of dimethyl ether and methyl bromide yielded little intensity in the C 1s core level region. Control experiments using dimethyl ether alone gave no indication of strong adsorption or reaction of this material with Mg(0001); at exposures of Me_2O greater than 300 L trace amounts of oxygen were detected on the surface by AES and may indicate the adsorption of a water impurity.

Electron Energy Loss Spectroscopy. High-resolution EELS studies on Mg(0001) surfaces cleaned and dosed as described

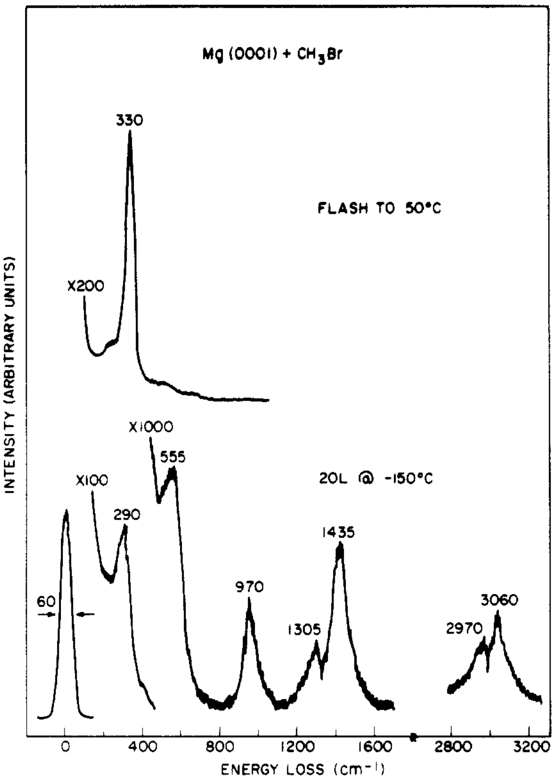

Figure 4. High-resolution EELS data for methyl bromide adsorbed on a Mg(0001) surface under varying conditions. The lower trace is that obtained for a phyisorbed multilayer (20-L exposure to MeBr at −150 °C) residing atop a reacted surface bromide produced by the cleavage of the initially contacting adsorbate (see text). The upper trace reflects the surface obtained by desorbing the multilayer.

Table I. Vibrational Spectra of Gas-Phase and Adsorbed MeBr[a]

mode	gas phase[b]	physisorbed[c] multilayer	matrix[d] isolation
nCH$_3$ s stretch	2972	2970	2800
CH$_3$ s deformation	1306	1305	541[e]
C–Br stretch	611	555	f
CH$_3$ d stretch	3056	3060	2886
CH$_3$ d deformation	1443	1435	g
CH$_3$ rock	955	970	g
Mg–C stretch		g	g
Mg–Br	371[h]	290	g

[a] All values in cm^{-1}. [b] Reference 6. [c] This work. [d] Reference 7. [e] CH$_3$ s deformation of the isolated methyl radical is observed at 611 cm^{-1}, reference 7. [f] C–Br bond cleavage. [g] Modes not detected. [h] Gas-phase diatomic stretching frequency, ref 8.

above revealed essentially two types of spectra. In the first ($\gtrsim$25 L MeBr at −150 °C), several broad loss features (Figure 4, lower trace) are observed. The intense mode at ~300 cm^{-1} is believed to be, based on evidence which follows, a Mg–Br stretch suggesting that at least part of the methyl bromide in the multilayer has, in fact, undergone bond cleavage on the surface. The relatively weak features in the 500–1500 and 2900–3100 cm^{-1} regions are readily ascribed to modes of a physisorbed species. Their assignments are summarized in Table I. Similar, but weaker spectra are seen for the deuterated species. We note, as a comparison to the above, that alkyl halides which chemisorb molecularly on metal surfaces are characterized by distinctly different vibrational spectra.[9]

