

**METAL CHLORIDE REDUCTIONS WITH AROMATIC RADICAL ANIONS. THE MAGNESIUM CHLORIDE CATALYSED CLEAVAGE OF TETRAHYDROFURAN BY SODIUM NAPHTHALENE RADICAL ANION**Barry R. STEELE<sup>1,\*</sup>, Georgios A. HEROPOULOS<sup>2</sup> and Constantinos G. SCRETTAS<sup>3</sup>

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*Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organometallic synthesis and catalysis.*

Activated metals for organic synthesis are often prepared by reduction of metal salts using alkali metal aromatic radical anions. The reduction of magnesium chloride has been examined by NMR. Whereas the expected reduction to the metal occurred with lithium or potassium naphthalene radical anion, under certain conditions, with sodium naphthalene radical anion, no metallic magnesium was precipitated and dark red solutions were obtained. It was also found that solutions of sodium naphthalene radical anion in tetrahydrofuran, in the presence of a catalytic amount of magnesium chloride, quickly became diamagnetic. A mechanism involving bimetallic species is postulated to explain the results.

**Keywords:** Radical ions; Reductions; NMR spectroscopy; Alkali metals.

Activated forms of metals are of special use in synthesis and several methods are available for their preparation<sup>1</sup>. In the case of magnesium, for example, these include vaporisation of the metal<sup>2</sup>, activation by electron-transfer reagents<sup>3</sup>, mechanical activation<sup>4</sup> and reduction of metal salts<sup>5</sup>. All these methods have their advantages and disadvantages, and the factors to be considered include the reactivity required, the scale of the synthesis and the apparatus involved. One of the most popular methods is that of the reduction of metal salts by alkali metals which has been pioneered and developed by Rieke<sup>6</sup>. This is of general applicability to the small or large-scale preparation of a wide range of activated metals and its use as a synthetic method has been amply demonstrated. The alkali metal may be used by itself or in conjunction with an electron transfer agent such as naphthalene. In the latter case, the active reducing agent is then the naphthalene radical

anion, although the nature of the counterion is often an important factor in deciding the reactivity and course of reaction.

It appears that the activation of the metal is not merely due to the increase in surface area. It has been suggested that absorbed anions generated from solvent cleavage during reduction or the alkali salts generated, or both, may facilitate electron transfer in the rate-limiting step and that also high densities of dislocations and imperfections may also increase reaction rates<sup>7</sup>. Magnetic titrations using NMR are a convenient method for determining the stoichiometry of reduction with aromatic radical anions<sup>8,9</sup>, and we have screened a number of metal compounds and found that in many cases the apparent stoichiometry of reduction is much more than the initial oxidation state of the metal<sup>10</sup>. This “over-reduction” may also contribute to the high reactivity of active metals produced in this way. Here we report some findings on the reactions with magnesium compounds.

## RESULTS AND DISCUSSION

As can be seen from the magnetic titration curve in Fig. 1, magnesium chloride underwent the expected two-electron reduction with lithium naphthalene radical anion in THF and gave a grey precipitate of “Rieke” magnesium. The reductions with most other reagents such as lithium and sodium stilbene, potassium naphthalene and sodium anthracene radical

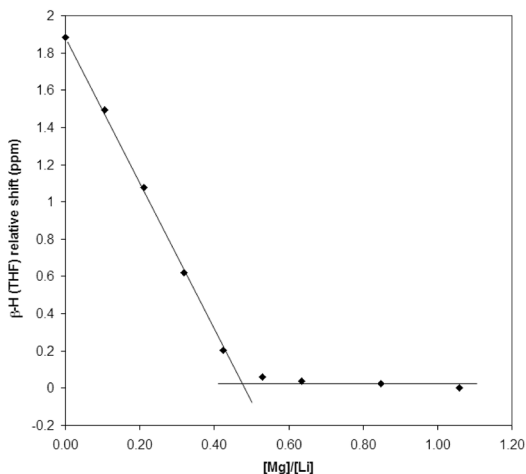


FIG. 1  
Magnetic titration of  $\text{MgCl}_2$  (0.5 M in THF) against lithium naphthalene radical anion (1.0 M in THF)

anions gave essentially the same results. An interesting and unexpected departure from this behaviour, however, was that of magnesium chloride with sodium naphthalene and biphenyl radical anions. The addition of a small amount of  $\text{MgCl}_2$  solution to a solution of sodium naphthalene or biphenyl radical anion caused a decay in the paramagnetism and a colour change from the dark green of the radical anion solution to a dark orange-brown.

