U.D.C. 542.957.1;547.52/.59

The Radical-anions and Dianions of Aromatic Hydrocarbons in Metallation Reactions

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The review gives a general account of the literature data on the behaviour of the radical-anions and dianions of aromatic hydrocarbons in reactions involving the metallation of aliphatic-aromatic compounds and discusses the mechanisms of these reactions, the role of the counterion, the degree of its solvation, and the type of ionic association complexes in solutions of the reactants being emphasised. Since the carbanions of dihydro-derivatives of aromatic hydrocarbons are formed in the course of the reactions, data are presented also on their involvement in the metallation processes. The relative propotophilic properties of the three types of metallating agents, established experimentally and determined from the localisation energies of their protonation reactions calculated by the Pariser-Parr-Pople method, are compared.
The bibliography includes 120 references.

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I. REACTIONS OF RADICAL-ANIONS AND DIANIONS AS REDUCING AGENTS AND BASES

Radical-anions (r.a.) of aromatic hydrocarbons are usually obtained in solution by electrochemical reduction at the cathode or by chemical reaction with an alkali metal [1,2]. Under favourable conditions, there is a possibility of the transfer of two electrons to the hydrocarbon molecule and the formation of a dianion (d.a.); trianions are generated much more rarely. The role of radical-anions and dianions in organic chemistry is very great and much attention has been devoted to the study of their formation, structure, properties, and reactivities (see the relevant reviews[1-13]).

As a result of intense study in recent years, it has been established that the transfer of one electron with formation of a radical-anion is the first step in many reactions (see the relevant reviews [9,11,14]). Such are, in particular, the reactions involving the metallation of aliphatic-aromatic compounds by alkali metals. The capacity of radical-anions to give up readily the unpaired electron in the non-bonding orbital of the aromatic hydrocarbon to compounds with a higher electron affinity permits numerous reduction reactions, including the sensitisation of anionic polymerisation leading to the formation of "live" polymers [7]. The protophilic properties of radical-anions are a consequence of the enhanced electron density at their carbon atoms. Dianions are more vigorous reducing agents and proton acceptors than radical-anions [15]. Adducts of aromatic hydrocarbons with alkali metals, which include radical-anions or dianions in their composition, have been used successfully for the metallation of a wide variety of organic compounds [16-20], behaving as proton acceptors, i.e. bases.

A mechanism of the protonation of aromatic radical-anions and dianions has been proposed by Laitinen and Wawzonek [21] and Hoijtink et al. [15], in relation to the electrochemical reduction of aromatic hydrocarbons (Ar) in aqueous dioxan. Initially the interaction of the primary reduction product, the radical-anion Ar^-, with the donor BH entails the formation of the radical ArH$^\cdot$:

$$Ar^- + BH \rightarrow ArH^\cdot + B^- . \quad (1)$$

Since it has a higher electron affinity [15], ArH$^\cdot$ combines with an electron and is converted into the carbanion of the dihydro-derivative of the aromatic hydrocarbon ArH^-:

$$ArH^\cdot + Ar^- \rightarrow ArH^- + Ar . \quad (2)$$

Apart from the radical-anion, the metal, cathode, etc. can behave as the electron donor. In the final stage, a proton adds to the carbanion and the dihydro-derivative is obtained:

$$ArH^- + BH \rightleftarrows ArH_2 + B^- . \quad (3)$$

Usually the rate of electron transfer [reaction (2)] is higher by several powers of ten than the rate of protonation [22] [reactions (1) and (3)].

The protonation of the dianion includes the stage involving the formation of ArH^-:

$$Ar^{=} + BH \rightleftarrows ArH^- + B^- \quad (4)$$

and then ArH_2:

$$ArH^- + BH \rightleftarrows ArH_2 + B^- . \quad (5)$$

The protonation of radical-anions and dianions of different structures by water, alcohols, and acids has been considered by a number of workers [23-35]. Weissman and coworkers [23] adopted the mechanism (1)–(3) for the reaction of sodionaphthalene with water. Its validity was demonstrated by Bank and Closson [25] using an isotopic method. Regardless of the rate of addition of tritiated water to the solution of sodionaphthalene in tetrahydrofuran (THF), a mixture of naphthalene, dihydronaphthalene, and a small amount of tetralin was obtained and only the last two products were radioactive.

In the discussion of this result, Bank and Closson noted that, if reaction (1) were followed by the disproportionation of the radicals ArH$^\cdot$,

$$ArH^\cdot + ArH^\cdot \rightarrow ArH_2 + Ar , \quad (6)$$

naphthalene would have been radioactive too.

Presumably the radical-anion could disproportionate initially:

$$Ar^{\cdot-} + Ar^{\cdot-} \rightleftarrows Ar^{=} + Ar, \quad (7)$$

and then the dianion would be protonated via reactions (4) and (5). Then, when the required amount of water is added slowly, one should expect the involvement of $Ar^{=}$, ArH^{-}, and Ar in the equilibrium. However, naphthalene would contain tritium under these conditions. Since there is no tritium in naphthalene, the mechanism (1)–(3) is correct.

The formation of the carbanions ArH^{-} in the reaction with the proton-donating dianions of a number of aromatic hydrocarbons was demonstrated spectroscopically by Velthorst and Hoijtink [26]. Krapcho and Bothner-By [36] applied the mechanism of the protonation of a radical-anion to the hydrogenation of organic compounds by an alkali metal in liquid ammonia with added alcohol (the Birch reaction). In liquid ammonia, the alkali metal M is ionised [37]:

$$M \xrightarrow{NH_3} M^{+} + e^{-}, \quad (8)$$

the cation and the electron (e^{-}) being solvated by ammonia. The addition of one or two electrons to the molecule of the organic substance converts it into a radical-ion or dianion, which then reacts with the alcohol [reactions (1)–(5)]. In addition to the dihydro-derivative, more highly hydrated compounds are frequently formed (see the relevant reviews [37-41]).

