Stoichiometry of protonation of aromatic hydrocarbon radical anions by weak proton donors. A marked discrepancy between the number of protons used and those incorporated into the aromatic structure

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Abstract

The stoichiometries of the reaction between alkali metal radical anions of biphenyl, naphthalene, phenanthrene and anthracene, and methanol and/or other proton donors have been determined by the magnetic titration technique. In the case of naphthalene radical anion and, for example, methanol as the proton source, the stoichiometry was found to be cation-dependent: Li, 2:1; Na, 1.75:1; K, 1.33:1. The reaction products using the experimentally determined stoichiometric conditions were ca. 95% naphthalene and 5% dihydronaphthalene(s). Thus, a marked discrepancy is observed between the protons used and those incorporated into the naphthalene molecule. Radical anions, at concentrations comparable with those of preparative reactions, react with carbon acids or amines according to the first-order kinetic law, although the initial concentrations of the two reactants were of the same order of magnitude or even equal. Lithium anthacene radical anion reacts with phenylacetylene and diethylamine at comparable rates, although the two "acids" differ in their acidities by ca. 10 orders of magnitude. A deuterium isotope effect of 2.49 ± 0.05 was observed in the reaction between lithium anthracene radical anion and diethylamine. A general reaction scheme is proposed that involves electron transfer to the proton donor and hydrogen-atom attack on the neutral hydrocarbon as the key reaction steps.

*Keywords:* Lithium; Sodium; Potassium; Alkali metals; Aromatic radical anions

1. Introduction

In 1956 Weissmann and coworkers [1] proposed a general mechanism for the reaction between naphthalene radical anion and electrophiles such as a proton or carbon dioxide, Scheme 1.

This mechanism, the so-called Weissman mechanism, assumes a 1:1 stoichiometry and requires a 50:50% mixture of neutral naphthalene and the corresponding dihydronaphthalene derivatives as the reaction products. There are two reports on the protonation of preformed naphthalene radical anion. The first was concerned with the elucidation of the mechanism of the reaction between sodium naphthalene radical anion and water [2] and was based on kinetic measurements. The most important findings of this study are: (a) the rate of disappearance of the sodium naphthalene radical anion

exhibits first-order dependence on the initial concentrations of each of the reactants, (b) the reaction with water of the dihydronaphthyl anion, an intermediate of the overall reaction, is considerably faster than that of the radical anion, (c) the reaction appears to have a small deuterium isotope effect. The authors concluded that the Weissman mechanism is in full agreement with the observed rate law. The other report was a CIDNP study of the protonation of various aromatic hydrocarbon radical anions, including sodium naphthalene radical anion with water and alcohols [3]. The results of the latter study also seemed to support the Weissman mechanism. Studies referring to the protonation of preformed aromatic hydrocarbon radical anions are, in general, relatively few. These concern sodium anthracene radical anion [4–6] and sodium perylene radical anion [7]. All these studies employed spectrophotometric techniques to measure kinetic, and therefore the initial concentrations of radical anions employed were very small.

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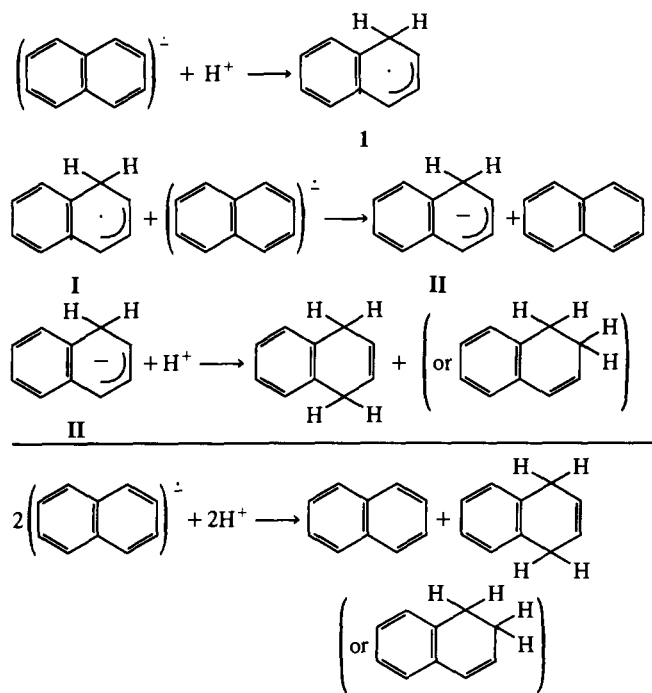
Scheme 1.

