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Reductive Cleavage of the Carbon−Halogen Bond in Simple Methyl and Methylene Halides. Reactions of the Methyl Radical and Carbene at the Polarized Electrode/ Aqueous Solution Interface

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Reactivities of methyl radical and carbene species, electrogenerated on the surfaces of group IB metals via reductive cleavage of simple methyl and methylene halides (bromides and iodides) in aqueous solution, are investigated using cyclic voltammetry associated with the products' identification by gas chromatography/ mass spectrometry. To appreciate specific changes in the electrochemical behavior of the above halides, related to the nature of the electrode material, similar measurements have also been carried out employing an inert glassy carbon electrode. The replacement of glassy carbon by the group IB metals Ag and Cu was found to lead to a sensible shift (several hundred mV) in their reduction potentials (E_p). Consequently, the reduction of CH_2Br_2, CH_2I_2, and CH_3I starts at potentials positive with respect to the potentials of zero charge (pzc) of Ag and Cu, producing significant amounts of ethylene and ethane, respectively. Methane becomes the dominant reaction product only at the potentials more negative than E_p. The extent of interaction between the reaction intermediates and the electrode surface clearly depends not only on the potential but also on the electronic structure of the electrode. This was confirmed by the results of experiments conducted using the Au and glassy carbon electrodes, having pzc values much more positive than Ag and Cu, at which methane was the only detected product of the CH_3X and CH_2X_2 reduction, over the entire range of potentials. The collected results demonstrate that the reactions undergone by the electrogenerated CH_2 and $^{\bullet}CH_3$ species can be oriented toward formation of either ethylene/ethane or methane by a suitable choice of the electrode material and of the range of applied potentials. The use in this study of Ag and Cu electrodes allows generation of the CH_2 and $^{\bullet}CH_3$ radicals above the onset potential for H_2 evolution, so that their reactivity can be investigated virtually in the absence of competing reactions.

1. Introduction

Carbene and methyl radicals are two important intermediates in Fischer−Tropsch synthesis of waxes, alcohols, and various chemicals used in the production of synthetic lipids and soaps.[1] The latter process is based on the catalytic hydrogenation of CO and CO_2 on transition metals (i.e., Ni, Pd, Fe, Co) and various mixed catalysts and leads to a variety of polymeric products. The yield of polymethylene depends on the surface coverage, mobility, and reactivity of the adsorbed carbene and methyl radicals on the catalyst surface. The adsorption of these reactive intermediates may vary from dissociative to practically nondestructive, depending on the electronic structure of a given substrate.[2,3] For example, chemisorption of methyl radicals on Ni(100) results in carbene, methylidyne, and up to 75% of atomic carbon.[4]

On the other hand, such dissociation reactions are practically absent on group IB metals. Traces of carbene may be formed from adsorbed methyl radicals on stepped Cu surfaces; however, this happens exclusively at very low surface coverages.[5] In fact, the main reason for the highly dissociative chemistry of methyl and carbene on some transition-group metals seems to be the strong interaction between the metal atoms and the C−H bonds of the adsorbate (back-donation from metal d-orbitals to an antibonding C−H orbital).[2,3,6,7]

Stability of an adsorbed carbon-centered radical toward dissociation is determined by the degree of filling of the antibonding adsorbate−metal d states and the size of the coupling matrix element.[7] The former increases to the right in the transition-metal series and is complete for the noble metals (Cu, Ag, and Au), whereas the amount of the coupling matrix element increases down through the groups of the periodic table, making 5d metals the most noble. As shown in early theoretical studies by Hoffmann and co-workers,[8] the $^{\bullet}CH_3$ coupling rate on group IB metals to give ethane is simply related to the position of the Fermi level of the catalyst relative to the M−CH_3 bonding orbital.

Although the adsorption behavior of methyl radicals and carbene on metal surfaces from the gas phase is relatively well understood, very little is known about the stability of these intermediates on the electrodes in contact with aqueous solutions. DeWulf et al.[9] and Hori et al.[10] proposed that electrochemical hydrogenation of CO_2 on polycrystalline copper in aqueous carbonate solutions might involve adsorbed carbene. More recently, we have suggested that carbene and methyl radicals are the reaction intermediates in the process of cyanide elec-

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troreduction on group IB metals and nickel.[11] One of the main goals of the present work was to generate these species directly at the group IB metal/solution interface from sources other than CO_2, CO, or HCN and to investigate how their reactivities change with the nature of the electrode and of the electrolyte. We choose for this purpose the reductive cleavage of methyl and methylene halides. It is quite common in ultrahigh vacuum (UHV) studies to generate carbene and methyl radicals on metal surfaces via thermal or photochemical cleavage of halogenated hydrocarbons such as CH_3I and CH_2I_2.[2,3,12] However, because of its hydrophobic nature the solubility of methylene iodide in aqueous solution is relatively low. On the other hand, methyl iodide is reasonably soluble in water, allowing preparation of, for example, a 16 mM CH_3I solution,[13] which largely exceeds the concentrations of ca. 2−5 mM normally used in kinetic studies related to the electroreduction of alkyl halides.[14,15] The solubilities of CH_3Br and CH_2Br_2 (ca. 1.75 and 11.8 g/100 g H_2O, respectively, at room temperature)[16] are larger than those of their iodinated analogues, and, consequently, their electrochemical behavior can be readily studied in the absence of any organic solvent added.[17]

The electroreduction of carbon−halogen compounds has been extensively studied in the past, especially on mercury electrodes, in view of applications to organic synthesis.[18,19] More recent research efforts fall into two categories: (i) outer-shell heterogeneous (and homogeneous) activation of aliphatic and aromatic halides and (ii) metal-assisted (inner-shell) activation of halogenated molecules. The experimental and theoretical work regarding (i) was mainly carried out by Savéant and co-workers, who used in most cases a glassy carbon electrode in polar aprotic solvents containing tetraalkylammonium salts.[14,20] The choice of glassy carbon was dictated by its relative inertness toward electrogenerated alkyl radicals, contrasting with the behavior of some metal electrodes (Hg, Sn, Cd, etc).[19,21,22] We are not aware of any previous kinetic studies which would compare rates of dissociative electron

transfer on solid electrodes in purely aqueous electrolytes (no organic solvent added). This might be simply due to a low solubility of the studied halogenated aromatic molecules,[21] n-, sec-, and tert-butyl halides,[14] and aliphatic peroxide molecules[23] in water.