Eisch and Kaska [18] suggested that the metallation of aliphatic-aromatic hydrocarbons (in particular tri- and di-phenylmethane) by an adduct of an aromatic hydrocarbon and an alkali metal (lithiobiphenyl) takes place similarly, i.e. via stages (1)–(3). This mechanism of metallation, involving radical-anions, is now generally accepted.

When the acidity of the proton donor BH is low (for example, when BH is a CH acid), the protonation may not go to completion owing to the reversibility of reactions (3)–(5). When Ar is a polycyclic hydrocarbon, an equilibrium is frequently established in the disproportionation reaction of two carbanions of the dihydro-derivative [25,42]:

$$ArH^{-} + ArH^{-} \rightleftarrows ArH_2 + Ar^{=}. \quad (9)$$

The protonation (metallation) process can also be complicated by electron transfer from the radical-anion or the dianion to the proton donor [19,43,44]:

$$Ar^{\cdot-} + BH \rightleftarrows Ar + BH^{\cdot-}. \quad (10)$$

The mode of reaction depends on factors such as the ionisation potential and the protophilic properties of the radical-anion or dianion, and the acidity and electron affinity of the proton donor. Cations, which are not indicated in the above reactions, and solvents in which the reactions are carried out play an important role. The position of equilibrium in the formation of the radical-anions and their conversion into dianions by reduction or disproportionation depend to a considerable degree on the counterion and the solvent [5,7]. Nevertheless, in certain cases the last reaction may actually cause the protonation of the dianion and not the radical-anion, as shown by Szwarc and coworkers [35] for the perylene radical-anion.

Like other anionic organic reactions, the metallation processes involving radical-anions and dianions are frequently carried out in ethereal solvents, since the latter are very weak proton donors and effectively solvate the cations. Since the dielectric constants (DC) of ethers are low, (3–7 at 25°C), ionic association effects are often of primary importance. In a general form, the equilibrium between the individual states of the organic derivative of the alkali metal (AM) in solution is described by mechanism (11), [45,46] which does not, however, take into account the solvation of the species:

$$(A^{-\delta}M^{+\delta})_n \rightleftarrows n\,A^{-\delta}M^{+\delta} \rightleftarrows A^{-}M^{+} \rightleftarrows A^{-} \| M^{+} \quad (11)$$
$$A^{-} + M^{+}$$

In glycol ethers and many cyclic ethers, the existence of the polar molecules $A^{-\delta}M^{+\delta}$ and their aggregates $(A^{-\delta}M^{+\delta})_n$ is atypical and two main types of ion pairs predominate, contact ion pairs ($A^{-}M^{+}$, c.i.p.) and separated ion pairs ($A^{-}\|M^{+}$, s.i.p.); on the other hand, the concentration of free ions (A^{-}, M^{+}) is low. The main difference between the separated and contact ion pairs is the presence of a layer of solvent molecules (usually the solvation shell of the cation) separating the ions, as a result of which the interionic interaction in a separated ion pair is of a Coulombic type and hardly depends on the radius of the cation.

In contact ion pairs, a decrease of the radius of the cation entails an appreciable enhancement of the interionic interaction and the exchange energy begins to play a decisive role in this process. The formation of separated ion pairs is favoured by an increase of the degree of solvation of the cation which may be a consequence of its reduced radius, the enhancement of the solvating capacity of the solvent, or a decrease of temperature. For large cations (K^{+}, Rb^{+}, and Cs^{+}), the existence of separated ion pairs in an ethereal medium is unlikely.

The different types of ion pairs are distinguished with the aid of many physicochemical methods—by the shift of the absorption band maximum in the spectrum of the carbanion; by the splitting of the components of the ESR spectrum as a result of the interaction of the unpaired electron with the magnetic moment of the nucleus of the cation; by the heat of dissociation of ion pairs, into free ions established by measuring the conductance of the solution as a function of temperature. Much information can be obtained also with the aid of the NMR method [47-50]. Contact ion pairs with unequal degrees of solvation of the cation may be distinguished spectroscopically [51] and by ESR [52] and it is also possible to detect the so called peripherally solvated [7,53] contact ion pairs which are isomeric with separated ion pairs. More detailed information about the state of organic compounds of alkali metals in solution is given in other reviews [5,7,13,49,53-56].

The extensive literature on the structure and properties of radical-anions and dianions and on the state of the adducts in solution has been summarised in other reviews [3-9,12,13]. The problem of the reactivities of radical-anions and dianions has been less thoroughly considered and general accounts of the information about their behaviour in metallation reactions, particularly as a function of the counterion, the properties of the solvent, and the type of ionic association complexes, are altogether lacking. The aim of the present review is to fill this gap. Since in the course of metallation reactions involving radical-anions and dianions the carbanions of dihydro-derivatives of aromatic hydrocarbons are formed, one of the sections of the review is devoted to the metallation of aliphatic-aromatic compounds by such species.

II. RADICAL-ANIONS AS METALLATING AGENTS

Normant and Angelo [16] were the first to note the possibility of using radical-anions for metallation. They showed that in THF sodionaphthalene, sodiobiphenyl, and

other adducts metallate in the CH bond aliphatic-aromatic hydrocarbons (fluorene, triphenylmethane, etc.), various derivatives of acetylene, nitriles, carboxylic acids, and certain heterocyclic compounds, both rapidly and in high yields. It has been established for the metallation of diphenylmethane that the naphthalene radical-anions are more effective than the phenanthrene radical-anions and that the rate of reaction increases when the sodium cation is replaced by potassium.