It is relevant here to mention the reactions between alkali metal radical anions and relatively strong carbon acids such as fluorene [8], acetylenic compounds [9] and thiophene [10], which lead to metallation products. In the metallation of thiophene by lithium aromatic hydrocarbon radical anions, the maximum yield of 2-thienyllithium, based on the available lithium, was 50%. It thus appeared that metallation by stable radical anions followed a 2 : 1 stoichiometry, a conclusion that had been substantiated by carrying out a magnetic titration of lithium biphenyl radical anion against thiophene [10]. Specifically, it takes one molecule of thiophene to consume two molecules of the radical anion. This result was explained on the basis of the fact that a stable chemical system has all its spins paired, and all its charges neutralized. This, in turn, means that one needs at least two odd-electron species in order to obtain reaction products with an even number of electrons [10]. The latter result was made more emphatic by carrying out metallations of thiophene with unstable radical anions that dimerize or polymerize faster than they metallate thiophene, for example the radical anions of 1,1-diphenylethylene or styrene. In the latter cases the unpaired spins are "taken care of" by the spin-pairing in the formation of the C–C bond(s) in the dimer of 1,1-diphenylethylene or the polymer of styrene, thus giving yields of metallation products corresponding to 1 : 1 stoichiometry, that is up to 100%, based on the available lithium.

Radical anions, due to their dual nature, that of a radical and a carbanion, have been considered as strong

bases, capable of abstracting protons from appropriate sources [2]. Considering radical anions as strong bases has created some confusion. For example, a method for determining the concentration of naphthalene radical anion has been employed, using a titration against a standard solution of acetic acid in toluene [11]. The authors assumed that the reaction exhibited a 1 : 1 stoichiometry, whereas the stoichiometry was found by magnetic titration to actually be 4 : 1. It appears useful, then, to determine the stoichiometry of reactions involving radical anions, which find considerable use in synthesis [12].

In this work we report on the stoichiometry of protonation of biphenyl, naphthalene, anthracene and phenanthrene radical anions, in some cases with more than one counterion and more than one proton source. We also report on the product distribution in the protonation reaction as well as giving a brief kinetic study of the reaction of potassium naphthalene radical anion with diphenylmethane and of lithium anthracene radical anion with diethylamine, phenylacetylene and fluorene. In our study we used NMR spectroscopy, enabling us to employ radical anions at concentrations approaching those of preparative reactions, i.e. around 1 M [10,13,14].

2. Results and discussion

2.1. Lithium naphthalene

Lithium naphthalene radical anion, on reaction with protonating agents possessing one available proton, such as methanol, sec-butanol and diethylamine, exhibited a 2 : 1 stoichiometry (Fig. 1). Thus it takes one proton equivalent to consume two moles of the radical anion. Lithium naphthalene radical anion titrated against n-
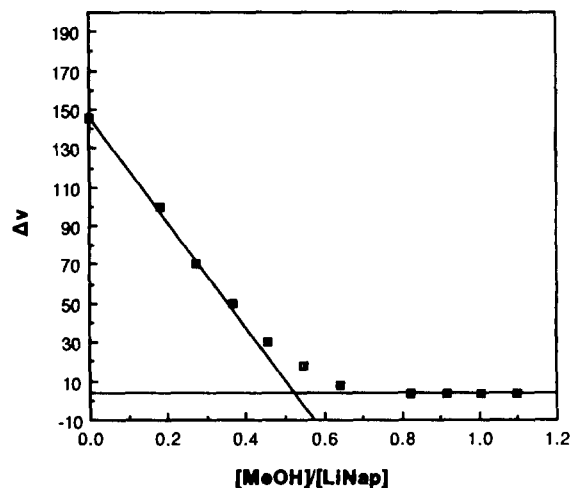

Fig. 1. Magnetic titration of lithium naphthalene radical anion against methanol.

butylamine gave a stoichiometry of 4:1. In this case there are two available protons and, therefore, the latter result appears to be in accordance with the results obtained with monoprotic agents. With dicyclohexyl-amine, however, a rather unexpected stoichiometry of 4:1 was obtained. By varying the counterion a new point emerged from this study. Namely, that the stoichiometry of protonation of the naphthalene radical anion with methanol appears to be cation-dependent 2:1 with lithium, 1.75:1 with sodium and 1.33:1 with potassium. Table 1 summarizes the relevant data.

It was then of interest to examine the distribution of the products resulting from the protonation of naphthalene radical anion. Reacting lithium naphthalene radical anion with methanol at ambient temperatures, in a molar ratio of 2:1, and working up the reaction mixture after 24 h, produced 95% naphthalene and 5% 1,4-dihydronaphthalene. By adding one equivalent of methanol to two equivalents of lithium naphthalene at 0–5°C, and then keeping the reaction mixture at −20 to −23°C until complete discharge of paramagnetism, a brown–red solution was obtained which, on carbonation, afforded ca. 75% of dihydronaphthoic acid, based on the available protons. In the latter experiment, the neutral fraction from the carbonation mixture was shown by NMR spectroscopy to be naphthalene with a small percentage of dihydronaphthalenes. By doubling the quantity of methanol, i.e. 1:1 molar ratio, the distribution changed substantially: 77% naphthalene, 5% 1,4-dihydronaphthalene, 10.8% 1,2-dihydronaphthalene and 7.2% di- or polymeric material. Reaction between sodium naphthalene radical anion and methanol in a molar ratio of 1.75:1 (i.e. the stoichiometric ratio determined by NMR); gave 94.3% naphthalene, 2.8% 1,4-dihydronaphthalene and 2.9% 1,2-dihydronaphthalene. The corresponding reaction with water, either in a molar ratio of 1.7:1 or with a large excess of water, gave approximately 70% naphthalene and ca. 30% dihydronaph-