The rate of loss of paramagnetism can be readily followed by observing the change in the bulk paramagnetic solvent NMR shift. For a given paramagnetic species this shift is proportional to the concentration and thus kinetic studies are possible<sup>11</sup>. In the present reaction a typical decay curve is shown in Fig. 2 together with the corresponding curves for the lithium and potassium systems where no such decay was observed.

Any explanation for the observed reaction must explain not only these differences in behaviour for sodium naphthalene radical anion (or for sodium biphenyl radical anion which behaves similarly) compared with the lithium or potassium systems, but also the fact that no decay is observed for the more weakly reducing sodium anthracene radical anion. In the latter case, the expected 2:1 stoichiometry for the reduction is observed (Fig. 3). Catalysis was also effected by  $\text{MgBr}_2$  and  $\text{Mg}(\text{OCH}_2\text{CH}_2\text{OEt})_2$  but not by analogous compounds of Zn, Mn or Ni.

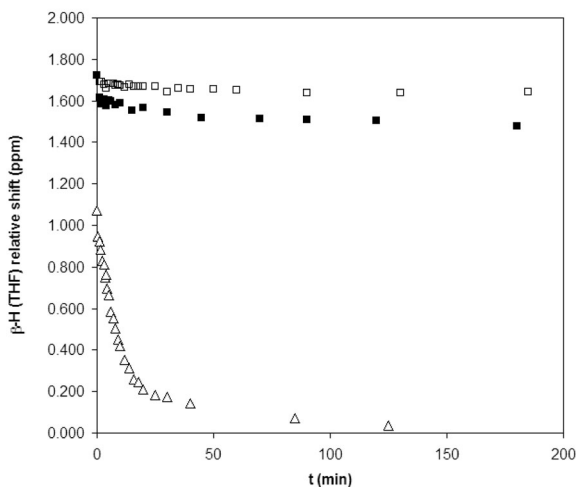


FIG. 2

Decay of paramagnetism for lithium (■), sodium (△) and potassium (□) naphthalene radical anion solutions (0.5 ml of 1.0 M in THF) on addition of  $\text{MgCl}_2$  (5  $\mu\text{l}$  of 0.5 M in THF)

While we have not examined the kinetics of the decay at length, there is an initiation period followed by an almost linear time/concentration relationship in the initial stages of the decay. The overall data, however, do not fit in with any simple order of reaction although an examination of the initial rates for three runs, carried out with different concentrations of sodium naphthalene radical anion but under otherwise identical conditions, shows that the rate decreases slightly as the concentration of the radical anion increases (Fig. 4).

Thus, the rate appears to be determined to a large extent by the concentration of THF and that of the active intermediate. The latter concentration, however, must be small and probably effectively constant. We suggest that the initial step in the reaction sequence gives, as the reactive intermediate, a mixed sodium/magnesium species which reacts with THF but the subsequent reactions are not clear in detail. Gas chromatographic and mass spectrometric analysis of the product mixture indicated the presence of a large number of components including alkylnaphthalenes and corresponding hydrogenated derivatives which could arise either by homolytic or carbanionic ring cleavage processes.

The dihydronaphthalenes are presumed to arise from the protonation of the corresponding carbanions. These are known to aromatise to naphthalene via loss of metal hydride. In the present case, the decrease in the