Koper and Voth[24a] have recently reported quantum chemistry and molecular dynamics simulations on the reductive cleavage of methyl halide at the electrode/solution interface. Their work[24] also provides some new insights into the mechanism of C−X and X−X (X = halogen) cleavage as well as into the nature of stabilization of the reaction intermediates on the metal surface.

2. Experimental Section

All solutions were freshly made from analytical reagent grade chemicals. Water of 18 MΩ resistivity was obtained with a Milli-Q system (Millipore). Methylene bromide, methylene iodide, and methyl iodide were obtained from Aldrich and methyl bromide was obtained from Merck and were of highest available purity. The measurements were performed at room temperature, 22 ± 1 °C, using a two-compartment cell in which a platinum counter-electrode (large area Pt grid) was separated from a working electrode by a ceramic frit. A cross section of metal (Ag, Cu, or Au) rods, 3 mm in diameter, (Specpure 99.999%, Johnson Matthey) served as a working electrode. The electrode surface was prepared by mechanically polishing the metals with fine emery papers and then with suspensions of 1.0 and 0.3 μm alumina powders. Alumina was removed from the electrode surface via sonication in an ultrasonic bath and washing with copious amounts of distilled water. Before the measurements, the electrode surface was cleaned by cycling the potential into the hydrogen evolution region (two voltammetric scans from −0.4 to −1.8 V and back in a 1 M $NaClO_4$ solution). Potentials were monitored using an Amel potentiostat against a Ag/AgCl/Cl⁻ reference electrode and are reported versus normal hydrogen electrode (NHE).

The electrochemical quartz microbalance, purchased from the Institute of Physical Chemistry (Polish Academy of Sciences, Warsaw), employed AT-cut mass-sensitive quartz crystals (Phelps Electronics) with 10 MHz resonant frequency.

Gaseous reaction products were analyzed with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) (Haysep R and Carbosieves S II column, respectively). The formation of hydrocarbons was followed by gas chromatography/mass spectrometry (GC/MS) performed using the HP 5890 instrument connected to a MSD 5971A quadrupole and interfaced with a capillary column (Carboxen 1006 PLOT). Electron impact spectra were recorded at 70 eV with helium carrier gas.

3. Results and Discussion

3.1. Kinetics of CH_3I Reduction on Glassy Carbon.
Figure 1 shows a cyclic voltammogram[25] recorded during reduction of CH_3I in 1 M $NaClO_4$(aq) on a glassy carbon electrode (curve a) and its numeric simulation (curve b).

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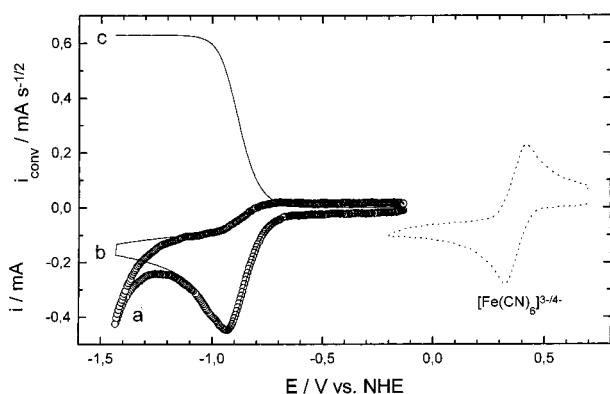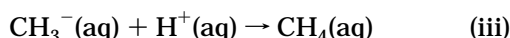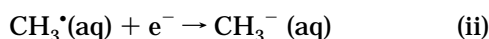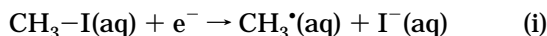
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(25) The cyclic voltammogram presented in Figure 1 was recorded at a glassy carbon rod, $d = 7$ mm (Sigradur K, Germany) embedded in Teflon. Prior to use, the electrodes were polished mechanically to a mirror polish using an alumina powder (0.3 and 0.05 μm, Buehler) on a polishing cloth (WELL-Walter Ebner, Switzerland) and were rinsed several times with distilled water. The electrode potential was cycled in 1 M $NaClO_4$ from 0 to 1.9 V and back and between 0 and −1.6 V, at 50 mV s⁻¹.

Figure 1. Recorded experimental and simulated cyclic voltammograms (circles and solid line, respectively) for the reduction of 5.45 mM CH_3I at a glassy carbon electrode in aqueous solution containing 1 M $NaClO_4$. Curve c represents a convoluted cathodic current. The scan rate was 50 mV s^{-1}.