Table 1
Stoichiometries of radical anion protonation determined by magnetic titration

Arene	Counterion	Proton source	Stoichiometry
Naphthalene	Li	MeOH	2:1
Naphthalene	Li	s-BuOH	2:1
Naphthalene	Li	n-BuNH₂	4:1
Naphthalene	Li	Et₂NH	2:1
Naphthalene	Na	MeOH	1.75:1
Naphthalene	Na	H₂O	1.7:1
Naphthalene	K	MeOH	1.33:1
Anthracene	Li	MeOH	1:1
Anthracene	Na	MeOH	1:1
Anthracene	K	MeOH	1:1
Phenanthrene	Li	MeOH	1.09:1
Phenanthreene	Li	n-BuNH₂	2.8:1
Biphenyl	Li	MeOH	1.18:1
Biphenyl	Na	MeOH	1.39:1

Table 2
Product distribution in radical anion protonation under the experimentally determined stoichiometric conditions and the respective theoretical yields

System	Products (%)	Theoretical (yield %)
Nap–Li–MeOH	naphth.(95); dihydro-(5)	75–25
Nap–Na–MeOH	naphth.(94.2); dihydro-(4.8)	70–30
Nap–Na–H₂O	naphth.(70.4); dihydro-(29.6)	70–30
Nap–K–MeOH	naphth.(95.2); dihydro-(4.6)	81–19
Ant–Li–MeOH	anthrac.(50); dihydro-(50)	50–50
Ant–Na–MeOH	anthrac.(50); dihydro-(50)	50–50
Ant–K–MeOH	anthrac.(50); dihydro-(50)	50–50
Phen–Li–MeOH	phenanthr.(63); dihydro-(37)	50–50
Biph–Li–MeOH	biphenyl(75.8); hydrogenated biphenyls(24.2)	57–43 *

* As dihydrobiphenyls which is not the case. See relevant discussion.

thalenes. Potassium naphthalene radical anion and methanol in a molar ratio of 1.33:1 gave 95.2% naphthalene and 4.8% 1,4-dihydronaphthalene. These results indicate that, when the reaction is carried out under the experimentally determined stoichiometric conditions, the protonating agent is methanol and the mixture is hydrolyzed after 24 h at room temperature, the distribution appears to be nearly independent of the counterion and is 95% naphthalene with the rest being dihydroderivatives.

In the protonation of lithium naphthalene radical anion with methanol under stoichiometric conditions, and provided that all the available protons are incorporated into the naphthalene molecule, the expected maximum yield of dihydronaphthalenes ought to be 25%. Thus, the 5% yield of dihydronaphthalene indicates that only 20% of the added protons have been incorporated into the naphthalene molecule. By protonating lithium naphthalene radical anion with an equimolar amount of methanol, the protons incorporated into the naphthalene became 40% of those available ones (Table 2, entry 2). Sodium naphthalene radical anion, on reaction with a stoichiometric amount of methanol, produced only 19% dihydronaphthalenes based on the expected theoretical yield of 30% (Table 2, entry 3). When the proton source changed to water, at the stoichiometric molar ratio almost all the available protons were used to produce dihydronaphthalenes (Table 2, entry 4). It is interesting to note that, by using a rather large excess of water in the protonation of sodium naphthalene radical anion, the distribution of products was the same as for protonation with a stoichiometric amount of water (Table 2, compare entries 4 and 5). In the case of protonation of potassium naphthalene radical anion with the stoichiometric amount of methanol, only 12.5% of the available protons were incorporated into the naphthalene molecule to produce dihydronaphthalenes (Table 2, entry 6). Therefore, *in no case has the 50:50% molar distribu-*

tion of naphthalene and dihydronaphthalenes been observed, as required by the Weissman mechanism.

The discrepancy between the smallest number of protons necessary to bring about complete destruction of the naphthalene radical anion, and the number of protons incorporated into naphthalene, is an important finding of the present study. It is an issue that had been overlooked in previous studies. Therefore, any mechanistic scheme proposed must take into consideration this result.

Reaction of alkali metal naphthalene radical anions with any of the alcohols or amines were employed in this study is too fast to be followed by our method [10,13,14] at ambient temperatures. We were able, however, to follow the rate of reaction between potassium naphthalene radical anion and diphenylmethane, a carbon acid $(pK_a = 32.2$ in DMSO [15]). Disappearance of potassium naphthalene radical anion in the presence of an excess of diphenylmethane obeys the first-order rate law (Fig. 2). It should be stressed that the initial concentrations of the radical anion and of the carbon acid were of the same order of magnitude. That is, the observed first-order kinetics are real. In this respect, potassium naphthalene radical anion behaves like lithium anthracene radical anion, whose reaction with, for example, fluorene or diethyl amine also follows first-order kinetics, see Fig. 3. Bearing in mind that lithium radical anions of biphenyl, naphthalene, phenanthrene stilbene and anthracene react with thiophene according to first-order kinetics [10], it seems that this kinetic behaviour could be common among the aromatic hydrocarbon radical anions in their reaction with any proton donor.