Table 1. Rate constants ($10^3 k$, litre mole^{-1} s^{-1}) for the reaction of radical-anions (K^+ cation) with triphenylmethane at 20°C.[57,58]

Radical-anion	DG	DME	DEE	DMP
Biphenyl	55	25	10	12
Napthalene	1.6	1.3	2	5
Anthracene	—	0.6	~0.1	—

Eisch and Kaska[18] observed that metallation with the aid of lithiobiphenyl in THF at 30°C is quantitative for triphenylmethane, takes place to the extent of 50% for diphenylmethane, and not more than 1% for toluene. The metallation reaction was accelerated by the addition of metallic lithium to lithiobiphenyl, which was explained by the formation of the biphenyl dianion more reactive than the radical-anion.

Table 2. Rate constants ($10^3 k$, litre mole^{-1} s^{-1}) for the reaction of radical-anions (Na^+ cation) with 9-phenylxanthene at 20°C.[58]

Radical-anion	DG	DEE
Biphenyl	16	200
Naphthalene	7	11

Later studies were made[57-60] on the dependence of the rate of metallation of certain aliphatic-aromatic compounds on the structure of the radical-anion, the substrate, and the cation on the solvating properties of the ether.

Usually the protophilic properties (or in the more general case the nucleophilic properties) of the carbanion become more pronounced as the interaction with the counterion weakens. This has been demonstrated in numerous instances of anionic polymerisation reactions[7,61], metallation by organolithium compounds[54], hydrogen isotope exchange between the CH bonds of two hydrocarbons in catalysis by bases[62], etc. The same cause is responsible for the acceleration of the majority of anionic organic reactions in solvents which effectively solvate cations and thereby activate the anions[5,63-65].

However, Tables 1 and 2 show that the effect of interionic interaction in metallation reactions involving radical-anions does not always obey the above rule and is related in a specific manner to the structure of the reactants.

Thus, in the reaction with triphenylmethane, the protophilic properties of the biphenyl radical-anion become more pronounced on passing from 1,3-dimethoxypropane (DMP) and 1,2-diethoxyethane (DEE) to solvents with a higher solvating capacity[5]—[1,2-dimethoxyethane? (Ed. of Translation)] (DME) and diglyme (DG) (Table 1). At the same time the opposite variation of the effect of the medium on the rate of reaction has been observed for the naphthalene radical-anion under the same conditions, i.e. an unusual behaviour has been observed, the protophilic properties of the radical-anion proving to be more marked the more intense its interaction with the cation. In the metallation of 9-phenylxanthene by sodium adducts the same behaviour is shown also by the biphenyl radical-anion (Table 2). It has been demonstrated[58] that the biphenyl and naphthalene radical-anions form with the Na^+ cation separated ion pairs in DG and contact ion pairs in DEE, i.e. contrary to the usual belief, the reactivity of the separated ion pairs is inferior to that of the contact ion pairs.

Table 3. Rate constants ($10^4 k$, s^{-1}) for the reaction of naphthalene radical-anions with triphenylmethane at 22°C.[57]

Solvent	Na^+	Li^+	K^+	Cs^+
DME	0.5	1	1	>10
DEE	0.8	1.2	2.5	>10

Essentially the same conclusion can be reached also on the basis of data for the effect of the cation on the rate of metallation of triphenylmethane by the naphthalene radical-anion in DME and DEE (Table 3). In DME, sodionaphthalene is present predominantly in the form of separated ion pairs and potassionaphthalene and caesionaphthalene are mainly in the form of contact ion pairs[5], but the rate of metallation is in fact higher for the contact ion pairs.

The above findings suggest that the cation enters into the composition of the activated complex for the reactions involving the metallation of aliphatic-aromatic compounds with participation of radical-anions.

An unusual dependence of the protophilic properties of the radical-anion on the intensity of interionic interaction has been observed also in certain other reactions with an acid-base mechanism. Thus weaker protophilic properties of the radical-anions entering into the composition of the separated ion pairs compared with the contact ion pairs were noted by Bank, who measured the rate of reaction of sodionaphthalene[38] and sodioanthracene[34] with water (Table 4).

For example, when tetraglyme (0.01% in relation to sodionaphthalene) is added to THF, the sodionaphthalene contact ion pairs are converted into separated ion pairs[7,53] and the rate of reaction with water then decreases by two powers of ten. The addition of tetraglyme (13 mole %) to THF causes a similar decrease (by a factor of 110) of the rate of protonation of the anthracene radical-anion. The type of dependence of k_1 and k_2 on the solvent is not altogether the same (cf. k_1 and k_2 for THF + DME and DME in Table 4). Bank and Bockrath attribute this to differences in the structure of the transition states[34].

Smid[49,55] showed that, when 1,4-dioxan (DO) is replaced by THF, the interionic interaction in the fluorenylsodium contact ion pairs is weakened. The protophilic

properties of the fluorene carbanion should then become more marked; however, measurements of the rate of reaction of fluorenylsodium with 1,2-benzofluorene [66] (Table 5) have shown that the protophilic properties of this anion become weaker. The addition of tetraglyme to THF causes the formation of separated ion pairs as for sodionaphthalene, but the rate of transfer of the proton to fluorenylsodium decreases by a factor of six, whereas in DME the formation of separated ion pairs is accompanied, as usual, by an enhancement of the protophilic properties of the carbanion.