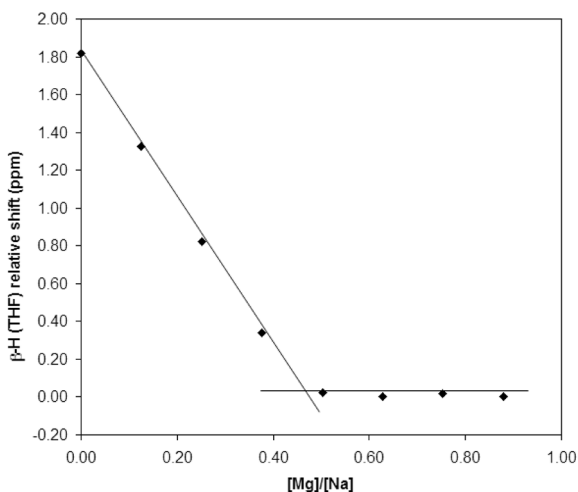


FIG. 3  
Magnetic titration of  $\text{MgCl}_2$  (0.5 M in THF) against sodium anthracene radical anion (1.0 M in THF)

amount of dihydronaphthalenes produced as the reaction progresses is not accompanied by a corresponding increase in the amount of naphthalene observed and, taking into account the substantial amounts of alkylated material produced, we are led to the conclusion that the dihydronaphthylcarbanions are producing and reacting with solvent cleavage products. The reaction of THF with carbanions to give ethene and the enolate anion of acetaldehyde is well-known<sup>12</sup>. Another reaction of THF which may also be of relevance here is the insertion of activated magnesium into the THF ring to give a magnesa-oxacycle<sup>13</sup>.

The possible formation of bimetallic species in the  $\text{MgCl}_2/\text{Na}/\text{C}_{10}\text{H}_8$  system was indicated by experiments using non-catalytic quantities of magnesium chloride. When 2 equivalents of sodium naphthalene radical anion in THF were treated either slowly or rapidly with 1 equivalent of  $\text{MgCl}_2$  in THF, either at  $-40\text{ }^\circ\text{C}$  or at room temperature, a grey precipitate of metallic "Rieke" magnesium was formed. A similar precipitate was also formed on the slow addition of 1 equivalent of  $\text{MgCl}_2$  in THF to 4 equivalents of sodium naphthalene radical anion in THF. Rapid addition, however, at room temperature<sup>14</sup> with the same reactant ratio produced a clear dark red solution. The colour of this solution is reminiscent of the dark red solutions containing the naphthalene dianion  $[\text{C}_{10}\text{H}_8]^{2-}$ . Carboxylation of this reaction mixture with  $\text{CO}_2$  produced 1,4-dihydro-1-naphthoic acid in 34%

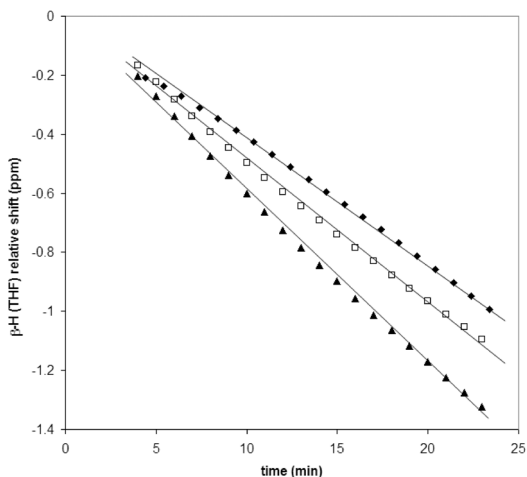


FIG. 4

Initial decay of paramagnetism for 1.08 (◆), 0.80 (□) and 0.50 M (▲) sodium naphthalene radical anion solutions in THF on addition of  $\text{MgCl}_2$  (5  $\mu\text{l}$  of 0.5 M in THF)

yield whereas the yields from the previously mentioned experiments were of the order of 5–10% of a mixture of 1,4-dihydro-1-naphthoic acid and alkylated derivatives. Thus there appears to be an ideal ratio of 4:1 of sodium to magnesium for the formation of a stable species. At lower ratios, as in the rapid addition of 1 equivalent of  $\text{MgCl}_2$  to 2 equivalents of sodium naphthalene radical anion there is a simple reduction to the metal, whereas at ratios higher than 4:1 there seems to be no suitable configuration for the formation of a stable species and the magnesium is precipitated as the metal. For the 4:1 stoichiometry of the reactants but with slow addition of the  $\text{MgCl}_2$  solution, the high initial radical anion/ $\text{MgCl}_2$  ratios would produce Mg metal which could then aggregate to form particles of a size unfavourable for redissolution as the final 4:1 ratio is reached, whereas with rapid addition the aggregation process can be averted. As to the nature of the soluble species, we can infer that the chloride must somehow be involved in the complex, since normally sodium chloride is insoluble in THF. Part of the naphthalene is presumably present in a reduced carbanionic form. Again, in contrast to the above, in the analogous reactions with lithium naphthalene radical anion, a metallic magnesium mirror was deposited.