On warming ($T > -130$ °C), a much simpler spectrum is observed. As shown in the upper trace of Figure 4, the EELS spectrum is dominated by an intense mode at 330 cm^{-1} (assigned to the Mg–Br stretch, see below) with weaker shoulders at both higher and lower frequency. Control experiments suggest that the high-frequency shoulder is most likely due to a minor, dissociatively chemisorbed oxygen contaminatn on the surface. The origin of the low-frequency shoulder (ca. 210 cm^{-1}) is unknown at present, but it may be due to a phonon arising from the growth of small, 3-dimensional MgBr$_2$ crystallites.[10] There is no evidence for the presence of chemisorbed hydrocarbon fragments (i.e., surface methyl groups). It is important to note that qualitatively similar spectra can be obtained directly by either *limiting the exposure of the surface to methyl bromide* for temperatures where multilayers form or *dosing the surface at higher temperatures.* In this regard, we consider explicitly the EELS data which we obtained for extremely limited exposures of the surface to methyl bromide. First, at exposures of methyl bromide less than 1 L (0.2 L was the smallest value which we were able to measure accurately), spectra virtually identical with that presented in the upper trace of Figure 4 were obtained. As above, these spectra were dominated by an intense (although less strong than those obtained at saturation coverages) mode at 310 cm^{-1}, supporting the assignment of the 330-cm^{-1} band in Figure 4 to that of a surface magnesium bromide (i.e., *not* bulk MgBr$_2$). These same spectra, when examined at extreme sensitivity, did not reveal any features which might derive from a stable, surface-bound methyl group.[11] Further discussion of this latter finding is deferred to later in the manuscript.

Temperature-Programed Desorption Spectroscopy Studies. Figure 5 shows a representative TPD spectrum which is obtained from a clean Mg(0001) surface after exposure to 25 L of MeBr at −150 °C. The two ions monitored, m/e 94 and 30, are diagnostic of methyl bromide and ethane, respectively. As is clearly shown, the excess alkyl bromide desorbs at a low temperature ($T \simeq -125$ °C) concurrent with the loss of ethane from the surface. This suggests that this latter reductive dimerization product is, in fact, dissolved in the physisorbed multilayer ice. We note that such spectra must be obtained quickly, as ethane appears to leach continuously from the multilayer even at the low temperatures used for dosing the sample.[12] We have seen no evidence which suggests that the surface bromide desorbs in any form at a temperature less than that at which the crystal itself begins to evaporate at an appreciable rate ($T \simeq 200$ °C).

LEED and Auger Electron Spectroscopy Studies. Careful examination of Auger spectra taken of the sample yielding either the XPS data in Figure 3a or the EELS data in the upper trace of Figure 4 and those similarly derived shows no evidence for the presence of carbon on the surface. Extremely small quantities of oxygen (presumably derived from the adsorption of impurities) were noted occasionally. LEED did not reveal any ordering in the chemisorbed monolayer, the physisorbed multilayer, or the resulting surface bromide layer. In the case of the latter material, the LEED data suggest that any three-dimensional MgBr$_2$ crystallites which may form (see above) must be smaller than the coherence length of the LEED experiment. The bromide monolayer itself must be disordered. We also note that most organic overlayers are very sensitive to electron beam stimulated chemistry and/or desorption.

Co-adsorption Studies with Oxygen. Given that oxides are a major contaminant in the magnesium used in large-scale preprative

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(9) See, for example, the chemisorption of CH$_3$Cl on Cu(100); Dubois, L. H.; Zegarski, B. R. *Chem. Phys. Lett.* **1985**, *120*, 537–541.

(10) Anderson, A.; Lo, Y. W. *Spectrosc. Lett.* **1981**, *14*, 603–615.