Table 4. Rate constants (k, litre mole^{-1} s^{-1}) for the reactions of sodionaphthalene [33] (k_1) and sodioanthracene [34] (k_2) with water at 20°C.

Solvent	$10^{-4}k_1$	$10^{-4}k_2$
THF	1.06	0.66
THF + DME (50 vol.%)	0.79	0.013
DME	0.31	0.017
THF + tetraglyme	0.023	0.006

In a study of the kinetics of the isotope exchange of molecular deuterium with the adduct of an alkali metal and benzonitrile, Japanese workers [67] established that the rate of reaction increases with the radius of the cation in the adduct and on weakening of the solvating capacity of the solvent (Table 6).

Table 5. Rate constants (k, litre mole^{-1} s^{-1}) for the reactions of fluorenylsodium with 1,2-benzofluorene at 25°C. [66]

Solvent	Type of ion pair	$10^{-3}k$
DO	c.i.p.	4.2
THF	c.i.p.	3.5
THF + tetraglyme	s.i.p.	0.6
DME	s.i.p.	50

Consequently in this case the enhancement of the interionic interaction of the radical-anion with the counterion tends to increase the reactivity of the adduct (see Refs. 68–70 for other studies on these lines).

All that has been said concerning the anomalous dependence of the protophilic properties of the radical-anions and carbanions on the intensity of the interaction with the cations suggests that the cation can play a significant role in the transition state of the rate-limiting step of the proton transfer process. In particular, the observed effects can be accounted for if it is assumed [33,34,58,66] that the cation activates the bond which functions as the proton donor. An increase of the cation radius and a decrease of the solvating capacity of the solvent are accompanied by a decrease of the degree of solvation of the cation, which should entail an increase of the electrophilic properties of the latter. This leads to an acceleration of the reaction, in agreement with experimental results. The idea of an electrophilic attack by the cation on the CH bond of the substrate is not new—it was put forward and defended long ago by Morton [71]. Experimental data failed to confirm this hypothesis for reactions involving the substitution of hydrogen by a metal under the action of strong bases and it was justly criticised [72]. However, in relation to protonation reactions of radical-anions, the idea is supported by data for the kinetic isotope effect (KIE).

Table 6. Rate constants (k, ml h^{-1}) for isotope exchange between D_2 and the benzonitrile radical-anion [68].

Cation	Solvent	k	Cation	Solvent	k
Li$^+$	THF	0.1	K$^+$	DME	2.0
Na$^+$	THF	4.8	K$^+$	DG	0.58
K$^+$	THF	10.0	K$^+$	triglyme	0.32

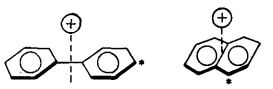
Usually, in metallation reactions involving a protophilic hydrogen substitution mechanism, the rate-limiting stage is the dissociation of CH bonds [72]. In this case a high KIE is observed [73]. For example, a KIE close to the maximum possible value $k_H/k_D = 10$ has been observed [74] for the metallation of triphenylmethane by n-butyl-lithium in ethyl ether and THF. However, in reactions of potassiobiphenyl and potassionaphthalene with triphenylmethane in DEE [58] at 25°C, the ratio $k_H/k_D \simeq 1$. A low value of KIE was also established by Bank in the reaction of sodionaphthalene ($k_H/k_D = 1.37 \pm 0.44$) [33] and sodioanthracene ($k_H/k_D = 2.02 \pm 0.68$) [34] with water in THF at 20°C. The author adopted the concept of the involvement of the counterion in the transition state of the protonation reaction and emphasised that it remains important in the interaction of the radical-anion with acids such as triphenylmethane, and water which differ greatly in acid strength.

According to Melander [73], a low KIE should be observed in reactions where the electrophilic attack by the cation precedes or takes place simultaneously with the dissociation of the CH bond. This has in fact been established [33,34,58].

The reason why the cation must be involved in the proton transfer process may be the considerable degree of delocalisation of the charge in the radical-anions of aromatic hydrocarbons [3,13]. Therefore the electron density at the reaction centre of the radical-anion is low and its protophilic properties are comparatively weak. The available literature data for KIE in metallation reactions suggest that the degree of involvement of the cation in the transition state increases with decrease of the protophilic properties of the carbanion. For example, in the metallation of triphenylmethane by organolithium compounds in THF, [75] a tendency was observed towards a decrease of the k_H/k_D ratio on decrease of the basicity of the anion (alkyl > phenyl > benzyl) of the metallating agent. According to West et al. [75], the lithium cation is involved in the transition state, the degree of its involvement increasing on passing to less basic carbanions. However, under these conditions the dissociation of the CH bond remains the rate-limiting stage of the reaction ($k_H/k_D \simeq 9-4$).

On the other hand, one cannot restrict the role of the cation to electrophilic attack alone. In our view, one cannot rule out the possibility that the change of electron

density distribution, caused by the cation, in the radical-anion in the transition state, giving an increased electron density at the reaction centre, is also important. Then, if the cation is near the reaction centre, a decrease of the degree of its solvation and the increase of electrophilicity will promote such redistribution (the dissociation of the CH bond will probably not be [will probably be?] the rate-limiting stage, as before). On the other hand, if the cation and the reaction centre are far from one another, the decrease of the degree of solvation of the cation may retard the reaction. When the location of the cation in relation to the radical-anion is symmetrical, the reaction centre (designated by an asterisk) in the biphenyl radical-anion is further away from the cation than in the naphthalene radical-anion. This difference may be the reason for the opposite influence of solvents on the reactivity of potassiobiphenyl and potassionaphthalene:



On the other hand, if one remembers that the cation can fulfill a dual function—that of an electrophilic agent in relation to the CH bond and of a polarising agent in relation to the radical-anion—it becomes evident that the dependence of the rate of reaction with the given substrate on the structure of the radical-anion, the size of the cation, and the solvating capacity of the solvent may become complicated and difficult to predict.