Convolution of the simulated voltammogram (curve c)[26] is consistent with an irreversible one-electron process having the apparent rate constant at zero overpotential $k^0(app) = 2 \times 10^{-4}$ cm s^{-1} and $\alpha = 0.48$ (note that the observed deviation of the current from the simulated limiting current at the plateau of the cathodic wave is due to the onset of hydrogen evolution (curve a) at glassy carbon). This suggests an extremely fast kinetics of CH_3I reduction as compared to the glassy carbon/dimethylformamide (DMF) system where reaction kinetics were found to be several orders of magnitude slower.[27] Apparently, electron transfer to the antibonding orbital of CH_3I results in the formation of a methyl radical (reaction i); the further reduction of the methyl radical (reaction ii) and its chemical reaction with water (formally, with H$^+$(aq) ions) (reaction iii) are not perceptible over the investigated potential range.

$$CH_3-I(aq) + e^- \rightarrow CH_3^\bullet(aq) + I^-(aq) \qquad (i)$$

$$CH_3^\bullet(aq) + e^- \rightarrow CH_3^-(aq) \qquad (ii)$$

$$CH_3^-(aq) + H^+(aq) \rightarrow CH_4(aq) \qquad (iii)$$

The standard redox potential ($E°$) for the reduction of a methyl halide to a methyl radical (reaction i) can be obtained from eq 1:

$$FE°_{CH_3X/^\bullet CH_3+X^{-aq}} =$$
$$-D_0 - T(\bar{S}_{CH_3X} - \bar{S}^\bullet_{CH_3} - \bar{S}_{X^\bullet}) + FE°_{(X^\bullet/X^-)}{}^{aq} \quad (1)$$

where D_0 is the dissociation energy of the C−X bond, F is the Faraday constant, T is the temperature (K), and $\bar{S}$ is the molar entropy of the species involved in the bond-breaking process (J K^{-1} mol^{-1}). The resulting $E°$ value for reaction i is about −0.73 V.[27] The formal redox potential for reaction ii can be simply estimated as the difference in the Gibbs energies of formation of the CH_3^- carbanion and of the methyl radical in water. In fact, the reduction of the methyl radical to form methane can even be expected to occur already at potentials positive to the onset of the CH_3I reduction because the electron affinity of $^\bullet CH_3$ in a

vacuum is positive ($E_A = 0.08$ eV),[28] and its hydration energy is rather small and comparable to that of CH_4 (ca. 8 kJ/mol).[29] The formal potential for the reaction

$$CH_3^\bullet(aq) + H^+(aq) + e^- \rightarrow CH_4(aq)$$
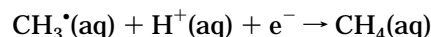
can be derived from the free energies of the methyl radical and methane formation in water and from the pK_a of the CH_4/CH_3^- couple:

$$FE°_{CH_4/^\bullet CH_3} = \Delta G^{f,aq}{}_{^\bullet CH_3} - \Delta G^{f,aq}{}_{CH_4} - RT \ln pK_a \quad (2)$$

However, the experimental data indicate that the CH_3I reduction in aqueous solution on a glassy carbon electrode is a pH-independent process. Thus, the cathodic peak remained unchanged after adjustment of the solution pH from 7.0 to 2.0. This observation is consistent with the transfer of the first electron to CH_3I as being the rate-determining step of the electrode reaction. The electron affinity of the hydroxyl radical is close to 1.8 eV, and $E°(OH^\bullet/OH^-) \approx 1.82$ V versus NHE,[30] so at potentials at which the CH_3I reduction occurs at the carbon electrode the hydroxyl radical should be immediately converted to OH$^-$ anion. Benderski[31] has concluded that the CH_3^- carbanion reaction with water, rather than the H-abstraction reaction, is responsible for the methane evolution from CH_3Cl under the photoemission-into-solution conditions. Note also that we have not observed any deuterium abstraction from deuterated methanol in the case of CD_3I reduction in a CD_3OD/H_2O mixture (1:1). CD_3H (rather than CD_4)[32] evolution accompanying methyl iodide reduction over the range of potentials studied was detected by GC/MS. This confirms the lack of hydrogen abstraction reactions and is consistent with the previous suggestion that the reduction of a methyl radical to a methyl carbanion is easier than the transfer of the first electron to CH_3I.

3.2. Reductive Cleavage of CH_2Br_2 and CH_3Br on Silver. Cyclic voltammograms corresponding to the electroreduction of methylene bromide (curve a) and methyl bromide (curve b) at a silver electrode in 1 M $NaClO_4$ solution are represented in Figure 2A. The peak potential for the CH_2Br_2 reduction in 1 M $NaClO_4$(aq) at the silver cathode is about 0.6 V more positive than at the glassy carbon electrode. The value of E_p associated with the CH_3Br reduction on silver is relatively negative, close to −1.1 V (cf. Table 1), whereas on glassy carbon the reaction cannot be observed, being apparently shifted into the hydrogen evolution region. The electroreduction of CH_3Br takes place at potentials negative to the potential of zero charge (pzc) of silver (−0.716 V vs NHE, according to ref 33) and leads to the formation of methane. Almost quantitative formation of CH_4 was confirmed by gas chromatography over the entire potential range of CH_3Br reduction. On the other hand, the CH_2Br_2 reduction occurs on positively charged silver ($E_p = -0.432$ V vs NHE) and

