A Quantitative Study of Enrichment of K+ in Radical–Ion Pairs generated by Sodium Reduction

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ESR spectroscopy and atomic absorption measurements establish that K+ enrichment up to four orders of magnitude may occur when reduction reactions are performed using even highly pure Na sources.

Sodium has been used as a standard reducing agent for the generation of radical anions[1] or in chemical reactions.[2] Spectroscopically, the interaction of the anions and Na+ counterions formed upon reduction can be followed by changes in electronic[3] and, particularly, ESR[4] spectra; e.g. tight (or contact) ion pairs[5] are readily identified by the appearance of hyperfine coupling constant of the ^{23}Na nucleus ($m_I = 3/2$).

After Na-reductions, occasionally two superimposed ESR spectra have been detected.[6,7] It was assumed that the two ESR spectra originate in the Na+ and the K+ ion pair of the radical ion formed after reduction. It was suspected that the K+ source was either the glassware[6] or impurities.[7]

To distinguish clearly between the two hypotheses, we present results based on ESR and atomic absorption spectroscopy which, for the first time, quantitatively establish the amount of K+ enrichment; furthermore, we give rationalisations which are responsible for the prominent increase of the K+ concentration.

Metal reduction is usually performed by the heterogeneous reaction between an alkali metal mirror and an organic solution. The mirror is produced either by direct sublimation of the metal onto the walls of an ESR cell, or by anterior decomposition of the corresponding metal azide followed by sublimation. However, when Na+ is the desired counterion one has to avoid enrichment with K, which always exists as an impurity in all sources of Na (e.g. NaN$_3$, Fluka Microselect contains: Na > 99.5%, K < 0.005%). As NaN$_3$ is the most pure, it was used as the Na source. The reductions were performed under high vacuum (10^{-5} Torr, 1 Torr =133.322 Pa) on Na mirrors obtained by decomposition of NaN$_3$ followed by sublimation.

Thiophene 2,5-dicarbaldehyde 1 was selected as the species to be reduced. The radical anion of 1 is rather stable and thus can be studied over a broad temp. range. The reduction potential of 1 is relatively low ($E_{1/2} = -1.040$ V vs. Ag/AgCl) and therefore the conversion into its radical anion should be rather effective. In addition, the Na+ and K+ ion pairs of 1·$^-$ possess almost identical stability and dynamics[8] and thus there should be no preference for either of the counterions based on thermodynamics.

When 1 was dissolved in THF and reduced on the Na mirror, the ESR spectrum (Fig. 1) was detected. It is composed by a ca. 1 : 1 superposition of two spectra possessing almost identical proton ($m_I = 1/2$) hyperfine coupling constants, a_H†) but two distinctly different ones of 0.038 and 0.014 mT for nuclei with $m_I = 3/2$. The two simulations shown above and below the experimental spectrum indicate the two components.[8] This observation mirrors either a simultaneous formation of two different (tight and/or loose) ion pairs with Na+ counterions or the coexistence of a Na+ and K+ ion pair.‡) As both Na and K have the same nuclear spin quantum number, $m_I = 3/2$, a definite distinction between these two cases can not be made based on the ESR spectral data.
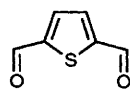
To establish the correct composition of the ion pairs, we prepared two highly concentrated samples of 1 in DME (ca. 0.002 mol dm^{-3}) and performed the reductions on two differently prepared Na mirrors: (A) A high amount of NaN$_3$ was decomposed and a thick metal mirror was produced. (B) Only a low amount of NaN$_3$ was decomposed and a thin Na mirror was achieved by careful sublimation.
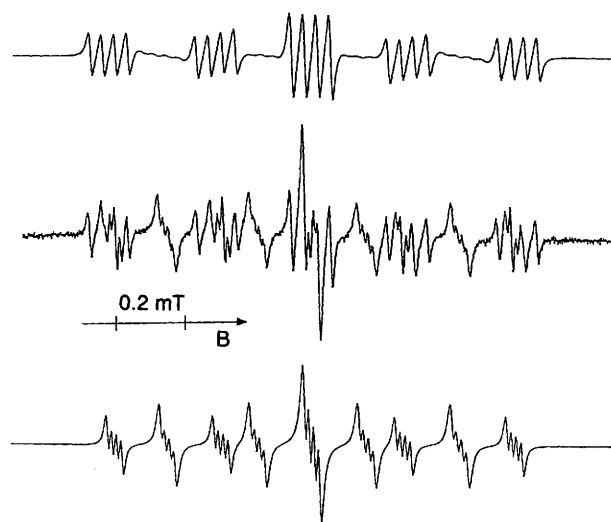