Therefore, any mechanistic scheme should take into consideration: (1) the observed stoichiometry, (2) the discrepancy between the minimum number of 'protons' required for the complete destruction of the radical
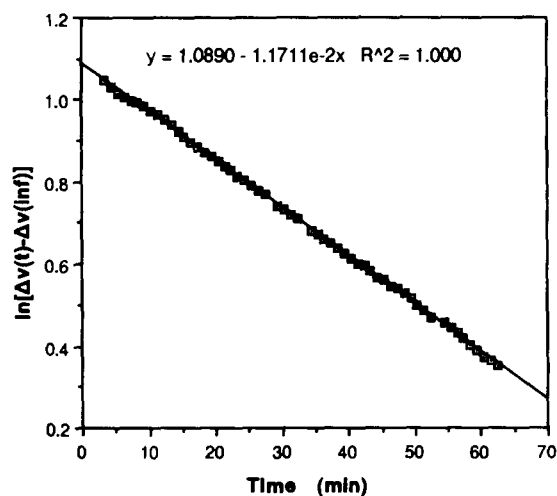

Fig. 2. First-order kinetic plot for the decay of paramagnetism in a solution being initially 0.61 M in potassium naphthalene radical anion and 2.23 M in diphenylmethane at 27°C.
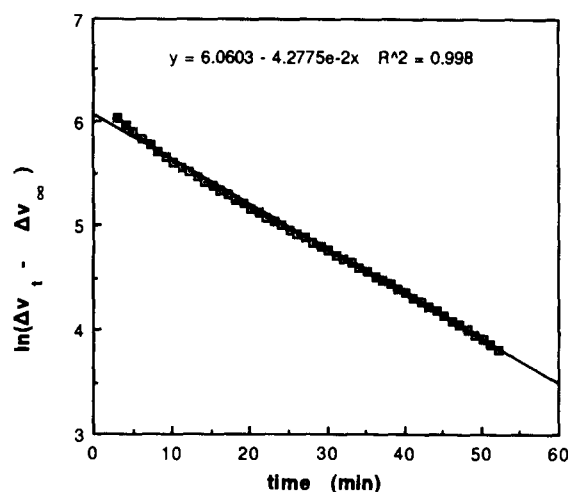

Fig. 3. Kinetic plot for the reaction between lithium anthracene radical anion and fluorene with initial concentration 0.50 M each at 27°C.

anion and the number of protons actually used to produce dihydronaphthalenes, and (3) the observed kinetic order in radical anion.

Perhaps, the most reasonable explanation of issue (2) is the elimination of alkali metal hydride from a species such as **II** (Scheme 1). It is already known that 1,4-dihydronaphthalene, on attempted metallation with phenyllithium in diethyl ether, is aromatized by LiH elimination [16]. We have also confirmed the formation of metal hydride in the lithiation of 9,10-dihydrophenanthrene with butyllithium in THF-methylcyclohexane solvent, see Experimental section.

Now let us examine some possible reaction schemes.

(a) Reaction through a dianion. Radical anions may undergo disproportionation to the corresponding dianion, e.g.

$$2N \cdot^- \xrightleftharpoons[N = naphthalene]{} N^= + N \qquad (1)$$
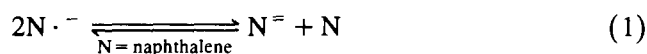
This reaction has been shown to occur upon adding a poor solvent to a solution of, for example, potassium naphthalene radical anion in tetrahydrofuran (THF) [14]. However, aromatic hydrocarbon dianions are sufficiently reactive to cause THF cleavage [14], somewhat like alkyllithium reagents [17]. Therefore, a dianion could be capable of abstracting a 'proton' from a substrate such as diphenylmethane (Scheme 1).

$$2N \cdot^- \xrightleftharpoons[N = naphthalene]{} N^= + N \qquad (i, slow)$$

$$N^= + 2MeOH \longrightarrow NH_2 + 2MeO^- \qquad (ii, fast)$$
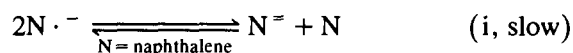
It appears reasonable to assume that, if a dianion were involved in the reaction, the disproportionation step, Eq. (1), should be rate-determining. Therefore, second-order kinetics ought to be operable, which is not the case.