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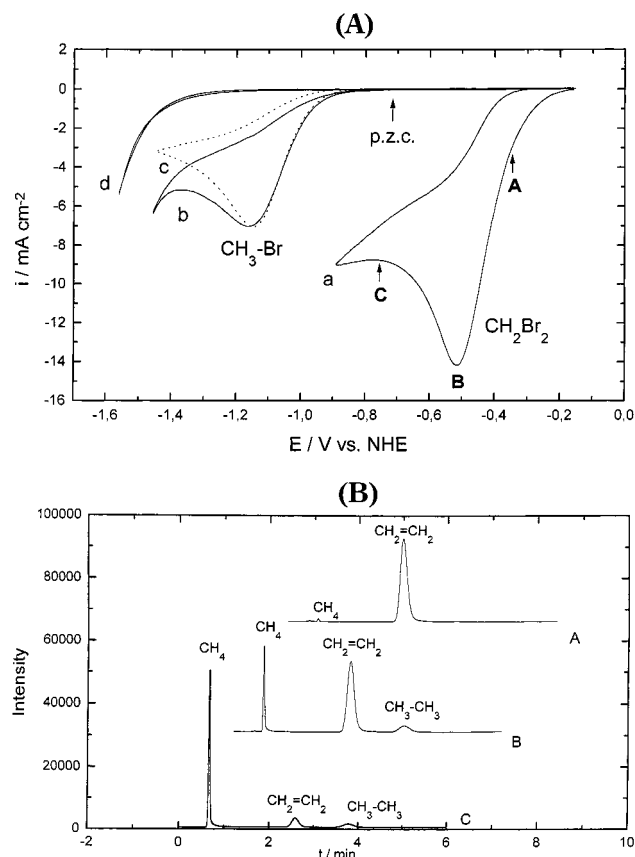(27) Fedurco, M.; Jorand Sartoretti, C.; Augustynski, J. *J. Phys. Chem.*, in press.

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Figure 2. (A) Cyclic voltammetric (CV) profiles for reduction of CH_2Br_2 and CH_3Br (ref 45) at a polycrystalline silver electrode in 1 M $NaClO_4$(aq). The dotted curve (c) represents a simulated voltammogram for the one-electron reduction of methyl bromide. Curve d was recorded in the solution of the supporting electrolyte. The letters A, B, and C indicate three electrode potentials at which gaseous reaction products were taken for GC analyses. The scan rate was 50 mV s^{-1}. The potential of zero charge of polycrystalline silver is indicated by pzc. (B) Gaseous products formed during constant-potential (indicated as A, B, and C in Figure 2A) electrolyses of CH_2Br_2. They were removed from the cell by purging the cathodic compartment with argon at a rate of 8 mL/min and analyzed using a FID detector and a Haysep R column.

Table 1. Effect of the Electrode Material upon the Peak Potential, $-E_p$ (V vs NHE) for the Dissociative Reduction of Selected Aliphatic Halocarbons in H_2O/1 M $NaClO_4{}^a$

	n-BuI	*n*-BuBr	CH_2I_2	CH_3I	CH_2Br_2	CH_3Br
GC	nsw	nsw	0.609	0.932	1.047	
Cu			0.500	0.80	0.588	1.092
Ag		1.080^c	0.398	0.762	0.432	1.082
				0.840^b		

^{a} Reactant concentration was 5.45 mM; measured at a scan rate of 0.05 V s^{-1}; nsw, nonsoluble in water. ^{b} Measured at a Ag(111) electrode. ^{c} Recorded in H_2O/*n*-propanol (4:1) containing 1 M $NaClO_4$.

results in the formation of C_2 and/or C_1 hydrocarbons, depending on the electrode potential. In this case, the electrogenerated bromide anions and reaction intermediates (i.e., carbene) are stabilized by the positively charged silver surface much more strongly than are the $^{\bullet}CH_3$ radicals formed during CH_3Br reduction on the negatively charged silver.

Labels A, B, and C in Figure 2A indicate three potentials of the Ag electrode at which gaseous samples were analyzed by gas chromatography (the corresponding chromatograms are shown in Figure 2B). Ethylene appears as the main reaction product at potentials close to the
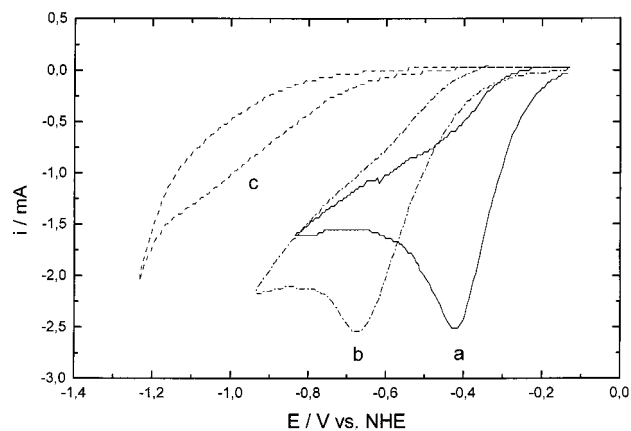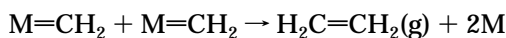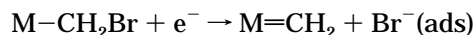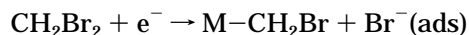

Figure 3. CV profiles showing the marked effect of the electrode material upon the potential range of CH_2Br_2 reduction. Curves a, b, and c represent the electroreduction of 28.5 mM CH_2Br_2 in 1 M $NaClO_4$(aq) at Ag(111), polycrystalline Cu and Au (A = 0.38 cm^2), respectively. The scan rate was 50 mV s^{-1}.

onset of CH_2Br_2 reduction (A); both ethylene and methane (with small amounts of ethane) are formed in the intermediate region (B), and methane (accompanied by traces of ethylene and ethane) becomes the principal product at potentials more negative than E_p (C). The fact that CH_3Br is reduced at much more negative potentials than CH_2Br_2 excludes its involvement as an intermediate of the CH_2Br_2 reduction.

The formation of C_2H_4 at potentials more positive than E_p for the CH_2Br_2 reduction would suggest that both C–Br bonds in methylene bromide are broken to give adsorbed carbene. The reaction in this potential range may occur through the following steps:

$$CH_2Br_2 + e^- \rightarrow M-CH_2Br + Br^-(ads)$$

$$M-CH_2Br + e^- \rightarrow M=CH_2 + Br^-(ads)$$

$$M=CH_2 + M=CH_2 \rightarrow H_2C=CH_2(g) + 2M$$

The latter scheme is supported by the identification by GC/MS of C_2D_4 as the main product of the CD_2Br_2 reduction over this range of potentials.