(11) These spectra did show, in addition to some variable but low levels of oxygen contamination, two *extremely low intensity losses* centered at 1200 and 1600 cm^{-1}, frequencies which do not correspond to the well-documented positions of a methyl moiety but perhaps originate from a low concentration surface carbonate. This finding suggests what, in fact, is a difficult experimental problem in a study such as this. Methyl bromide is very efficient at displacing reactive contaminants from the walls of the UHV chamber. It is thus important that reasonable care be exercised when examining data obtained for limited fluxes of reagents.

(12) High reagent fluxes were used so as to improve the efficiency, as best as is experimentaly feasible, of the physical entrainment of reaction products in the multilayer ice. It is not expected, if in fact the rate constant for decomposition of a surface bound methyl group at −150 °C were fast, that such a process could be completely efficient even at very high fluxes of adsorbate. It also must be emphasized that the ethane we observe need not derive from a bimolecular elimination as opposed to resulting from the coupling of radical decomposition products trapped in the multilayer.

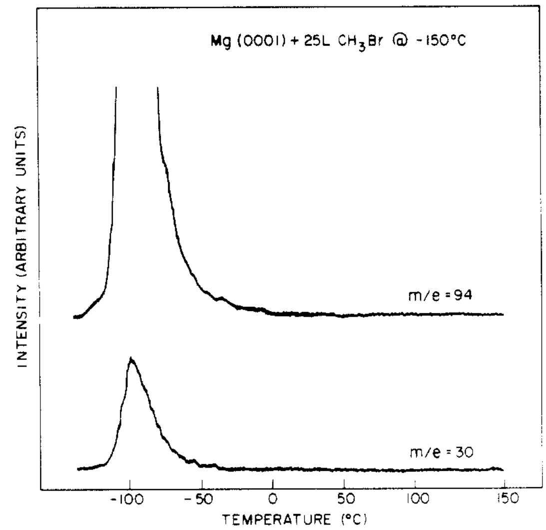


Figure 5. TPD data showing the concurrent desorption of methyl bromide (*m/e* 94) and ethane (*m/e* 30) from a Mg(0001) surface. The initial exposure was 20 L of MeBr at −150 °C.

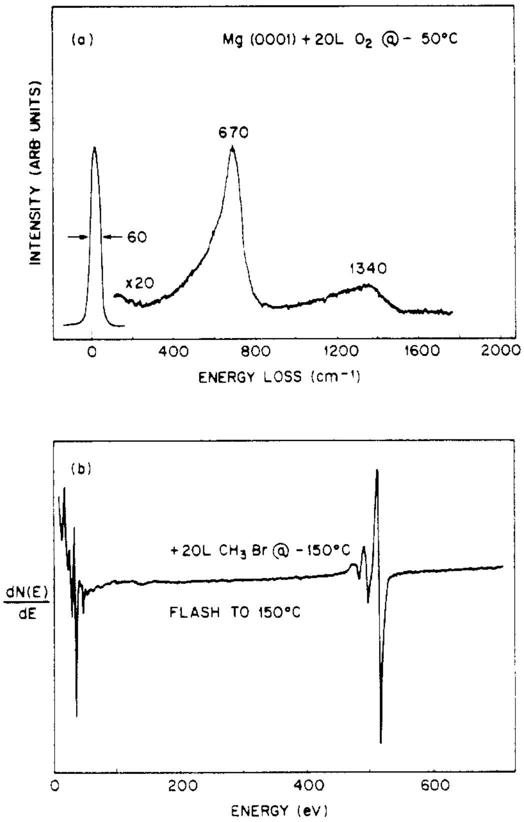
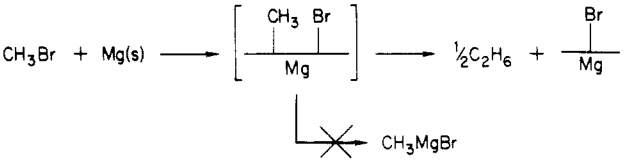