(b) Reaction by an electron transfer mechanism. We consider a reaction scheme in which the primary step is electron-transfer from the radical anion to the protonating agent. This alternative mechanistic scheme appears to be more attractive from the point of view of energetics. Indeed, loss of the unpaired electron by the radical anion regenerates the neutral aromatic hydrocarbon, i.e. a system with marked thermochemical stability, whereas direct protonation of the radical anion should result in partial disruption of the extended conjugation, which should be more costly in terms of energy. Evidence based on contact shift measurements [18] indicates that radical anions can donate their odd electron to a substrate such as an alkyl halide through the mediation of the cation. This requires 'coordination' of the substrate to the sphere of the metal. Therefore, we propose step (i) (Scheme 2) in which methanol enters the coordination sphere of the metal in a fast and reversible step, followed by a rate-determining step ((ii), Scheme 2) in which the electron that is lost by the radical anion causes fission of the methanol molecule to a methoxide anion and H-atom in a process similar to the reaction between solvated electron and water, alcohols or ammonia [19]. The H-atom attacks the neutral naphthalene [20] before the latter diffuses away, thereby producing a radical of dihydronaphthalene which, in turn, is converted to the corresponding carbanion by accepting an electron from the radical anion. Finally, elimination of metal hydride from the dihydronaphthalene carbanion would explain the observed distribution of products. Alternatively, the H-atom could be converted directly to H^- by accepting an electron from the radical anion. In order to decide between these two possibilities, we reasoned that, on reacting naphthalene radical anion with, for example, Et_2ND, some deuterium should be found in the naphthalene provided that the reaction goes through the attack of the H(D)-atom on the neutral naphthalene and the regeneration of the latter by MH(D)-elimination. The alternative, i.e. attack of $H^+(D^+)$, is excluded on the basis of lack of correlation between the pK_a of 'protonating' agents and the respective rate constants (see the relevant discussion for the anthracene radical anion, below). Deuterium incorpora-
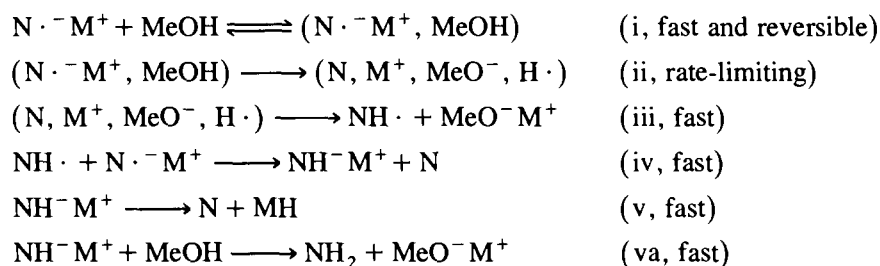
tion did occur, as shown by ^2H NMR as well as by mass spectrometry. Scheme 2, explains also the observed kinetic order with respect to naphthalene radical anion, see below. The different stoichiometries that have been observed for lithium, sodium and potassium naphthalene radical anions could possibly be explained by considering the relative abilities LiH < NaH < KH to compete against the corresponding alkali metal naphthalene radical anion $M^+C_{10}H_8^-$ for the protonating agent. Indeed, the pK_a of methanol, as well as of any other acid, is highly solvent-dependent; 16 in water, 29 in DMSO, and it should be even higher in THF. The acidity then of methanol in THF could be low enough to make the above-mentioned competition possible for sodium and potassium hydride but not for lithium hydride (Eq. (2)), thus shifting the stoichiometry towards 1 : 1.

$$MH + MeOH \longrightarrow H_2 + MeOM \qquad (2)$$

Scheme 2 seems to explain more satisfactorily the results with sodium naphthalene radical anion and water, where almost 100% of the available protons were incorporated into naphthalene, producing dihydronaphthalenes. Water is a stronger acid than methanol and a sodium derivative of the dihydronaphthalene carbanion NH^-Na^+ should react with water before undergoing NaH-elimination. The weakness of this scheme is the indirect evidence for the formation of alkali metal hydride and the lack of evidence for the formation of dihydrogen from the (supposed) reaction between the protonating agent and the alkali metal hydride. However, we have confirmed that the lithium hydride eliminated from lithiated 9,10-dihydrophenanthrene does react with a proton donor like water to form dihydrogen, see Experimental section.

2.2. Lithium, sodium and potassium anthracene

Lithium, sodium and potassium anthracene radical anions, on titration against methanol, gave stoichiometries very close to 1 : 1. A stoichiometry of 1.7 : 1 was obtained when lithium anthracene radical anion was titrated against n-butylamine. This result corresponds to

$N \cdot {}^-M^+ + MeOH \rightleftharpoons (N \cdot {}^-M^+, MeOH)$	(i, fast and reversible)
$(N \cdot {}^-M^+, MeOH) \longrightarrow (N, M^+, MeO^-, H \cdot)$	(ii, rate-limiting)
$(N, M^+, MeO^-, H \cdot) \longrightarrow NH \cdot + MeO^-M^+$	(iii, fast)
$NH \cdot + N \cdot {}^-M^+ \longrightarrow NH^-M^+ + N$	(iv, fast)
$NH^-M^+ \longrightarrow N + MH$	(v, fast)
$NH^-M^+ + MeOH \longrightarrow NH_2 + MeO^-M^+$	(va, fast)

