N.M.R. Spectra of Na^- and Rb^- in Solutions of Sodium and Rubidium in 1,4,7,10-Tetraoxacyclododecane (12-Crown-4)

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We report the n.m.r. spectra of sodide (Na^-) and rubidide (Rb^-) ions in the title solvent; these two-component metal solutions represent a convenient, stable source of high concentrations of alkalide ions in solution.

The reaction of organic compounds with dissolving metals,[1,2] the so-called dissolving-metal-reduction (DMR), is of considerable current interest.[3] The ultimate aim of a DMR is the selective reduction of functional groups. The classic DMR employs metal–ammonia solutions, known to consititute a powerful reducing system of considerable synthetic utility. However, a major drawback with M–NH_3 systems is their lack of specificity,[4] arising from the extreme reactivity of both the solvated electron (e_s^-) and its weakly bound association complexes $M_s^+e_s^-$ and $(e_s^-M_s^+e_s^-)$.

Recently, solutions of Na in neat 12-crown-4 (12C4)[5] and of NaK alloy in tetrahydrofuran in the presence of 18-crown-6[3,6] have been used as selective DMR systems, both in the reduction of CO and several organic compounds. Also, Dewald *et al.*[5] have converted triphenylmethane into the carbanion Ph_3C^- in Na–12C4 solutions, a reaction which is not possible using the M–NH_3 reducing system. However, little is known of the precise nature of the active reducing species in these solutions. Here we draw attention to the potential of n.m.r. for identifying metal anions as effective reductants. We show that the title system, alkali metals in neat 12-crown-4, represents a convenient source of high concentrations of M^-, rather than e_s^-, in solution. Furthermore, the n.m.r. data reveal fundamental differences in the electronic structure of Na^- and Rb^- in these solutions, possibly arising from an enhanced solvent interaction in the rubidide ion.

Solutions of Na and Rb in 12C4 were prepared under high vacuum conditions. N.m.r. spectra were recorded at room temperature on a Jeol FX90Q pulsed Fourier transform

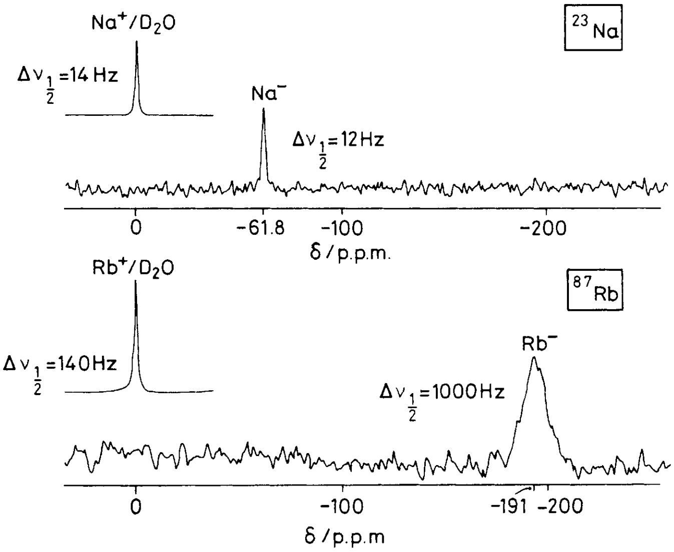

Figure 1. ^{23}Na and ^{87}Rb N.m.r. spectra of solutions of sodium and rubidium in 1,4,7,10-tetraoxacyclododecane (12-crown-4). Negative chemical shift values correspond to an increase in nuclear shielding compared to M^+ (reference) in D_2O, see Table 1.

Table 1. ^{23}Na and ^{87}Rb Chemical shifts and linewidths.

Ion	Temp./K	Solvent	δ/p.p.m.	$\Delta\nu_{\frac{1}{2}}$/Hz	Ref.
Na^+ (NaCl)[a]	300	D_2O	Reference	14	[b]
Na^- ($Na^+C.Na^-$)[c]	258	$MeNH_2$	−61.9	11	7
Na^-	300	12C4[d]	−61.8 (±0.1)	10	[b]
Na^-	—	Gas	−63.1 (calc.)	—	7
Rb^+ (RbCl)[a]	300	D_2O	Reference	140	[b]
Rb^- ($Rb^+C.Rb^-$)	233	$EtNH_2$	−185	220	7
Rb^-	300	12C4	−191(±2)	1000	[b]
Rb^-	—	Gas	−213.6 (calc.)	—	11

[a] Infinitely dilute salt soltuions. [b] This work. [c] C = 2,2,2-Cryptand. [d] 12C4 = 12-Crown-4.

spectrometer. Chemical shifts were determined relative to solutions of the appropriate metal chloride in D_2O at infinite dilution.

The ^{23}Na and ^{87}Rb n.m.r. spectra obtained are shown in Figure 1. Sodium–crown solutions exhibit a single, narrow line ($\Delta\nu_{\frac{1}{2}}$ = 10 Hz) located at 61.8 p.p.m. to low frequency of the Na^+/D_2O reference. This signal is diagnostic of the sodide ion[7—9] and establishes conclusively the existence of a genuine long lived 'gas-like' sodium anion in this system (Table 1).

The ^{87}Rb signal in 12C4 solutions has a chemical shift (δ −191 p.p.m.) similar to that found in the three-component $Rb^+C.Rb^-$/solvent systems[7] (C = cryptand), but the linewidth here is much broader than in the cryptand solutions (Table 1). However, assignment to the rubidide ion, Rb^-, is once again unambiguous because of the extremely large diamagnetic shift from the Rb^+ reference.[7] This represents the first report of Rb^- in a two-component metal solution. Cation resonances were not detected in the Na- and Rb-12C4 solutions; in NaCl–12C4 solutions the $^{23}Na^+$ resonance is 1200 Hz wide and further broadening of this absorption is anticipated in the paramagnetic metal solutions.

The chemical shift of Na^- in 12C4 is virtually identical (Table 1) with that of the gaseous free anion.[10] The absence of any solvent-induced decrease in the nuclear shielding for Na^- and the narrow n.m.r. width are indicative of a high symmetry arrangement of solvent molecules around the sodide ion. Hence the sodium 2p (core) electrons are effectively shielded from specific solvent interactions by the paired 3s electrons on the metal. In contrast, the n.m.r. absorption of Rb^- in Rb–12C4 solutions is substantially shifted from that calculated[11] for a genuine, gaseous rubidide ion (Table 1). This represents a significant decrease in the nuclear shielding of Rb^- when in the liquid state. Both the chemical shift and linewidth of the rubidium anion, therefore, suggest a considerable degree of interaction with the solvent.

We have demonstrated unequivocably the presence of high concentrations of alkalide ions in solutions of Na and Rb metals in 12-crown-4. This system offers considerable potential as a DMR reagent, representing a convenient source of M^- which is stable at room temperature. In addition, our e.s.r. studies[12] indicate that these crown solutions contain low concentrations of solvated electrons compared with M^- at ambient temperature.

Metal–crown solutions, therefore, should be particularly useful for two-electron reductions[13] and other synthetic tasks not effected by $M–NH_3$ solutions.[5] We suggest that DMR mechanisms need to be re-examined in the light of recent work on metal anions; at least some of the considerable reducing power[1] of M–amine and M–hexamethylphosphoramide solutions, for example, may be attributable to M^- rather than e_s^-.

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