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Richard V. C. Carr, Leo A. Paquette*
Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210
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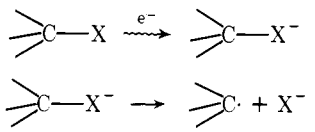
Bond Cleavage of the Solvated Methyl Chloride Anion: A Primary Electrochemical Event

Sir:

Although the specificity of electrochemical reactions lies in the facile reaction pathways provided by removal or addition of electron(s) to the reactants at the electrode,[1] little is known about the actual potential surfaces for these pathways. As an example, the cathodic reduction of alkyl halides has been the topic of ample mechanistic discussion.[2] There seems to be general agreement that the first step involves capture of an electron from the cathode together with, or followed by, cleavage of the halide radical anion:



(1)

One prerequisite to the understanding of the mechanism of eq 1 is the knowledge of the detailed form of the potential surface for dissociation of the anion.[3] We have therefore calculated, using the ab initio GAUSSIAN 70 program,[4] the energy surface for cleavage of CH_3Cl^-, with a crude "solvation shell" of two water molecules.

The choice of basis set is a compromise beteen several requirements: that it include the orbitals appropriate for describing both starting anion CH_3Cl^- and terminal anion Cl^-, while at the same time it be not too large (<50 orbitals) to handle by the available configuration interaction package for doublet states along the dissociation pathway. We therefore used a minimal basis STO-3G set *augmented* by (a) a group of very diffuse s,p Gaussians on carbon to describe the initial anion, with the extra electron trapped in the dipole field of the molecule;[5] (b) a group of semidiffuse "expanded" s,p Gaussians on chlorine, to describe adequately the valence shell of Cl^-, expanded by Coulombic self-repulsion. Diffuse orbitals on Cl added to the previous set give no improvement (<0.03 eV). Extra diffuse s orbitals on the hydrogen atoms do lower the energy (by 0.7 eV), but the configuration interaction becomes intractable because of the great number of very low-lying vacant configurations built on intermixing diffuse orbitals; also diffuse orbitals on hydrogens are not expected to contribute significantly to the dissociation process.

Table I. Energy of CH_3Cl^- and Electron Affinity (Relative to CH_3Cl Calculated with the Same Orbital Set) as a Function of ζ_c, the Gaussian Exponent of the Diffuse Carbon Orbital ($\zeta_{Cl}^{s,p} = 0.5$)

	ζ_c			
	0.1	0.05	0.01	0.005
$E(CH_3Cl^-)$, au	−493.7191	−493.8026	−493.8852	−493.8918
$EA(CH_3Cl)$, eV	−5.35	−2.97	−0.45	−0.23

We first varied the Gaussian exponent ζ_c of the diffuse orbital on C, $\sigma_{Cl}^{s,p}$ being fixed. The results for CH_3Cl^- are shown for $\zeta_{Cl}^{s,p} = 0.5$ in Table I.[6] Although the energy of the anion decreases quite rapidly at first and approaches more and more closely that of the neutral, there is no minimum in the energy. The odd electron tends to "fall off" the molecule and become free. It is possible that a very elaborate set of diffuse orbitals would finally yield a bound anion,[7] as required by the "dipole theorem" for $\mu > 1.625$ D.[5] Here we cannot answer the difficult question of whether CH_3Cl^- is very weakly bound;[8] we can, however, choose a carbon exponent $\zeta_c = 0.01$ which already provides an energy for the anion within 0.5 eV of the neutral calculated with the same basis set. This corresponds to a radius of 4.2 Å for the diffuse orbitals on carbon. Finally we choose for the expanded orbitals on chlorine the exponents $\zeta_s = 1.30$ and $\zeta_p = 0.09$ which optimize the energy of Cl^- at −454.8297 au. This gives a 2.82-eV electron affinity for Cl (calculated with the same basis set as Cl^-)[9] compared with the experimental value of 3.61 eV.[10]