N = naphthalene, NH $\cdot$ = dihydronaphthyl radical, either 1,2- or 1,4-, NH^-M^+ = 1,2- or 1,4-dihydrometallonaphthalene, NH_2 = 1,2- or 1,4-dihydronaphthalene.
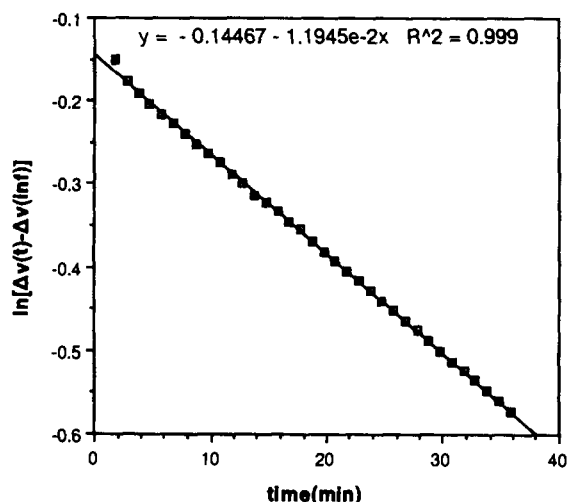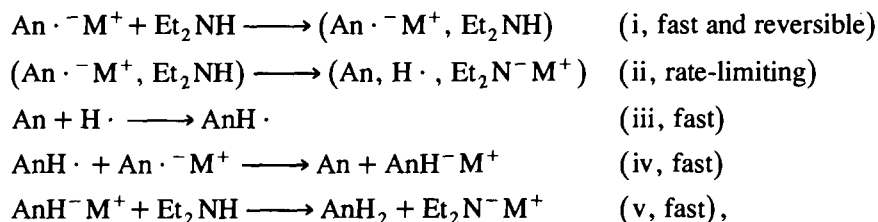
Scheme 2.

Fig. 4. Kinetics of the reaction between lithium anthracene radical anion and diethyl amine N-d, at 27°C, see the text.

a per-available-proton stoichiometry of ca. 1 : 1.2. Analysis of the protonation products indicated a 50:50% mixture of anthracene and 9,10-dihydroanthracene. Thus the anthracene case is the only one in which there is no discrepancy between the number of available protons and the number incorporated into the aromatic system, in accordance with the Weissman mechanism.

Lithium anthracene radical anion reacts with phenylacetylene, fluorene or diethylamine at convenient rates that can be followed by our NMR technique. The reactions with phenylacetylene and fluorene represent 'direct' metallation reactions, e.g. Eq. (3), and follow first-order kinetics, as does the reaction between lithium anthracene radical anion and diethylamine (Figs. 3, 4). Thus, in a solution of 0.94 M in lithium anthracene radical anion and 1.153 M in phenylacetylene a value $k_{obs} = 3.16(\pm 0.04) \times 10^{-3}$ s^{-1} at 34°C was obtained.

$$PhC\equiv CH + Li^+(anthra)^{\cdot -} \longrightarrow PhC\equiv CLi \qquad (3)$$
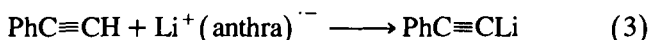
Similarly, lithium anthracene radical anion and diethylamine at initial concentrations of 0.96 M and 2.23 M respectively, gave a first-order rate constant $k_{obs} = 1.83(\pm 0.03) \times 10^{-3}$ s^{-1} at 34°C. One can notice that

although diethylamine is a weaker acid than phenylacetylene by at least 8 orders of magnitude [21], they both still react with lithium anthracene radical anion at comparable rates. This indicates the lack of a Brønsted-type relationship which, in turn, precludes the involvement of protonation in the rate-determining step.

Since, in the reaction of radical anions with proton donors, a particle of small mass could be involved, we examined the possibility of the operation of tunnelling. We measured (in duplicate runs) $k_H = 4.96(\pm 0.05) \times 10^{-4}$; $4.99(\pm 0.05) \times 10^{-4}$ s^{-1} and $k_D = 1.99(\pm 0.03) \times 10^{-4}$; $1.97(\pm 0.03) \times 10^{-4}$ s^{-1} at 27°C, employing equal initial concentrations of the two reactants, i.e. lithium anthracene radical anion and $Et_2NH(D)$, 0.90 M each. Thus, a primary isotope effect, $k_H/k_D = 2.49 \pm 0.05$, can be calculated which appears to be quite normal. This result precludes the involvement of tunnelling, but it does indicate the cleavage of the N–H bond in the rate-limiting step. We propose the following Scheme 3 which is consistent with the experimental evidence.

Scheme 3 is closely analogous to Scheme 2, proposed for the naphthalene radical anion case. The only difference is that the intermediate 9-hydro-10-metalloanthracene, (AnHM) cannot undergo a facile aromatization by elimination of MH. This is the fundamental reason for the observed 1:1 stoichiometry with all alkali metal anthracene radical anions. Scheme 3 is also consistent with both the kinetic order in lithium anthracene radical anion and the observed isotope effect. Moreover, Scheme 3 could explain the 'unexpected' 4:1 stoichiometry observed in the case of lithium naphthalene radical anion and the sterically-hindered secondary amine, dicyclohexyl amine, see relevant results. In the latter case, the involvement of the highly basic dicycloxexyl amide could alternatively attack solvent molecules producing molecular fragments capable of consuming radical anions. We investigated the possibility of formation of products resulting from combination of the amine and the aromatic molecule. Lithium naphthalene radical anion quenched with di-iso-propylamine gave only traces of amination product.