Thus the study of the reactions of various proton donors with radical-anions led to the formulation of many new hypotheses concerning the relation between the state in solution and the reactivity of adducts of alkali metals and aromatic hydrocarbons. Similar phenomena have been observed also for the radical-anions of aliphatic-aromatic hydrocarbons formed in the reactions of the latter with alkali metals.

III. RADICAL-ANIONS IN REACTIONS OF ALIPHATIC-AROMATIC COMPOUNDS WITH ALKALI METALS

The interaction of alkali metals with various compounds containing a CH bond in which the hydrogen atom is mobile entails [1,72] the substitution of the latter by the metal. Liquid ammonia [37,76,77], in which alkali metals readily dissolve, and other electron-donating solvents, for example THF, [78] are convenient media for reactions of this kind. The effectiveness of these solvents is due to the solvation of the alkali metal cation, which facilitates the conversion of the metal atom into an ionised form. This conclusion follows, in particular, from the studies of Scherf and Brown [79,80], who showed that the reaction of fluorene with lithium, sodium, and potassium becomes easier in a sequence corresponding to the solvating capacity of the ethers [5,62]: DME > THF ≥ DEE > DO.

It was suggested initially that the reaction has an acid–base mechanism [72] with dissociation of the CH bond and ionisation of the metal atom in a single elementary step (here and henceforth the aliphatic-aromatic compound will be denoted by AH in contrast to the purely aromatic compound Ar):

$$AH + M \rightarrow A^{-\delta}M^{+\delta} + H\cdot . \qquad (12)$$

The evolution of hydrogen, quoted by a number of workers [77-79], in the reactions of hydrocarbons with alkali metals is at first sight consistent with this view. However, later investigations [18,81,82] suggested that the reaction may be more complicated—it may proceed via a one-electron transfer stage with formation of a radical-anion $AH^{\cdot-}$:

$$AH + M \rightleftharpoons AH^{\cdot-} + M^{+} . \qquad (13)$$

The first ESR studies [83,84] already confirmed the formation of the radical-anions of aliphatic-aromatic hydrocarbons in their interaction with alkali metals in an ethereal medium. Comparatively stable (as a rule at low temperatures) radical-anions of indene [83], fluorene [83-86] and its derivatives [87-89], isomeric benzofluorenes [84,90], and 4,5-methylenephenanthrene [84,90-92] were obtained.

The mode of further reactions of the radical-anions in many ways depends on the structure of the hydrocarbon. Thus the radical-anions of arylmethanes mainly undergo the dissociation of the C–C bond with elimination of the benzene ring [81, 93-95]. The conversion of the radical-anion into a metallation product (the carbanion A^-) with dissociation of the CH bond and elimination of a hydrogen atom is possible [93-96]:

$$AH^{\cdot-} \rightarrow A^- + H^{\cdot} . \qquad (14)$$

Reaction (14) is more typical for the radical-anions of indene, fluorene, and similar compounds [82-84,97-98]. Hydrogen is evolved in a gaseous form and is consumed in the hydrogenation of the radical-anion,

$$AH^{\cdot-} + H^{\cdot} \rightarrow AH_2^- \qquad (15)$$

or of the initial hydrocarbon AH, or it remains in solution [83,84]:

$$AH + H^{\cdot} \rightarrow AH_2^{\cdot} \qquad (16)$$

and

$$AH_2^{\cdot} + AH^{\cdot-} \rightarrow AH_2^- + AH . \qquad (17)$$

When the reaction mixture contains sufficient of the initial compound AH, the latter may react with the radical-anions in accordance with Eqns. (18) and (19):[18,82-84]

$$AH^{\cdot-} + AH \rightarrow AH_2^{\cdot} + A^- , \qquad (18)$$

$$AH_2^{\cdot} + AH^{\cdot-} \rightarrow AH_2^- + AH . \qquad (19)$$

Eqns. (18) and (19) are analogous to Eqns. (1) and (2), AH playing the role of the proton donor BH in relation to its own radical-anions. The AH_2^- carbanions are usually more basic than A^- and are protonated by the initial hydrocarbon with formation of the dihydro-derivative AH_3:

$$AH_2^- + AH \rightarrow AH_3 + A^- . \qquad (20)$$

Thus the mechanism of the reaction in a system containing an aliphatic-aromatic hydrocarbon and an alkali metal is very complicated. One should note that the metal cation, the role of which in the process may be very considerable, as already demonstrated above, has been omitted from the equations.

It is usually almost impossible to obtain an unambiguous idea about the mechanism on the basis of kinetic data determined by any one method (for example from measurements of the electronic and ESR spectra and from the amount of hydrogen evolved). It is also difficult because all three modes of reaction of AH^- [reactions (14) and (15), (14)–(17), and (18)–(19)] are equivalent from the standpoint of the final result (the formation of the carbanions AH_2^- and A^-) and can be formally represented by the same overall equation for the disproportionation of two radical-anions:

$$AH^{\cdot-} + AH^{\cdot-} \rightarrow AH_2^- + A^- . \qquad (21)$$

The detection of AH_3 among the reaction products indicates the involvement of the initial AH in the reactions of the radical-anion but it is not clear in what capacity—as a hydrogen atom acceptor [Eqn.(16)] or as a proton donor [Eqn.(18)]. Nevertheless, it is important to know this also from the point of view of the characteristics of the reactivity of the radical-anion, which in the first case behaves only as an electron donor [Eqn.(17)] and in the second as a proton acceptor [Eqn.(18)]. In the determination of the activation parameters for the decomposition of $AH^{\cdot-}$, it is difficult to rule out the presence of AH, since equilibrium (13) shifts to the left with increase of temperature. However, even when the hydrocarbon AH is not present in solution, the possibility of the consumption of the radical-anion via two pathways [reactions (14) and (15)] remains. Taking this into account, we shall examine the available literature data for the effect of the metal and solvent on the course of the reaction involving the metallation of aliphatic-aromatic hydrocarbons by alkali metals.