Initially, the methyl group carries most of the negative charge (−0.59 at $R_{C-Cl} = 2.05$ Å), with less charge (−0.41) on chlorine. At the end, of course ($CH_3\cdot + Cl^-$), all of the charge is on chlorine. Because of the movement of charge, there will certainly be an important solvent motion accompanying the dissociation, with the water molecules moving from carbon to chlorine. Several test calculations show, however, that little or no stabilization (1-2 kcal/mol) is obtained by placing discrete OH_2 molecules initially near carbon (whether along the CC axis or in a direction perpendicular to it): apparently the carbon charge is so very diffuse that it is smeared out over a large volume, and any electrostatic stabilization in solution must come from the macroscopic long-range effect of the solvent. We therefore placed the two OH_2 molecules on either side of the C-Cl bond, on an axis running through the chlorine atom and perpendicular to the bond (optimized distance $R_{Cl-O} = 3.5$ Å,[11] Figure 1), where they interact with a more compact, albeit smaller, net charge. As the C-Cl bond is stretched, the OH_2 molecules are made to accompany the Cl atom. The energy curves for CH_3Cl^- and for $CH_3Cl^-\cdot 2H_2O$ were then calculated including configuration interaction between all singly and doubly excited configurations built by excitation from σ_{CCl}, and from the odd-electron orbital, to the five lowest vacant orbitals (including the diffuse orbitals and σ^*_{CCl}). Figure 1 shows that the energy first rises in a way which parallels that for neutral molecules,[12] reaches a maximum, and then descends. For isolated CH_3Cl^- there is a 24.6-kcal/mol calculated barrier to dissociation at $R_{C-Cl} = 2.65$ Å. Its calculated enthalpy of dissociation is +10 kcal/mol, compared with the "experimental" value ($E(CH_3Cl) = 84$,[13] $EA(Cl) = -83$ kcal/mol) of +1 kcal/mol. For the solvated $CH_3Cl^-\cdot 2H_2O$ the barrier drops to 16 kcal/mol, with a shorter transition state (R_{C-Cl} near 2.45 Å).

The change in behavior of the potential energy at $R = 2.65$ Å can be readily traced to the intersection between the diffuse orbital on carbon, which initially contains the odd electron, and

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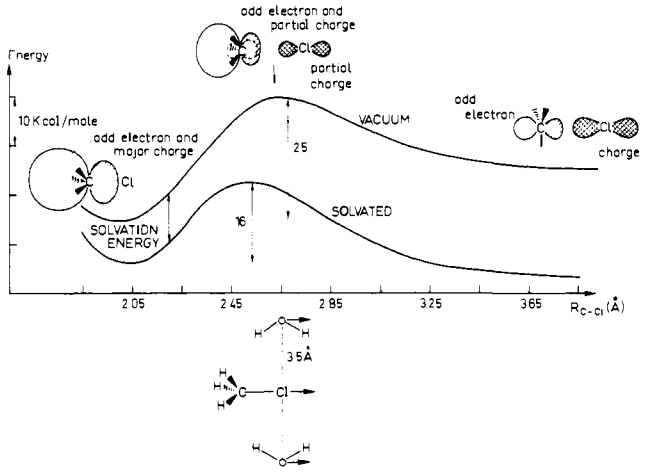

Figure 1. Potential curves for dissociation of CH_3Cl^- (a) under vacuum and (b) solvated by two OH_2 molecules which accompany the Cl atom during the dissociation. The methyl group is depyramidalized progressively along the reaction coordinate while the OH_2 molecules remain directly above and below Cl. Odd-electron position and net charge are also shown. Points are calculated every 0.20 Å starting at 1.85 Å.

the σ^*_{CCl} orbital which descends as it is stabilized by bond stretching. The odd electron is then transferred from diffuse orbital to σ^*_{CCl} and the dissociation is precipitated. The first part of the reaction is dominated by the energy increase as the bonding σ^2_{CCl} pair is destabilized, while the second half is dominated by the stabilization of the odd σ^*_{CCl} electron. At this stage the bonding pair is already well located near Cl and is little affected by further stretching. Figure 1 shows the amplitude of the unpaired electron at the initial, middle, and final stages of the reaction. The odd electron stays on carbon throughout, being initially diffuse, with sp character directed toward the hydrogens, and terminating essentially as a p valence electron in $\cdot CH_3$. At the transition state, the odd electron is in a half-diffuse sp, half-valence sp-like orbital (illustrated in Figure 1 by dotted contours for the inner part).

The behavior of the *net charge* is also illustrated in Figure 1. A full charge is transferred smoothly from C to Cl, while at the same time charge *contraction* occurs: from totally diffuse on C at the beginning to slightly expanded, but valence-like, on Cl at the end. The contraction is well on its way at the transition state, since partial transfer to charge (50%) to Cl has already occurred. Charge transfer and charge contraction account for the lowering of the barrier in the presence of the solvent molecules: the solvation energy of reactant *increases progressively* along the reaction coordinate and the *dissociation is "solvent enhanced"*. Comparison of calculated CH_3Cl^- and $CH_3Cl^-\cdot 2H_2O$ shows the reactant, transition state, and products to have respective "solvation energies" of −8.2, −17.7, and −21 kcal/mol. The full solvation energies should be nearer −23.3 kcal/mol for reactant[14] and −76.3 kcal/mol for product (Cl^-),[15] with a transition-state value somewhere in between (−36 to −50 kcal/mol).[16] Relative to reactant the barrier could be lowered by an additional ~10 kcal/mol, and our calculated barrier must be an upper limit to the true barrier.