A possible general mechanistic scheme is the following:



The “normal” behaviour observed in the case of sodium anthracene radical anion is no doubt due to the formation of the known stable magnesium anthracene<sup>3</sup>. The stoichiometric behaviour of lithium naphthalene radical anion could be interpreted as being due to the reduced reactivity of the lithium/magnesium intermediate towards either metallation or cleavage of THF, since it is well-known that organolithium compounds are more stable in THF than their sodium or potassium analogues<sup>12,15</sup>. However, in view of the results from the preparative stoichiometric reactions described above, it seems more likely that the observed behaviour of both the lithium and potassium radical anions arises from a lower stability, compared with that of sodium, of the proposed mixed metal reactive intermediate, and that this intermediate, if formed at all, decomposes rapidly to produce metallic mag-

nesium, naphthalene and the alkali metal chloride. Further investigations are planned into the nature and possible applications of the intermediate in organic synthesis.

## EXPERIMENTAL

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AC-300 MHz instrument. Analytical GC was carried out using a Varian 3400 CX instrument using a 30 m  $\times$  0.53 mm DB5 column and preparative GC was carried out using a Pye Unicam GCV chromatograph using a 10% Apiezon L column on Chromosorb GAWBMCS. GC-MS analysis was performed with a Varian Saturn 2000 instrument using a 30 m  $\times$  0.25 mm DB5-MS column. Naphthalene, anthracene, and biphenyl were commercial products, 98% or better, and were recrystallised before use. Tetrahydrofuran was doubly distilled from  $\text{LiAlH}_4$  under argon before use. Magnesium 2-ethoxyethoxide was prepared as described elsewhere<sup>16</sup>. Other starting materials were analytical grade commercial products used as received. Radical anion solutions were prepared in ca. 1 M concentrations under an atmosphere of argon by stirring equivalent quantities of alkali metal and aromatic hydrocarbon in THF overnight. The concentration of the radical anion was determined both by determination of total alkalinity of hydrolysed aliquots and by the reaction of an aliquot of the radical anion solution with 1,2-dibromoethane under argon and titrating the liberated bromide.

### Magnesium Chloride Solution

To magnesium turnings (2.4 g, 100 mmol) were added under argon a few ml of a solution of 1,2-dichloroethane (9.9 g, 100 mmol) in THF (200 ml). Once the reaction had started, the remainder of the solution was added so as to maintain gentle reflux. After the addition, the reaction mixture was heated at reflux for 4 h. The concentration of magnesium chloride was determined by EDTA complexometric titration. Magnesium bromide solutions were prepared in a similar way using 1,2-dibromoethane.

### Magnetic Titrations

Radical anion solution (0.5 ml) was transferred with syringe into an argon-filled NMR tube protected by a septum and with a capillary containing  $\text{C}_6\text{D}_6$ . For a full description of the techniques used, see ref.<sup>8</sup>. Aliquots of a THF solution of the metal compound were added and the chemical shifts of the  $\alpha$  and  $\beta$  protons of THF measured. The shifts relative to neat THF, corrected for dilution, were plotted against the ratio of metal compound added to the initial amount of radical anion present. The stoichiometry of the reduction was determined from the break in the plot (disappearance of paramagnetism).

### Kinetic Studies

Radical anion solution (0.5 ml) was transferred into an NMR tube as above, and a small amount (5–10  $\mu\text{l}$ ) of a THF solution of  $\text{MgCl}_2$  (typically 0.4–0.5 M) was added. The chemical shifts of the  $\alpha$  and  $\beta$  protons of THF were measured as a function of time.