$$An \cdot {}^-M^+ + Et_2NH \longrightarrow (An \cdot {}^-M^+, Et_2NH) \qquad (i, \text{ fast and reversible})$$

$$(An \cdot {}^-M^+, Et_2NH) \longrightarrow (An, H\cdot, Et_2N^-M^+) \qquad (ii, \text{ rate-limiting})$$

$$An + H\cdot \longrightarrow AnH\cdot \qquad (iii, \text{ fast})$$

$$AnH\cdot + An\cdot {}^-M^+ \longrightarrow An + AnH^-M^+ \qquad (iv, \text{ fast})$$

$$AnH^-M^+ + Et_2NH \longrightarrow AnH_2 + Et_2N^-M^+ \qquad (v, \text{ fast}),$$

$AnH_2 = 9,10$-dihydroanthracene. $AnH\cdot = 9,10$-dihydro-9-anthracenyl radical, $AnH^-M^+ = 9,10$-dihydro-10-metalloanthracene.

Scheme 3.

2.3. Lithium phenanthrene

Lithium phenanthrene radical anion, titrated against methanol, exhibited a stoichiometry of ca 1.09:1, whereas against n-butylamine a stoichiometry of ca. 2.8:1, or ca. 1.4:1 per available proton was obtained. The product distribution was 63% phenanthrene and 37% 9,10-dihydrophenanthrene when the radical anion was quenched with one mole equivalent of methanol. When the radical anion solution was poured into a large volume of methanol, then the product distribution changed to 55% phenanthrene and 45% 9,10-dihydrophenanthrene. The expected maximum yield of 9,10-dihydrophenanthrene on the basis of the observed stoichiometry of 1.09:1 should be 46%, which is not the case. We notice, however, that, in the case of lithium phenanthrene radical anion, the number of unaccounted protons is only 20%, a percentage considerably lower than that for lithium naphthalene radical anion in which the respective percentage is 80%.

These results indicate that lithium phenanthrene radical anion exhibits a behaviour intermediate between that for the corresponding radical anions of anthracene and naphthalene. The smaller percentage of unaccounted protons in the phenanthrene case, as compared with that of naphthalene, can reasonably be explained by the less facile elimination of LiH from a 9,10-dihydro-10-lithio-phenanthrene intermediate.

2.4. Lithium biphenyl

Lithium biphenyl radical anion, on titration against methanol, exhibited a sharp break at a ratio (methanol)/(lithium biphenyl) = 0.85. This corresponds to a stoichiometry of 1:1.18. The respective stoichiometry with sodium biphenyl radical anion was 1:1.39. The distribution of the products under stoichiometric conditions in the lithium biphenyl radical anion case was 75.8% biphenyl and 24.2% hydrogenated biphenyls. On the basis of the consumed protons, and provided that the reduction product is a dihydro-derivative of biphenyl, the expected yield should be 57% biphenyl and 43% dihydrobiphenyls. Although no efforts were made to identify the individual reduction products, the actual yield of the biphenyl, being in substantial excess of the expected 57%, suggests that the reaction could involve steps leading to aromatization either by alkali metal hydride-elimination or by a base-catalyzed hydrogen redistribution among the dihydro derivatives [22].

3. Concluding remarks

The alkali metal radical anions of biphenyl, naphthalene, phenanthrene and anthracene exhibit stoichiometries of protonation with alcohols and amines, which,

with the exception of the anthracene case, all deviate from the 1:1 stoichiometry required by the Weissman mechanism. The product distribution is also in marked disagreement with that expected on the basis of 1:1 stoichiometry. Specifically, in all cases except that of anthracene, when protonation is effected with the experimentally-determined stoichiometric amount of alcohol, the yield of the neutral hydrocarbon is always larger than the theoretical one, based on the available protons. This novel finding has been interpreted as arising from the aromatization by metal hydride-elimination from the intermediate, e.g. 1,2-(or 1,4-) dihydro-metallo-naphthalene. This latter process is the one that differentiates anthracene from the other aromatic hydrocarbons studied, simply because elimination of metal hydride from the intermediate 9,10-dihydro-metallo-anthracene is energetically unfavourable. A general mechanistic scheme has been proposed which involves electron-transfer from the radical anion to the protonating agent, followed by hydrogen atom attack on the neutral hydrocarbon and production of, for example, a 1,2 (or 1,4-) dihydronaphthyl radical intermediate. The formation of the latter intermediate can explain the observed chemistry, including the formation of di- or polymeric material.