Undoubtedly part of this lowering could be obtained by optimizing the distance and angular positioning of the two OH_2 molecules at each point of the pathway. But the calculation would not be very meaningful since additional OH_2 molecules (presently beyond our reach) would be expected to give much larger effects. Even with its relatively crude features (for the solvent) our calculation does give a clear-cut qualitative result: the *lowering of activation energy in solution* goes contrary to many reactions (S_N2), where the charge is more spread out in transition state than in reactants and where the activation energy rises in solution.[17]

Hence we find CH_3Cl^- to have a low barrier to dissociation when solvated by water molecules which "accompany" the dissociation. These results serve to illustrate the difference between CH_3Cl^- under vacuum and CH_3Cl^- in aqueous solution.[18] In the gas phase the anion is difficult to observe[8] in spite of its *deep minimum* because it lies *quasi-degenerate* with the neutral and can easily lose its electron. In solution, on the other hand, the solvated anion lies *well below* the solvated neutral (because of the differential solvation energy due to the charge); however, it is still not observed because the *small calculated barrier* to dissociation (16 kcal/mol, an upper limit) predicts a short lifetime (4.10^{-4} s, our upper limit, but closer to 10^{-8} s).[19,20] Whether or not other organic halide anions can be observed during mechanism 1 will depend crucially on the height of their dissociation barrier and hence on the energy of their σ^*_{CCl} orbital and the position of its intersection with the orbital initially containing the extra electron.[21]

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E. Canadell, P. Karafiloglou, L. Salem*

Laboratoire de Chimie Théorique (E.R.A. 549)
Université de Paris-Sud, 91405 Orsay, France

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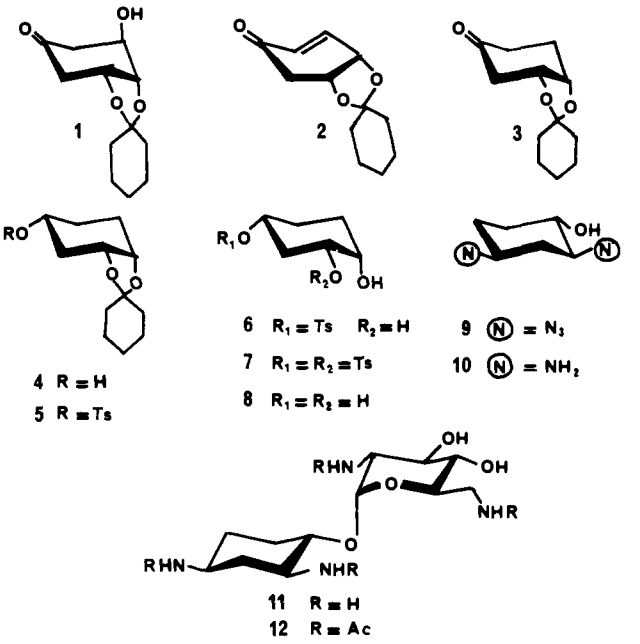

Synthesis of 2,5,6-Trideoxystreptamine and Its Transformation into Bioactive Pseudodisaccharides by Microbial and Chemical Methods

Sir:

The intrinsic toxicity and enzymatic inactivation of known aminocyclitol glycoside antibiotics makes the discovery of new drugs a goal of prime importance. Until the present time, most of the research efforts in this field were directed toward soil screening, chemical modifications of naturally occurring antibiotics, and mutasynthesis utilizing idiotrophs.[1-3] An alternative approach to the development of new amino glycosides would be total chemical synthesis. However, owing to the complex molecular architecture of the natural amino glycosides, this route has not been greatly utilized.

It is noteworthy that recently discovered amino glycosides such as Fortimicins[4] and Sporaricins[5] are composed of only two cyclic nuclei (aminocyclitol-*epi*-purpurosamine). Furthermore 4-O-substituted 2-deoxystreptamines are the antibacterial determinants of a variety of microbial products.[6] Therefore, it was envisaged that the preparation of relatively "simple" analogues of naturally occuring amino glycoside antibiotics could afford novel bioactive substances.

In this respect, it appeared to us that the chiral 2,5,6-trideoxystreptamine[7] **10** would be an interesting aglycon. Accordingly, we report here its synthesis from quinic acid and its microbial and chemical transformation into two bioactive pseudodisaccharides, **11** and **18**.