Figure 6. (a) High-resolution EELS spectrum of a clean Mg(0001) surface exposed to 20 L of O_2 at −50 °C. The two intense modes at 670 and 1340 cm^{-1} correspond to the fundamental and double loss of the MgO surface optical phonon.[13] When this surface is exposed to 20 L of MeBr at −150 °C and then warmed, no evidence for chemisorbed bromine is found as shown by the Auger spectrum in part b. This latter result is confirmed by EELS and XPS.

reactions of Grignard reagents, we have undertaken a qualitative study of the influence of oxygen monolayers on the UHV chemistry of Mg(0001) with methyl bromide. These results proved unexceptional and are summarized below. Dosing a clean magnesium sample with 20 L of O_2 at −50 °C produced a surface characterized by the EELS spectrum shown in Figure 6a. Two strong loss features, asymmetrically tailing to lower frequencies and centered at 670 and 1340 cm^{-1}, are clearly observed. The modes correspond closely to the fundamental and double losses of the MgO surface optical phonon,[13] suggesting the development of bulklike characteristics in the thin oxide produced by this procedure. XPS studies are also supportive of the formation of such a thin surface oxide film. Cooling this surface to −150 °C, dosing with MeBr (exposures ≥20 L), and warming so as to desorb the multilayer produces a material whose Auger spectrum (Figure 6b) is identical with that obtained before dosing, strongly suggesting that bromide was not extruded from MeBr on this surface. This conclusion was further supported by XPS and EELS data which showed no evidence of either Br or a Mg–Br stretch, respectively. Thus, even very thin oxides strongly decrease the reactivity of Mg toward MeBr in UHV.

Scheme I



Discussion

The study described above establishes several important features about the fundamental reactivity of an atomically clean magnesium surface with methyl bromide. While these observations do not directly address the most central question—that is, what is the exact nature of the surface reaction mechanism(s) leading to the formation of Grignard reagents—they do provide constraints as to the nature of the processes and intermediates which might be involved. In the discussion which follows, we will review what we have learned about the reactivity of magnesium under UHV conditions and make reasonable inferences as to how these results might relate to heterogeneous reactions in solution.

The most striking feature of the data presented above is that the intrinsic reactivity of Mg(0001) toward methyl bromide is quite high. At −150 °C, the temperature at which most of the low-temperature adsorption data was obtained, cleavage of the carbon–bromine bond is facile. At this temperature ($RT \simeq 0.24$ kcal/mol), bond cleavage appears to be instantaneous. Even if we presume a significant half-life ($t_{1/2} \simeq$ several seconds) and a normal preexponentional factor of 10^{13} s^{-1}, the limiting activation energy we predict is low, of the order of 6–8 kcal/mol.[14,15] It is likely that the real value is significantly lower than this (in complementary matrix isolation studies by Ault[7] and Klabunde and co-workers,[16] Mg atoms and clusters were shown to cleave the C–Br bond at temperatures near −257 °C, see below). The data presented above also suggest that this process is largely insensitive to solvation effects; bond cleavage is equally facile at both low (monolayer) and high (multilayer) exposures of methyl bromide and proceeds comparably in the presence of significant quantities of dimethyl ether. It further is observed that clean Mg(0001) is not particularly reactive toward dimethyl ether; it physisorbs at −150 °C but is not observed to chemisorb strongly. The presence of oxides does seem to perturb this, however, in that some persistant chemisorption is noted.[17]

The second striking feature of this study is that carbon–halogen bond cleavage on clean Mg(0001) does not lead to the formation of a *stable* magnesium–carbon bond when this specific alkyl bromide is used. This latter conclusion (based on XPS, EELS, Auger, and TPD data which show little or no carbon uptake as

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(13) Thiry, P. A.; Liehr, M.; Pireaux, J. J.; Caudano, R. *Phys. Rev.* **1981**, *B29*, 4824–4826. Thiry, P. A.; Ghijsen, J.; Pireaux, J. J.; Caudano, R. *J. Electron Spectrosc. Rel. Phem.* **1983**, *29*, 193–198.