In this connection, the question arises of why the reduction of CH_2Br_2 takes place apparently as a two-electron process, accompanied by carbene recombination to ethylene, rather than as two separate one-electron processes giving rise to two cathodic waves. It seems plausible that the electron transfer from silver to an antibonding orbital of CH_2Br_2 leads to an immediate dissociation of one of the C–Br bonds (which may occur on the subpicosecond time scale) and is followed by the transfer of the second electron to the adsorbed $^{\bullet}CH_2Br$ radical to give bromide anion and carbene, both being stabilized via adsorption on the positively charged silver surface. Another scenario, involving abstraction of the hydrogen atom from a water molecule by an electrogenerated $^{\bullet}CH_2Br$ radical (which would result in the formation of CH_3Br and of an $^{\bullet}OH$ radical) appears unlikely for the reasons already mentioned above.

3.3. Influence of the Electrode Material upon Reduction of CH_2Br_2. As shown in Figure 3, cathodic reduction of CH_2Br_2 is strongly affected by the nature of the electrode material. Thus, in comparison with polycrystalline Ag the peak maxima for Ag(111) and for polycrystalline Cu are shifted negatively by 0.08 and 0.15 V, respectively. In the case of a Au electrode, the CH_2Br_2

reduction starts only at a potential ca. 0.4 V more negative than on Ag and occurs at lower current densities. Such a behavior is clearly attributable to a lacking adsorption of carbene and bromide anion on the negatively charged gold surface. In fact, the potential of zero charge for polycrystalline gold is about 1 V more positive than that of polycrystalline silver (pzc of gold in contact with a nonadsorbing electrolyte such as $NaClO_4$ was indicated as -0.05 V vs saturated calomel electrode).[34] Consequently, the Fermi level of the positively charged gold is located much below the lowest unoccupied molecular orbital (LUMO) of CH_2Br_2, so direct electron transfer to this energy level can start only at potentials more negative than pzc. The small cathodic currents associated with the CH_2Br_2 reduction on gold (Figure 3, curve c) may be due to a poor electronic coupling between the halocarbon and the metal. The fact that the reduction process occurs on Au in the H_2-evolution region implies that at least a fraction of CH_2Br_2 molecules may get activated on the electrode surface via reaction with adsorbed hydrogen atoms rather than by a direct electron transfer. The situation is similar to that for the d-group metal cathodes having even lower overpotentials for hydrogen evolution than gold.

In their recent calculations, Koper and Voth[24a] have assumed, in the case of CH_3Cl reduction on Pt(111) in aqueous solution, that intermediates and/or products of the reaction do not interact with the metal surface. However, they allowed for the overlap of the antibonding carbon—halogen orbital with the metal. Similarly, one could assume that the reductive cleavage of CH_2Br_2, CH_3Br, and $^•CH_2Br$ on silver, investigated in the present work, occurs also in the vicinity of the electrode surface with no adsorption of reaction intermediates or products. However, in such a case, it would be difficult to explain the fact that the $^•CH_2Br$ radical undergoes one-electron reduction on Ag in the same potential range as CH_2Br_2, especially if one considers that according to a theoretical estimate $E^°_{^•CH_2Br/CH_2+Br^-}$ is more negative than $E^°_{CH_2Br_2/^•CH_2Br+Br^-}$ by ca. 0.570 V![27]

Our ab initio and density functional theory (DFT) calculations[35] suggest that the energy of the LUMO orbital of $^•CH_2Br$ is lower than that of triplet carbene CH_2 ($^3B_1$) as well as the lowest electron acceptor level in CH_2Br_2. This is consistent with the fact that electron affinity of the $^•CH_2Br$ radical in the gas phase is very positive ($+0.82$ eV)[28c] and exceeds that of the free $^3B_1$ ($E_A = 0.65$ eV).[30] Hydration energy for such species is not expected to be high; however, one certainly cannot neglect their stabilization by adsorption at the electrode surface. In fact, in the absence of adsorption of the intermediates at the metal surface, the reduction potentials for a given halocarbon at copper and silver should be very close (note that these two metals have quite similar pzc values). As shown in Table 1, the peak potentials for all the studied halogenated molecules are actually 0.1–0.2 V more negative at copper than at silver (except for CH_3Br, undergoing reduction at the negatively charged silver and copper practically at the same potential). Although we cannot make any definite conclusion as regards the strength of carbene adsorption

on the silver surface, some insight may be obtained into the extent of its stabilization on copper.

3.4. Interaction of Carbene with the Metal Surface. Carbene adsorption on copper powder during diazomethane (both CH_2N_2 and CD_2N_2) decomposition in an argon matrix was studied by Fourier transform infrared spectroscopy.[36] The problem was also treated theoretically in ab initio[37] and DFT[38] calculations on $M=CH_2$ and M_5-CH_2 clusters (where M = Cu, Ni, and Fe). Accordingly, carbene CH_2 ($^3B_1$) in the ground state reacts with Cu (^2S) giving doublet $CuCH_2$ ($^2B_1$) having a covalent σ bond between the carbon and copper atoms, while an unpaired π electron is localized on CH_2. The density functional calculations[38] predict the transfer of $0.2e^-$ from copper to carbene and the Cu—C dissociation energy of 280 kJ mol^{-1} for $CuCH_2$ ($^2B_1$). The latter authors suggest that involvement of metal p- and d-electrons in carbene clusters containing five copper atoms can lead to a decrease in the Cu—C bond energy to 242 kJ mol^{-1} in the case of Cu_5CH_2 ($^2B_1$) and, even, to 105 kJ mol^{-1} for Cu_5CH_2 ($^2B_2$), respectively. Clearly, the bond energy, vibrational frequencies of the adsorbate molecule, and the relative position of its electron-acceptor level are expected to vary substantially with the spin state and arrangement of metal atoms on the surface.