Scherf and Brown [79] showed that the effectiveness of alkali metals in the reaction with fluorene decreases in the sequence K > Li > Na. The rate of conversion of fluorene radical-anions into carbanions, measured [83] by the ESR method in DME, decreases in the same sequence.

Since the kinetic data [79,83] characterise the overall reaction of the radical-anion [Eqns.(14)–(19)], it is difficult to derive from them a clear idea about the effect of the cation on the behaviour and reactivity of the radical-anion.

The results obtained by Tabner, who made a detailed investigation of the kinetics of the conversion of the radical-anions of fluorene [86] and its derivatives [88–90] into the corresponding carbanions, suffer from the same deficiency. The kinetic parameters were determined in a system containing the radical-anions prepared at a low temperature (−80°C) in the presence of an excess of the alkali metal. Therefore it was postulated that the free hydrocarbon is absent from the solution and reactions (16)–(19) were excluded from consideration *a priori*. Nevertheless, a certain amount of AH might have formed in the system on raising the temperature in consequence of a shift of equilibrium (13). Moreover, the rate of evolution of hydrogen was not determined and the conclusions concerning the mechanism and the role of the cation in it were reached on the basis of kinetic data obtained spectrophotometrically or by the ESR method. In view of this, a detailed analysis of Tabner's data is pointless, and we shall consider only the most important results.

Table 7 presents the free energies of activation ($\Delta G^{\neq}$, kcal mole^{-1}) for the conversion of the fluorene radical-anions into carbanions, the temperature ranges (t_1 and t_2, °C) in which the rate constants k were measured, the values of k corresponding to the extreme temperatures (k_1 and k_2), and the order of the reaction n with respect to the radical-anions.

It is difficult to infer the effect of the cation from the rate constants, since the measurements were made in different temperature ranges. Sometimes the k cannot be compared as they have different dimensions. Since the rate decreases as the temperature is reduced, it follows, judging from the value of k with the same dimensions, that the dependence of the rate of reaction in THF on the cation is represented by the following sequence: $Li^+ < Na^+ < K^+ < Cs^+$. In the case of Cs^+, the rate of reaction was so high that it could not be measured. The activation energy for the first-order reaction in THF also decreases with the radius of the cation. Tabner's results differ from the data of Scherf and Brown [79] and Bilevich et al. [83] by the position of lithium in the series of cations. Possibly this is due to the difference between the solvents and temperatures. The effect of the cation depends also on the structure of the hydrocarbon. Thus the rate of decomposition of the 1,2- and 2,3-benzofluorene radical-anions [90], obtained by the reaction with sodium, is higher than that of the radical-anions obtained by the reaction with lithium, while for 4,5-methylenephenanthrene the most stable radical-anions were in fact obtained in THF by the reaction with sodium.

Table 7. Effect of the cation and the solvent on the kinetics of the conversion of the fluorene radical-anions into carbanions [8].

Cation	Solvent	t_1,°C	t_2,°C	$k_1\cdot10^3$	$k_2\cdot10^3$	n	$\Delta G^{\neq}_{25}$
Li^+	THF	+9.4	−6.1	1.2	0.415	1	20.8
Li^+	THF	−20.2	−37.5	60.2*	21.3*	2	17.9
Na^+	THF	−30.7	−41.2	1.6	0.46	1	18.1
K^+	THF	−38.7	−53.2	25	1.8	1	14.8
Li^+	DME	−18	−43.3	25.8*	0.24*	2	16.9
Li^+	THP**	−17.8	−48.4	9.95	0.39	1	18.3
Li^+	MTHF**	−23.2	−43.4	10.1	0.66	1	18.8

*The dimensions of the constants are litre mole^{-1} s^{-1}; in the remaining cases the dimensions are s^{-1}.
**THP = tetrahydropyran; MTHF = 2-methyltetrahydrofuran.

Tabner observed that the reaction may be of first or second order with respect to the radical-anion [86] (Table 7). Analysis of the conditions under which the reaction was carried out led him to the conclusion that a first-order reaction is observed for contact ion pairs and a second-order reaction for separated ion pairs. Admittedly the type of ion pairs was not identified, but Tabner's conclusion appears likely, since a second-order reaction was observed either at low temperatures (in THF) or in solvents with a relatively high solvating capacity (DME). In addition, a second-order reaction with respect to the radical-anion was observed also for isomeric benzofluorenes [90], where an appreciable delocalisation of the charge also favours the formation of separated ion pairs.

The second-order reaction may be a consequence of the fact that the transition state of the rate-limiting stage [it is believed that this is reaction (14)] has the structure of a contact ion pair, i.e. the cation is actively involved in its formation. In relation to the free radical-anion or the radical-anion forming part of the separated ion pair, the cation behaves in this case like a kinetically independent species, which leads to a second-order reaction.