Fig. 1 ESR spectrum of 1·$^-$ (middle) generated on a Na mirror (from NaN$_3$) and simulations of the two components possessing different splittings from nuclei with $m_I = 3/2$
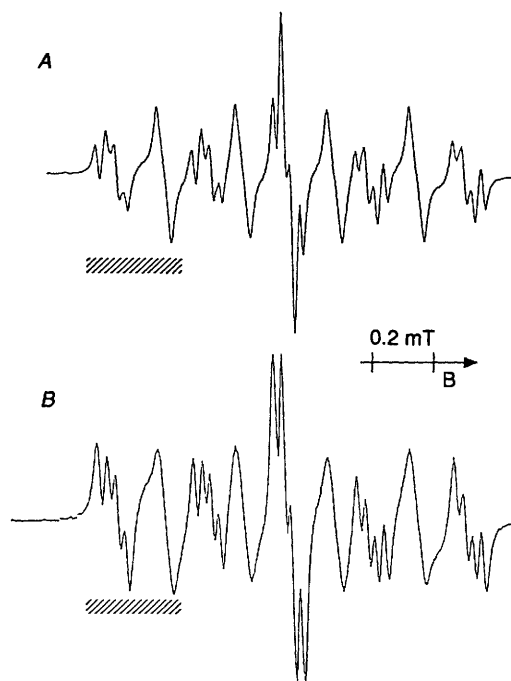

Fig. 2 ESR spectra of 1·$^-$ generated on two differently prepared Na mirrors

Table 1 Concentrations of K$^+$ and Na$^+$ determined by atomic absorption spectroscopy in two samples of **1** in DME (0.002 mol dm^{-3}) after reduction on Na mirrors. The experimental error is ±0.2 µg/ml throughout.

Mirror Generation	[Na$^+$]/µg ml^{-1}	[K$^+$]/µg ml^{-1}
A	9	7
B	9	1

The ESR spectra taken from *A* and *B* are shown in Fig. 2. Although the line patterns of both spectra are similar, the intensity ratios of the ESR lines are different. The ESR spectrum of **1**·$^-$ prepared by *A* (Fig. 2) indicates a pattern which is similar to that shown in Fig. 1. The two outermost groups of lines (marked with dashed area, Fig. 2) reveal a ratio of *ca.* 1:2. On the other hand, in the ESR spectrum of **1**·$^-$ by *B*, the corresponding ESR lines possess a ratio of 1:1 and the pattern is dominated by the splitting of 0.038 mT ($m_I = 3/2$). The ESR spectral resolution is worse than that shown in Fig. 1, as expected for such a high concentration (in terms of ESR spectroscopy) of the samples. However, this highly concentrated samples allowed the determination of the concentrations of the Na$^+$ and K$^+$ counterions with the help of atomic absorption spectroscopy. The results are summarised in the Table 1.

For *A* the Na$^+$ and the K$^+$ concentrations almost reach the same level whereas for *B* there is an almost ten fold excess of Na$^+$ over K$^+$. Thus, depending on the technique employed in the preparation of the Na mirrors for the reductions, a significant enrichment with K became apparent. This can be traced ·back to the followed factors: (*i*) The enthalpy of sublimation for K is lower than that of Na (89.24 *vs.* 107.32 kJ mol^{-1});[10] (*ii*) K is a stronger reducing agent than Na[10] [$E_{1/2}$ = −2.93 *vs.* −2.71 V *vs.* normal hydrogen electrode (NHE)] and thus electron transfer from K appears prior to Na.

Additional factors are different solubilities of the alkali metal cations as well as differently stable Na$^+$ and K$^+$ ions pairs of the reduced species (almost identical for **1**).[8]

It is very unlikely that the glassware is the source of the K$^+$ ion pairs, the more so as the Pyrex (Corning) glassware we use does not contain k-oxides but only Na$_2$O. Furthermore, even in K-reduced samples of **1**, no Na$^+$ ion pairs could be detected. It is noteworthy that it was convincingly shown that Na$^+$ impurity in Li reduced biphenyl stems from the Pyrex apparatus.[11] However, for the sublimation of Li temps. are

required at which the Pyrex glass already softens (enthalpy of sublimation = 159.37 kJ mol^{-1}),[10] therefore glass–metal ion exchange is advanced. Such reactions are impaired at the considerably milder temperatures necessary for Na or K sublimations.

Footnotes

† For the ESR spectrum of the ion pair with the metal hyperfine coupling constant, $a_{Me} = 0.038$ mT, the a_H are 0.513 (1 H), 0.335 (1 H), 0.239 (1 H) and 0.065 (1 H) mT, for that with $a_{Me} = 0.014$ mT, the a_H are 0.477 (1 H), 0.345 (1 H), 0.223 (1 H) and 0.084 (1 H) mT. The exchange rates used for the simulations in Fig. 1 agree to those given by Pedulli and coworkers.[8]

‡ The ratio of the two a_M is 2.7:1, which is comparable to the theoretical a_{Na}/a_K ratio of 4:1.[9]

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