In this connection, surface-enhanced Raman spectroscopy (SERS) often reveals a strong potential dependence of vibrational frequencies and band intensities for various molecules adsorbed on group IB metals.[39] Consequently, the extent of carbene stabilization may greatly differ, not only with the nature of specific metallic clusters but also with the potential.

The location of the electron acceptor level in adsorbed carbene is expected to vary as a function of the applied electrode potential. In other words, at potentials positive with respect to their pzc, the excess of positive charge borne on copper or silver should decrease the extent of metal-to-carbene charge transfer. The opposite is expected in the case of increasing cathodic polarization, during which the adsorbed bromomethyl radical, methyl radical, and carbene will undergo partial electron transfer. Here, by electron transfer we understand continuous charge transfer to various metal—adsorbate clusters with increasingly negative potential, rather than a single electron-transfer event in a classical sense. For the bromomethyl radical reduction, the amount of the metal-to-adsorbate charge transfer should result in a measurable cathodic current accompanied by the ethylene formation at the onset potential for the CH_2Br_2 reduction. In such a case, the amount of the cathodic current will be affected by altering the charge density at the metal side of the interface (at a given potential) through coadsorbing on the electrode surface species other than carbon-centered radicals, for example, additional bromide anions.

3.5. Effect of Bromide Anion Concentration. According to Stevenson et al.,[40] the Br^- adsorption on Ag-(111) is a fast and reversible process, in contrast to the formation of an ordered Br^- adlayer (phase transition), occurring at potentials approaching 0 V versus Ag/AgCl, which is kinetically slow. In Figure 4 are represented cyclic

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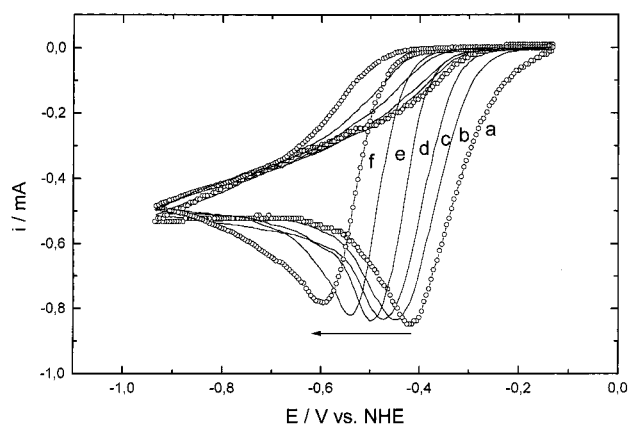
Figure 4. Series of CV profiles showing the effect of increasing bromide concentration upon dissociative reduction of 40 mM CH_2Br_2 at a Ag(111) electrode ($A = 0.070$ cm^2): 1 M NaClO$_4$-(aq) without (a) and with 0.005 (b), 0.015 (c), 0.115 (d), 0.3 (e), and 1 M (f) additions of NaBr. The scan rate was 50 mV s^{-1}.

voltammograms for the CH_2Br_2 reduction on a Ag(111) electrode recorded in the presence of increasing amounts of bromide anions (NaBr) added to the solution. With increasing bromide concentration, the voltammograms are progressively shifted toward negative potentials, the effect being particularly pronounced in the rising part of the cathodic peaks where ethylene is formed. Previous SERS studies indicate that in a 1 M NaBr solution bromide anions remain adsorbed on silver down to quite negative potentials exceeding −1 V versus NHE.[41] For all NaBr concentrations listed in Figure 4, ethylene was found to be the main reaction product at potentials positive of E_p, whereas methane formation always predominated at the plateau of the diffusion-controlled wave. The effect of Br$^-$ upon the onset potential of the CH_2Br_2 reduction cannot be explained as simply due to electrostatic double-layer effects because both methylene bromide and the bromo-methyl radical are neutral species. Furthermore, our experiments were conducted in quite concentrated per-chlorate solutions (1 M NaClO$_4$) in order to limit Frumkin type double-layer effects. Specifically adsorbed Br$^-$ ions will however cause a negative shift in pzc, making the silver surface (in the potential range where CH_2Br_2 undergoes reduction) charged more positively than in the absence of bromide anions.[42] This will in turn tend to diminish the extent of metal-to-carbene charge transfer, as observed experimentally.

3.6. Cleavage of CH_2I_2 and CH_3I on Silver and Copper. Also consistent with the surface-assisted electron transfer (ET) pathway are the results of electrochemical and GC/MS studies on the iodine-containing halocarbon reduction at silver and copper. In fact, despite their largely differing dissociation energies (220 vs 300 kJ mol^{-1}, respectively),[27] CH_2I_2 and CH_2Br_2 undergo reduction at silver from 1 M NaClO$_4$(aq) in the same potential range. In addition, D_0 of the C—Br bond in the $^\bullet CH_2Br$ radical is the largest of all the halocarbons studied in the present work (ca. 330 kJ mol^{-1}) and $E^\circ_{^\bullet CH_2Br/CH_2+Br^-}$ is the most negative of all the halides studied,[27] and yet its reduction to carbene occurs from the onset potential for the methylene bromide reduction (as shown by the formation of C_2H_4 at potentials positive to E_p). Clearly, the Savéant model of dissociative electron transfer (DET)[14b] does not apply in the present case, the electrogenerated $^\bullet CH_2X$