## Sodium Naphthalene Radical Anion/Magnesium Chloride: Preparative Scale Reactions

*Catalytic reactions.* (i) To a solution of sodium naphthalene radical anion, prepared as described above from 40 mmol of sodium, 0.5 ml of 0.5 M  $\text{MgCl}_2$  in THF was added. A gradual change in colour from dark green to dark red-brown was observed. The reaction mixture was analysed at room temperature after 16 h. Head-space volatiles were analysed by GC and chromatograms consistent with the presence of acetaldehyde and THF were obtained. There was no evidence for the presence of ethene. The volatile components of the reaction mixture were removed in vacuo. GC analysis indicated the presence of acetaldehyde, 1,2-dihydro- and 1,4-dihydronaphthalene, and naphthalene. No evidence was obtained for the presence of ethene or butan-1-ol. The residue was hydrolysed and extracted with dichloromethane. The extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to give 4.5 g of a yellow oily crystalline solid which was steam-distilled to remove most of the naphthalene. After the steam distillation, the content of the distillation flask was extracted with dichloromethane, dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to give 3.4 g of a yellow oil which GC-MS and  $^1\text{H}$  NMR indicated to be a very complex mixture containing naphthalene and di- and tetrahydronaphthalenes and their alkylated derivatives. No attempt was made to identify the individual components.

(ii) Using the procedure described in (i), the initially obtained red-brown solution was poured onto crushed dry ice in diethyl ether. After warming to room temperature, the volatiles were removed by rotary evaporation, water was added and neutral organic products extracted with  $2 \times 50$  ml of toluene and  $2 \times 50$  ml of hexane. The extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to give 3.8 g of a yellow oily solid which GC-MS and  $^1\text{H}$  NMR indicated to be a very complex mixture similar to that obtained above containing naphthalene and di- and tetrahydronaphthalenes and their alkylated derivatives. The aqueous solution was acidified and extracted with  $\text{Et}_2\text{O}$ . The extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated to give 1.0 g of a yellow-brown oil. The  $^1\text{H}$  NMR spectrum was too complicated for the analysis of individual components, but indicated the presence of alkylated (dihydro)naphthoic acids.

*Stoichiometric reactions.* (i) A solution of sodium naphthalene radical anion was prepared in the usual way from 20 mmol of naphthalene and 20 mmol of sodium in 18 ml of THF. The solution was cooled in a dry ice/acetone bath and 20 ml of a 0.5 M solution of  $\text{MgCl}_2$  in THF (10 mmol) were added dropwise. The suspension formed consisted of a black solid material and a red solution. The reaction mixture was allowed to warm slowly to room temperature. At ca.  $-30^\circ\text{C}$  the suspension became yellow, turning to grey-brown at room temperature. The reaction mixture was carboxylated by pouring onto dry ice in ether and worked up as above. An oily solid was obtained (0.27 g) which  $^1\text{H}$  NMR indicated to be probably a mixture of dihydronaphthoic acids and their alkylated derivatives. Similar results to the above were obtained when the reaction was carried out under the following conditions:

a. Stoichiometry as above (2:1 ratio of sodium naphthalene radical anion to  $\text{MgCl}_2$ ) at room temperature.

b. Stoichiometry 4:1 ratio of sodium naphthalene radical anion to  $\text{MgCl}_2$  with dropwise addition of  $\text{MgCl}_2$  solution at either low or room temperature.

c. Stoichiometry 2:1 or 4:1 ratio of lithium or potassium naphthalene radical anion to  $\text{MgCl}_2$  with either dropwise or rapid addition of  $\text{MgCl}_2$  solution at either low or room temperature.



(ii) A solution of sodium naphthalene radical anion was prepared in the usual way from 20 mmol of naphthalene and 20 mmol of sodium in 18 ml THF. 8.5 ml of a 0.58 M solution of  $\text{MgCl}_2$  in THF (10 mmol) were added rapidly at room temperature (ca. 25 °C). The reaction was not appreciably exothermic and a red-brown solution was formed. The reaction mixture was treated with carbon dioxide and worked up as above. An oily solid was obtained (1.17 g) which  $^1\text{H}$  NMR indicated to be mostly dihydronaphthoic acids together with a small amount of alkylated derivatives.

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