4. Experimental

Magnetic titrations and kinetic measurements were carried out with either a Varian FT-80A NMR spectrometer or a Bruker AC-300 MHz NMR instrument. The latter instrument was used for recording ^{1}H, ^{2}H and ^{13}C NMR spectra. For mass spectrometric analysis a Finnegan TSQ 7000 GC/MS/MS instrument was employed. Gas chromatographic analyses were performed with a Pye Unicam GCV chromatograph. Naphthalene, phenanthrene anthracene and biphenyl were commercial products, 98% or better, and were recrystallized from isopropanol or ethanol. Tetrahydrofuran was doubly distilled from LiAlH$_4$ under argon shortly before use. n-Butylamine, diethylamine, di-iso-propylamine and dicyclohexylamine were distilled from barium oxide under argon. Methanol was distilled from magnesium methoxide under an atmosphere of argon. sec-Butanol was 99% (or better) and distilled under argon shortly before use. Et$_2$ND was prepared by potassium carbonate catalyzed H/D exchange in mixtures of Et$_2$NH–D$_2$O. NMR analysis indicated a purity of 95% at least after three exchanges between 10 ml of diethylamine and 5 ml portions of D$_2$O. Standard solutions were handled with microsyringes. Alkali metal aromatic hydrocarbon radical anions were prepared in 20 mmol quantities and in concentrations of ca. 1 M under an atmosphere of argon by stirring strictly equivalent quantities of the alkali metal and the aromatic hydrocarbon overnight. The concentration of the radical anion was

determined by reacting an aliquot of the radical anion solution with ethylene bromide under argon and titrating the liberated Br⁻ and/or by total alkalinity on hydrolyzed aliquots.

4.1. Magnetic titrations

A 500 μl aliquot of a 1.0 M solution of lithium naphthalene radical anion in THF was introduced via a microsyringe into a 5 mm NMR tube [13b] filled with argon. Increments, 2 μl each, of neat methanol were added with a 10 μl syringe, and the corresponding solvent shifts referred to the low field THF proton signal were recorded. The results are given graphically in Fig. 1.

4.2. Kinetic runs

A 500 μl aliquot of 1.0 M lithium anthracene radical anion in THF was introduced into the NMR tube as described in the previous paragraph. The tube was placed in the NMR probe which had a temperature of 27°C and, after a few minutes, 70 μl diethylamine, freshly distilled and saturated with argon, was added to the radical anion solution. Thorough mixing was effected by shaking the NMR tube for a few seconds. The tube was again placed in the probe. The progress of the reaction was followed by observing the solvent shift (low field signal of THF) as a function of time. Points were collected around every 1 min. The data are plotted as $\ln(\Delta\nu_t - \Delta\nu_\infty)$ vs. time (min), see Fig. 3.

4.3. Product analysis

1. To a solution of lithium naphthalene radical anion in THF prepared from 2.56 g, 20 mmol of naphthalene, 0.140 g of lithium chips and 18 ml of THF, was added 0.405 ml, ca. 10 mmol, of methanol. A small exotherm was observed. The resulting mixture was stirred overnight. Hydrolysis and extraction with 3 × 50 ml of methylene chloride, etc. gave 2.5 g of product. Gas chromatographic analysis: column 10% Apiezon L on Chromosorb GAWBMCS, 6 × 18 ft², carrier gas argon, 42.85 ml min⁻¹, T_{col} = 130°C, T_{det} = 230°C, T_{inj} = 230°C, indicated naphthalene 95%, 1,4-dihydronaphthalene 5%.

2. The previous experiment was repeated with the only difference being that protonation was effected by 0.810 ml of methanol, i.e. by an equimolar quantity. The product, 2.55 g by gas chromatographic analysis, was shown to be a mixture of 5% 1,4-dihydronaphthalene, 10.8% 1,2-dihydronaphthalene, 77% naphthalene, and 7.2% di- or polymeric material. The assignment of the chromatographic peaks was based on preparative GC and NMR spectroscopy.

3. To a solution of lithium naphthalene radical anion,

prepared as in 1 above and containing 20 mmol, was added 10 mmol of methanol at 0–5°C. The reaction mixture was stirred for 24 h at room temperature. The solution was evaporated to dryness under vacuum and the solid residue was tested for the presence of lithium hydride by hydrolyzing the mixture under vacuum. Incondensable gas remained when the flask containing the hydrolysate was immersed in liquid nitrogen.

4. To a solution of lithium naphthalene radical anion, prepared as in 1 above and containing 20 mmol, was added 10 mmol of methanol at 0–5°C and the reaction mixture then kept at −20 to −23°C until paramagnetism had decayed completely. The resulting brown–red solution was carbonated. Usual work-up of the carbonation mixture afforded 0.65 g of a mixture of dihydronaphthoic acids (NMR), or 75% of the theoretical yield based on available protons. NMR analysis on the neutral fraction indicated it to be mainly naphthalene.

5. A 55:45% mixture of phenanthrene and 9,10-dihydrophenanthrene respectively, prepared by protonation of 20 mmol of lithium phenanthrene radical anion with a large excess of methanol, was dissolved in 20 ml THF and subjected to metallation with butyllithium in methylcyclohexane (6.0 ml, 1.80 M, 10.8 mmol) at an initial temperature of −60°C. The resulting brown–red solution was stirred at room temperature for 3 days, during which period the colour of the solution faded. On standing a white precipitate was formed which, after being freed from the supernatant, was reacted with methanol. A vigorous reaction took place, releasing a gas which did not condense at the liquid nitrogen temperature. NMR analysis of the hydrocarbon isolated from the supernatant indicated a ca. 85:15% mixture of phenanthrene and 9,10-dihydrophenanthrene, respectively.

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