(14) For a discussion of the interpretation of desorption data see: Redhead, P. A. *Vacuum* **1962**, *12*, 203–211.

(15) An additional bound can be provided by the heat of vaporization of the multilayer (~5.9 kcal/mol), a value close to the number we estimate above.

(16) (a) Tanaka, Y.; Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 1013–1016. Imizu, Y.; Klabunde, K. J. *Inorg. Chem.* **1984**, *23*, 3602–3605.

(17) For a general discussion of the chemisorption properties of oxidized magnesium surfaces see: Matrinez, R.; Barteau, M. A. *Langmuir* **1985**, *1*, 684–691.

well as ethane evolution for high-flux exposures) seems to suggest that the formation of Grignard reagents does not proceed by a simple insertion of magnesium into the carbon–halogen bond.

It is also instructive to consider the nature of the reactivity we observe. First, the surface is not restructured or corroded significantly by reaction with MeBr under the conditions used here. Second, due to the physical constraints of UHV experiments such as these, the initial reaction events must involve methyl bromide which is in direct contact with the surface (a condition which need not pertain to reactions in solution). Third, coverages of reacted material terminate at or near monolayer densities. With these constraints, we can draw a simple, yet descriptive, mechanistic picture for the reaction of a clean Mg(0001) surface with multilayer quantities of methyl bromide under UHV conditions (Scheme I). At low exposures, where only submonolayer quantities of MeBr contact the suface, a similar picture emerges with one notable uncertainty. The EELS data presented above strongly indicate that methyl moieties are not retained on this surface at −150 °C (even at methyl bromide exposures of substantially less than 1.0 L). How these methyl groups are lost from the surface is unclear; we have no data which suggests a dominant role for either ethane or methyl radicals. Intuitively, however, we would expect a bimolecular, surface-mediated process such as the reductive elimination of ethane to be unlikely at the lowest coverages. The only other candidate would thus appear to be a direct and facile homolytic cleavage of the Mg–C bond to give a weakly adsorbed methyl radical which is subsequently lost to the gas phase. Indeed, such gas-phase methyl radicals have been observed in the surface-moderated decomposition of trimethylaluminum.[18a] In addition, the literature contains many notable examples of facile, low activation barrier, homolytic bond cleavages characterizing the homogeneous decomposition pathways of metal alkyls.[18b]

An additional suggestion of Scheme I, as expressed in the traditional language of organometallic chemistry, is that the *formal* valence state of the reacted surface metal atoms is *less* than that of the Mg(II) in a stable RMgX product. The bonding between these surface metal atoms and both bond clevage products (the methyl and the bromide) thus more closely resembles bonding to magnesium in a reduced valence state (i.e., Mg(I)). As described above, structures such as these do not seem to yield stable organometallic products directly (under our reaction conditions). They might remain mechanistically viable, however, if *in solution* the reduction of a boundary-layer-trapped radical (generated by homolysis of the Mg–C bond) to the anion were to prove kinetically competent. Even though the data of Whitesides et al.[3] and others[4] strongly support the intermediacy of these radicals in the important product-yielding processes, in the absence of more detailed experiments, conclusions such as these must remain tentative. Be this as it may, our data strongly argues against the notion of a simple, *direct*, surface-mediated C–Br bond cleavage on Mg as a viable route to *stable* organomagnesium reagents.

The conclusions reached above are in excellent agreement with matrix-isolation experiments. For example, Ault has shown that the adduct formed from the reaction of MeBr with magnesium atoms at low temperatures has, at best, a very weak Mg–C bond (the vibrational spectrum of the methyl group is seen to be very close to that of the free methyl radical (see Table I);[7] Klabunde has also shown in similar experiments that a Mg–C stretch is not observed.[16] These metal atom/metal cluster experiments thus serve to confirm the high intrinsic reactivity of low-valent magnesium toward methyl bromide which we observe. The "weakness" of the Mg–C bond reported in these studies also parallels the absence of a surface hydrocarbon fragment as noted above. This may be circumstantial, however, as the analogy between free atoms or clusters and surfaces may not be explicit.[19,20]