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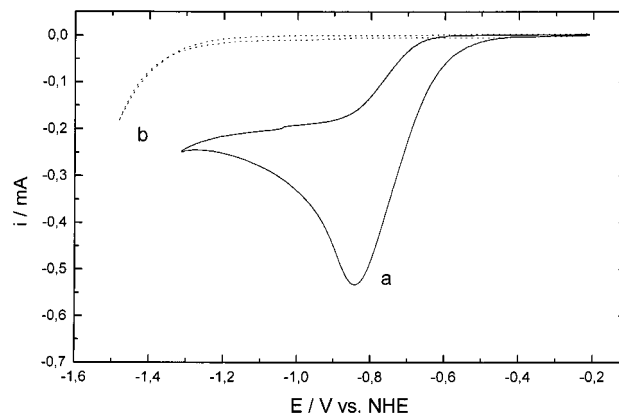

Figure 5. CV profile for the reduction of 5.45 mM CH$_3$I at a Ag(111) electrode in 1 M NaClO$_4$(aq). The dotted line was recorded in the absence of the halocarbon. The scan rate was 50 mV s^{-1}.

radicals being apparently stabilized by adsorption on the electrode surface.

Apparently, the CH$_3$I reduction at silver and copper also follows the inner-shell ET pathway. Although the latter molecule is reduced at Ag at a potential 0.36 V more negative than methylene iodide, at the onset of the reduction, silver still remains positively charged. Thus, again methyl iodide is reduced to ethane and/or methane, depending on the electrode potential.

Figure 5 shows a cyclic voltammogram recorded at a Ag(111) electrode for 6.5 mM CH$_3$I in 1 M NaClO$_4$(aq). The corresponding peak potential is 0.08 V more cathodic than E_p measured at the polycrystalline Ag. Gas chro-matographic analyses revealed that up to 25% of ethane was produced at Ag(111) close to the onset potential of the CH$_3$I reduction. An even larger proportion, accounting for 45−50% of the total hydrocarbon yield, was formed at a polycrystalline Cu electrode. This may be the conse-quence of the lower pzc of Cu as compared to Ag (in the presence of electrogenerated halide anions), favoring the recombination of $^\bullet$CH$_3$ radicals. The M−CH$_3$ bonding orbital is initially doubly occupied, and the CH$_3$ group can be viewed as CH$_3$$^{x-}$ (where $x = 0-1$) due to the charge transfer from the metal. When the methyl groups approach each other, the potential energy of the system initially increases as the C−C bonding and antibonding orbitals, both doubly occupied, begin to form. The potential energy continues to increase until the C−C bonding orbital rises above the Fermi level. At this point, the antibonding electrons can transfer to the metal, and the further C−C formation becomes attractive.[2,8]

On going from the onset potential for CH$_3$I reduction at silver, that is, from ca. −0.5 to −1 V, the electron transfer to the adsorbed methyl group (M−CH$_3$) becomes increas-ingly important. The M−CH$_3$$^-$ species readily react with water molecules coadsorbed on the electrode surface, leading to methane formation. Adsorption of iodide anions and other reaction intermediates during the CH$_3$I reduc-tion on polycrystalline silver was confirmed using elec-trochemical quartz crystal microbalance (EQMB). The observed frequency difference of 40 Hz, as compared to the signal measured in 1 M NaClO$_4$, is somewhat larger than expected for a half-monolayer coverage of Ag by I$^-$ anions. This could indicate that methyl radicals and, eventually, water molecules might be coadsorbed with I$^-$ on the electrode surface. Similarly, the mass change associated with the CH$_2$Br$_2$ reduction (max 30 Hz at −0.6 V) on silver could be explained as due to the simultaneous adsorption of Br$^-$ anions, $^\bullet$CH$_2$Br, CH$_2$, and water mol-
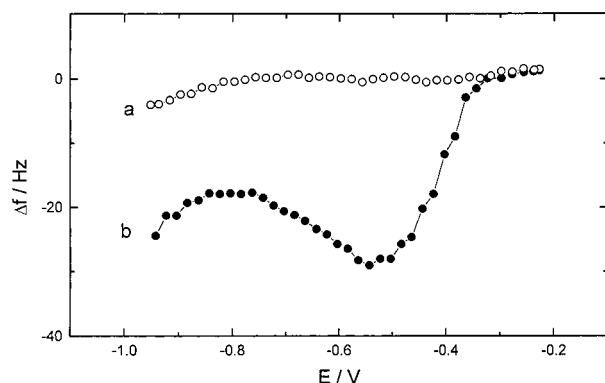
Figure 6. Changes in frequency ($\Delta f = 1$ Hz ~ 1.1 ng of the mass change) recorded at an EQMB (10 MHz) during the electroreduction of 40 mM CH_2Br_2 at a silver electrode (curve b), under similar conditions as in Figure 4a. The mass changes arise from the adsorption of bromide anions, electrogenerated in situ during the methylene bromide reduction, and, possibly, of some other intermediates formed in the course of dissociative ET reactions. Curve a represents a blank experiment in aqueous 1 M $NaClO_4$ solution.
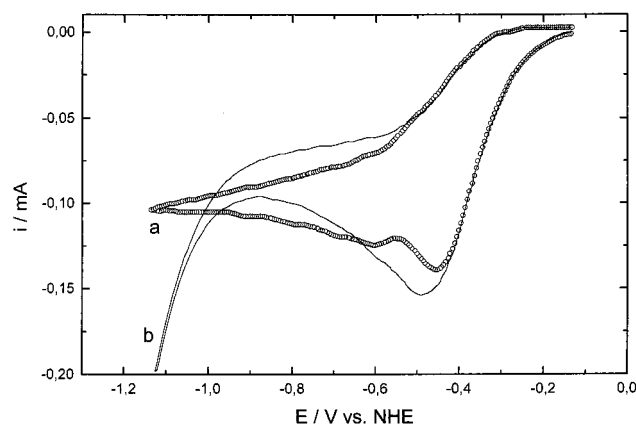

Figure 7. CV profiles illustrating the effect of pH upon the reduction of 6 mM CH_2Br_2 at polycrystalline silver (a) in 0.074 M CH_3COONa (pH 8.4) and (b) in a 0.074 M CH_3COONa/0.126 M CH_3COOH buffer (pH 5.0). Recorded at a scan rate of 50 mV s^{-1}. A sharp rise in the cathodic current at potentials negative of -1 V is due to the hydrogen evolution.

ecules (Figure 6). Moreover, the EQMB measurements have clearly demonstrated that neutral (unreduced) halocarbon molecules are not adsorbed on silver from aqueous solutions.