The authors believe that the role of the cation consists in the localisation of the negative charge near the carbon atom of the CH aliphatic bond [86], which is favoured by the intense interionic interaction in contact ion pairs. The necessity to localise the charge near the reaction centre is believed to be due to the fact that the structure of the transition state is closer to that of the reaction product (the anion A^-) then to the initial radical-anion [90]. In particular, this is indicated by the correlation between the acidity of the hydrocarbons and the rate of decomposition of their radical-anions (Table 8).

The decrease of the solvation energy of the cation, tending to increase its electrophilicity, should probably enhance the localisation of the charge by the cation.

Possibly this is one of the reasons for the acceleration of the decomposition of the radical-anion with increase of the radius of the cation, since the greater its radius the lower the degree of its solvation. We may note that, on passing from diglyme to dioxan, the degree of solvation of the cation falls and the rate of evolution of hydrogen in the reaction of cyclopentadiene with potassium rises [97].

Table 8. The acidity of the hydrocarbons (pK) [99] and the relative rate constants (lg k_{rel}) for the decomposition of their radical-anions (Li^+ cation) in THF at 25 °C. [90]

Hydrocarbon	pK	lg k_{rel}
1,2-Benzofluorene	20.0	0.91
4,5-Methylenephenanthrene	22.6	0.51
Fluorene	22.9	0.00
2,3-Benzofluorene	23.2	—1.67

Nevertheless, it would be premature to assume that there is a fully unambiguous relation between the type of ion pairs and the effect of the cation in the conversion of the radical-anions of aliphatic-aromatic hydrocarbons into carbanions. There are facts which are difficult to account for within the framework of the above hypothesis concerning the structure of the transition states; these include, in particular, data [86,89,90] indicating a dependence of the activation parameters for the reaction on the cation and on the solvent. Possibly this difficulty will be overcome after more detailed studies of the decomposition of the radical-anion.

The increased probability of decomposition of the radical-anion involving dissociation of the CH bond via reaction (14) with increase of the acidity of the hydrocarbon was noted not only by Tabner [86] but also by other workers. Bosch and Brown [82] established that, when indene is metallated by potassium and lithium in DME at 85 °C, a much greater amount of hydrogen is evolved than in the metallation of a less acid hydrocarbon—fluorene (50–60% and 2–14% of theoretical respectively). It has also been noted [83] that the fluorene radical-anion is more stable than the indene radical-anion. On the other hand, it is evident that an increase of acidity tends to accelerate the protonation of the radical-anion [reaction (18)], which competes with reaction (14). Since the kinetics of both processes depend in a complex manner on the cation, the solvent, and the structure of the radical-anion, it follows that the relative contributions of reactions (18) and (14) can vary in different ways depending on the specific experimental conditions. This is confirmed by measurements [98] of the rate of metallation of the same hydrocarbons by potassium in THF at 25 °C (Table 9).

Probably not only the acidity of the hydrocarbon but also its structure as a whole has a significant influence. It has been suggested [84] that, for a fairly high degree of delocalisation of the unpaired electron (for example in the ring fragment of the naphthyl or phenanthryl ion), the radical-anions of fairly acid hydrocarbons can also be stable. For example, the radical-anion of 4,5-methylenephenanthrene [92] (pK = 22.6) is stable at room temperature.

In conclusion of this section, we shall mention yet another reaction which may occur in a system containing an aliphatic-aromatic hydrocarbon and an alkali metal. In the presence of an excess of the latter, the anions A^- may, like those of aromatic hydrocarbons, combine with a further electron and give rise to radical-dianions (r.d.a.):

$$A^- + M \rightarrow A^{=} + M^+ . \qquad (22)$$

One of the first radical-dianions of this kind was detected in the reaction of cycloheptatriene with potassium in RHF. [100,101] However, radical-dianions were in fact obtained even earlier. Thus it has been noted [80] that the reaction of a second equivalent of potassium with fluorenylpotassium proceeds without the evolution of hydrogen. The authors could not account for this phenomenon, since they assumed that the second hydrogen atom in the 9-position must be substituted by the metal. It was not until later that Janzen and Gerlock [84] showed with the aid of ESR that the addition of a second potassium atom with formation of a radical-dianion takes place under these conditions and not substitution. Syrkin and coworkers [102] observed the formation of radical dianions in the polarographic reduction of aromatic compounds in DMF. So far, the radical-dianions of fluorene [84,103], 9-phenylfluorene [87,103,104], benzofluorenes [87,103], and diphenylmethane [95] have been identified by ESR; the ESR spectra of 4,5-methylenephenanthrene have been investigated in greatest detail [84,92,103–105].

Table 9. The acidity of the hydrocarbons (pK) [66] and the rate constants (k, s^{-1}) for the evolution of hydrogen in the course of their metallation by potassium in THF at 25 °C. [98]

Hydrocarbon	pK	$k \cdot 10^8$
Cyclopentadiene	15—17	1.0
Indene	21	1.5
Fluorene	25	1.9

Usually radical-dianions are formed readily when hydrocarbons are metallated by potassium and the reaction can proceed even in the melt in the absence of a solvent [95]. With sodium, it is not always possible to obtain radical-dianions even for hydrocarbons with an extensive π-conjugation system, such as benzofluorenes. From the standpoint of reactivity, the radical-dianions have been hardly investigated; it has only been stated that they may be protonated by the solvent (DME). [92] There is no doubt that the study of the chemical behaviour of these species, which combine properties of a radical-anion and a dianion, can yield very interesting and useful results.