It is also of interest to note that the surface passivates itself as a stable bromide under the reaction conditions used here. The nature of this "passivating" layer can be inferred from the data presented above. First, the core level data do not reveal a large perturbation of the Mg line shape other than that due to surface plasmon structure.[5] Second, both XPS and AES suggest that submonolayer to monolayer quantities of bromide are present on the "fully reacted" surface. Taken together, these results strongly preclude significant nucleation and growth of bulk $MgBr_2$ islands. This conclusion is further confirmed by the LEED and EELS experiments described above.

It is important to note that thin multilayer ices of methyl bromide (neat and with dimethyl ether) are in fact stable on the magnesium (0001) surface. In these particular systems, ones which most closely resemble the reactions conducted in solution, we have not seen evidence of Grignard formation up to the temperature at which the multilayer desorbs ($T \simeq -130$ °C). In this regard, the upper limit for the activation barrier for C–Br bond cleavage on a clean magnesium surface we described earlier warrants additional consideration. The data detailed above confirm that these stable multilayers must reside atop a brominated surface. In this sense, then, the *upper* limit above must also reflect the extreme *lower* limit for the activation barrier for the reductive cleavage of the C–Br bond in methyl bromide via an outer-sphere electron-transfer process (that is, across the brominated layer). It is likely that the true lower limit to this outer-sphere process is, in fact, several kcal/mol higher than this ($E_a > 6$–8 kcal/mol).

Why then do we not see Grignard formation in UHV? A simple answer which suggests itself is as follows. We are compelled to believe that the barrier to this process, *by whatever mechanism*, is greater than the barrier for the desorption of the multilayer. Is this inconsistent with the notion of a process whose rate in solution is at or near a transport limit (transport being a low activation energy process)? The answer here is no. We must remember that transport only reflects the flux of reagents to the surface. In such instances, consideration of activation barriers only is insufficient.

We would also note that surface bromination is not the only effective means of passivating Mg(0001) toward MeBr in UHV. As described above, surface oxides, even in monolayer quantities, greatly diminish the reactivity of this surface toward MeBr. While our data do not allow us to make definitive conclusions, we nonetheless remain curious as to how such so called "passivating overlayers" might be involved in the true processes by which Grignard reagents form. There is not doubt that oxides are a ubiquitous contaminant in bulk magnesium. It is also easy to envision processes by which a magnesium surface immersed in a solution might be continually maintained in a partially halogenated or complexed state with little consequence for the yield of reagent. The question suggested therein thus becomes one of whether outer-sphere electron-transfer processes mediated by such layers are important in the formation of organomagnesium reagents.[21] We simply do not know. Future studies may help establish the importance of such notions in this and related systems.

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Registry No. CH_3Br, 74-83-9; Mg, 7439-95-4; C_2H_6, 74-84-0.

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(18) (a) Squire, D. W.; Dulcey, C. S.; and Lin, M. C. *Chem. Phys. Lett.* **1985**, *116*, 525. (b) For leading references see: Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

(19) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91–137; Morse, M. D.; Geusic, M. E.; Heath, J. R.; Smalley, R. E. *J. Chem. Phys.* **1985**, *83*, 2293–2304.

(20) We note, based on the correct observations of one of the reviewers, that the extreme reactivity suggested by matrix isolation experiments can be misleading as reaction is likely to occur during the deposition process. The exact temperature which pertains thereto is somewhat higher than the limiting value and not well known.

(21) If, in fact, outer sphere electron transfers are important processes in the formation of Grignard reagents, it is easy to envision other reasons as to how an overlayer might influence the yield of a specific product. This process is corrosive—magnesium is lost to the solution—and, as such, the ease with which metal is removed might prove sensitive to the nature and concentration of ad- or over-layer atoms.