3.7. Effects of the Reactant Concentration and Solution pH. In the case of 6 mM CH_2Br_2 reduction on silver, one can clearly recognize a second cathodic wave at ca. -0.6 V versus NHE (Figure 7, curve a), which completely disappears when the bulk concentration of methylene bromide is increased to 30 mM. The second cathodic wave is also observable at the silver electrode in the case of 6 mM CH_2I_2 reduction. GC/MS experiments showed that both ethylene and methane were formed at E_p during the reduction of methylene halides, whereas methane was the main product at more cathodic potentials. One may expect that $M=CH_2^-$ reacts rapidly with surface water molecules to give methane, as already mentioned for the CH_3^- and/or $M-CH_3^-$ species. However, in contrast with the CH_3 radical, carbene is significantly more difficult to reduce than the parent molecule from which it has been produced, that is, CH_2Br_2 or CH_2I_2. In fact, there exists clear experimental proof that the CH_2X_2 reduction to carbene and the electron transfer to $M=CH_2$ to give $M=CH_2^-$ and CH_4 are two distinct electrode processes.

Thus, for the low CH_2Br_2 or CH_2I_2 concentrations (i.e., 6 mM CH_2X_2), the peak potential of the first cathodic wave corresponding to the methylene halide reduction to carbene is unaffected by the solution pH, but the second cathodic wave ($M=CH_2$ reduction) is shifted to more positive potentials when the pH changes from 8.4 to 5.0 (cf. Figure 7). A further decrease in pH from 5 to 2 (pH adjusted by dilute $HClO_4$) did not have any significant effect on either the peak potential or the shape of the cathodic wave.

In view of the results collected in the present work, the reduction of methyl and methylene halides appears as a typical electrocatalytic process with both its kinetics and the nature of the final products clearly affected by the employed electrode material. In this connection, we reported recently[27] even larger effects of the same kind observed during experiments conducted in an aprotic solvent, *N,N*-dimethylformamide, with the same reactants and electrode materials (cf. also ref 20a, regarding the reduction of CF_3Br in DMF).

4. Conclusions

The electrochemical cleavage of methylene and methyl halides on the group IB metals in aqueous solutions is addressed here for the first time. The reduction of CH_2I_2, CH_3I, and CH_2Br_2, having relatively low-lying LUMOs, when taking place on the positively charged metal surfaces (i.e., at potentials positive to the pzc of silver and copper) leads first to the formation of CH_2 and $\cdot CH_3$ radicals, respectively. Surface-assisted reactions of these species, resulting either in ethylene or ethane formation, are favored in the range of potentials close to the onset potential for the halocarbon reduction (there exists here an interesting similarity with the cleavage of CH_2X_2 and CH_3X occurring under UHV conditions, where ethylene and ethane are the unique reaction products on silver and gold surfaces).[43] On the other hand, methane becomes the only reaction product at potentials more negative than E_p. The insight into the mechanism of CH_2I_2, CH_3I, and CH_2Br_2 reduction, particularly at the Ag and Cu electrodes, was rendered possible by the fact that the latter reactions (including carbene and methyl radical conversion into methane) take place at potentials significantly more positive than the onset of hydrogen evolution from neutral aqueous solution. Consequently, one may reasonably expect that the adsorbed hydrogen atoms are not involved to any significant extent in the methane formation.

The situation is different for the molecules having high-lying LUMOs and, also, large C−X bond dissociation energies. Typical examples here are CH_3Br and CH_2Cl_2,[44] the reduction of which can start only at the negatively charged metal/solution interface. Thus, the suitable choice of the halocarbon molecule as well as of the electrode material allows one to reach conditions where, at sufficiently positive applied potentials, exclusively C_2- or C_1-hydrocarbons can be generated. This is apparently possible due to the stabilization of the electrogenerated carbon-centered radicals and halide anions by the positively charged metal surface. Once the charge on the electrode side of the interface gets reversed, the electrogenerated

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(44) It was found experimentally in the present work that the electroreduction of CH_2Cl_2 on Ag(111) in 1 M $NaClO_4$ takes place at the negatively charged electrode ($E_p = -1.23$ V vs NHE), close to the onset potential of hydrogen evolution, and results basically in the formation of methane and trace amounts of ethane.

(45) The concentration of CH_2Br_2 used in this experiment was 40 mM; however, no attempt was made here to find out the exact concentration of methyl bromide. The latter molecule is in the form of a highly volatile gas at room temperature.

halide must be strongly repelled from the cathode surface. However, the halocarbon cleavage might still be favored here because of the significant hydration energy for the bromide and iodide anions (ranging from -260 to -300 kJ/mol) and because of quite positive $E°_{(X^•/X^-)}$ potentials for the halide redox couples in water. However, significant deviation from the adiabatic condition of the electrode processes can be experienced in such cases, as illustrated in the present work for the CH_2Br_2 reduction on gold electrode.

The present work brings some important insights into the mechanism of the inner-shell electron transfer as-sociated with the halocarbon reduction on medium hydrogen overvoltage group IB metals. Future studies will be extended to d-group metals such as platinum, palladium, or nickel exhibiting relatively high hydrogen coverages.