The crucial intermediate for the synthesis of **10** was the hydroxy ketone **1** which was readily available from quinic acid.[8] Treatment of **1** with *p*-toluenesulfonyl chloride in pyridine (5 days, room temperature) gave the crystalline conjugated enone **2**, in 95% yield: mp 56–58 °C; $[\alpha_D]$ +135° (*c* 1.0, $CHCl_3$); UV max (95% C_2H_5OH) 217 nm (ϵ 8.8 × 10^3); IR (film) 1670 (C=O) cm^{-1}; ^{13}C NMR ($CDCl_3$) $\delta(C_1 \rightarrow C_6)$ 195.6, 38.6, 70.7, 73.0, 146.2, 128.8. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.21; H, 7.73. Catalytic hydrogenation (10% Pd/C) of **2** in ethyl acetate produced the saturated ketone **3** (85%), mp 86–87 °C, $[\alpha]_D$ +136° (*c* 1.11, $CHCl_3$), as a white solid. Lithium borohydride reduction of **3** in diglyme furnished exclusively the syrupy alcohol **4**, which was converted into its crystalline tosylate **5** (90% from **3**), mp 88–89 °C, $[\alpha]_D$ +42° (*c* 1.08, $CHCl_3$). The cyclohexylidene group in **5** was hydrolyzed in methanol using Amberlite IR 120 (H^+) resin to give the amorphous diol **6** which was selectively tosylated to produce the desired ditosyloxycyclohexanol **7** (80% from **5**), mp 134 °C, $[\alpha]_D$ +19° (*c* 1.25, $CHCl_3$). Alternatively, **7** was also obtained by acidic removal of the ketal group in **4**, followed by selective *p*-toluenesulfonylation of the cyclohexanetriol **8**, mp 137–138 °C, $[\alpha]_D$ +18° (*c* 1.0, EtOH). The overall yield was 55% based on **1**. Azidolysis of **7** in dimethylformamide (120 °C, 30 min) produced the oily diazide **9**, $[\alpha]_D$ +81° (*c* 1.0, $CHCl_3$), which was hydrogenated using Adams' catalyst in methanol to yield the 2,5,6-trideoxystreptamine **10**, isolated as its dihydrochloride salt, mp 305–310 °C dec, $[\alpha]_D$ +17° (*c* 1.15, H_2O). Anal. Calcd for $C_6H_{16}Cl_2N_2O$: C, 35.48; H, 7.94; Cl, 34.91; N, 13.79. Found: 35.32; H, 7.91; Cl, 35.04; N, 13.55.

Using the method of Rinehart and co-workers[3] for producing mutasynthetic amino glycoside antibiotics, exogenously added, 2,5,6-trideoxystreptamine **10** was converted by the idiotroph of *Streptomyces fradiae* (ATCC 21401) into bioactive 5,6-dideoxyneamine **11**, isolated as its disulfate salt, mp 280–283 °C dec, $[\alpha]_D$ +40° (*c* 1.0, H_2O). Anal. Calcd for $C_{12}H_{26}N_4O_4 + 2H_2SO_4$: C, 29.62; H, 6.2; N, 11.5; S, 13.18. Found: C, 29.40; H, 6.35; N, 11.32; S, 13.04. The culture medium was supplemented with **10** (250 μg/mL) and 10% inoculum of the mutant was added. The culture was further incubated at 30 °C for 5–6 days, until antibacterial potency reached a maximum. 5,6-Dideoxyneamine **11** and unchanged 2,5,6-trideoxystreptamine **10** were absorbed on Amberlite IRC 50 (NH_4^+ form) from which they were eluted with 1 N ammonium hydroxide. Further purification was accomplished by ion exchange chromatography on Amberlite CG50 (NH_4^+ form) or CM-Sephadex C-25 (NH_4^+ form) using an increasing concentration of ammonium hydroxide as eluant.

The structure of the bioactive pseudodisaccharide isolated was confirmed on the basis of the data obtained from its *N*-acetate derivative **12**: mp >270 °C dec; $[\alpha]_D$ +96° (*c* 1, H_2O); ^1H NMR [4-N-Ac(S)] δ 1.98, 1.96, 1.93 and 1.89; chemical ionization mass spectrometry[9] *m/e* 459 (MH^+), fragments 245, 227, 215, and 197. Anal. Calcd for $C_{20}H_{34}N_4O_8$: C, 52.39; H, 7.47; N, 12.22. Found: C, 52.31; H, 7.35; N, 12.02. This derivative was found to be identical with the tetra-*N*-acetyl-5,6 dideoxyneamine reported recently by Suami and co-workers.[10]

Biotransformation of **10** into **11** is consistent with our previous postulation[11] that neomycin biosynthesis proceeds via an intermediate of the neamine type rather than 5-O-substituted 2-deoxystreptamine. This hypothesis is consistent with

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