IV. DIANIONS AS METALLATING AGENTS

The dianions of aromatic hydrocarbons are stronger bases than the radical-anions. For example, the metallation of triphenylmethane by the dianions of naphthalene [106], biphenyl [107], and anthracene [57] is faster by several powers of ten than the metallation by radical-anions under the same conditions. The high reactivity of the dianions is to some extent an obstacle to its quantitative investigation. The protophilic properties of the dianions are so marked that they are protonated by the solvent and not only by fairly acid solvents such as ammonia [108] but also by much

weaker proton donors—ethers. Thus dilithionaphthalene cannot be obtained in an ethereal medium without admixture with an organic derivative of the alkali metal the absorption spectrum of which resembles that of the dihydronaphthalene carbanion [5,109,110]. It has been shown [106,111] that the diphenyl and anthracene dianions, obtained by the reduction of the corresponding radical-anions with potassium or lithium in DME and DEE, are converted after a time, in a solution free from acid impurities, into carbanions the spectroscopic properties of which resemble the carbanions of dihydro-derivatives.

It has recently been shown [112] that the protonation of the dianions by the solvent is the reason for the earlier observation [57] of the conversion of the naphthalene radical-anions into the carbanions of the above type in the presence of an excess of the alkali metal. This process is faster the lower the ionisation potential of the metal and the higher the solvation capacity of the solvent. In other words, this reaction is promoted by the same factors as those favouring the formation of the dianions [5]. Szwarc and coworkers showed that the protonation of the diphenylacetylene [113] and methylphenylacetylene [31] dianions in THF causes in the course of time a shift of the equilibrium in the reaction of these hydrocarbons with sodionaphthalene or sodiobiphenyl. A slow protonation of the naphthalene dianions by ethers (DO and THF) has been reported [28].

The low stability of solutions of the dianions hinders the study of the effect of the cation and the solvent on the reactivity of the dianions. One-electron transitions, which are more likely than in the case of radical-anions, give rise to an additional complication. For example, the interaction of the anthracene dianion with 2-methylnaphthalene leads to the formation of the carbanion of the latter. However, the naphthalene and biphenyl dianions convert 2-methylnaphthalene into radical-anions, while metallation does not take place [106].

Table 10. Rate constants (k, s^{-1}) for the reaction of diphenylmethane with anthracene dianions and the positions of the maxima (λ_{max}, nm) in the spectra of the dianions [106].

Cation	Solvent	k	λ_{max}
Li^+	DEE	$\gg 10^{-7}$	565
Na^+	DEE	$\sim 10^{-7}$	590
K^+	DEE	$2 \cdot 10^{-3}$	615
Na^+	DME	$1 \cdot 10^{-4}$	600
K^+	DME	$>10^{-3}$	615

The effects of the cation and the solvent on the reactivity of the dianion obey the usual relations governing the protophilic substitution of hydrogen, i.e. the reaction rate increases as the interaction between the dianions and the counterions is weakened. For example, the rate of reaction of the naphthalene dianion with diphenylmethane in THF ($k \simeq 10^{-2}$ s^{-1}) is much higher than in DEE ($k = 6 \times 10^{-4}$ s^{-1}), [106] where the lithium cation is less solvated. The interaction of the anthracene dianion with the cation becomes weaker with increase of the radius of the latter in the series $K^+ > Na^+ > Li^+$ or when the solvating capacity of the solvent is impaired (DME > DEE), as shown by the bathochromic shift of the absorption band in the spectrum of the anthracene dianion [111]. The rate of reaction of the anthracene dianion with diphenylmethane also increases in the same direction [106] (Table 10).

Apparently the protophilic properties of the dianion are fairly marked and there is no need for the activation of the metallated linkage by the cation or for the increase of the electron density at the dianion reaction centre in the transition state, as suggested for radical-anions. In this connection, it is interesting to note that a high KIE ($k_H/k_D \simeq 10$) [35] has been found for the reaction of the perylene dianion with alcohol in THF, as for metallation by lithium alkyls [74,75].

On the other hand, the problem of the effect of the cation on the reactivity of the dianion cannot be regarded as finely elucidated. According to the date of Ichikawa and Tamaru [114], the rate of isotope exchange of D_2 with anthracene dianions (it is assumed that the exchange involves an acid–base mechanism) increases when Li^+ and Na^+ cations are replaced by cations with a larger radius, in agreement with results [106] obtained in a study of metallation reactions. On the other hand, the adsorption of hydrogen in solutions of the dianions, leading to the formation of the carbanions of dihydroanthracene and the alkali metal hydride [70], is faster for cations with small radii [114].

V. CARBANIONS OF DIHYDRO-DERIVATIVES OF AROMATIC HYDROCARBONS AS METALLATING AGENTS

On reaction with proton donors, the radical-anions and dianions of aromatic hydrocarbons are converted into the carbanions of the dihydro-derivatives [mechanisms (1), (2), and (4)]. Until recently, special attention was not paid to the behaviour of these carbanions in the metallation or Birch reduction reactions and yet the final result of the process depends on them in many ways. For example, it has been shown [108] that, in the reductive alkylation of biphenyl in liquid ammonia, the species involved in the reaction with methyl bromide is not the biphenyl dianion formed in the first stage but its protonation product—the carbanion of dihydrobiphenyl.

In DME and DEE, the carbanions of dihydrobiphenyl are less protophilic than the biphenyl radical-anions, whereas in diglyme as a solvent, which has a higher solvating capacity, the opposite relation between their reactivities is obtained [106]. Therefore the metallation of triphenylmethane and 9-phenylxanthene in DME or DEE is complicated by the accumulation of dihydrobiphenyl carbanions in solution. In particular, the metallation of 9-phenylxanthene by sodiobiphenyl in DEE is on the whole slower for this reason than in diglyme, despite the fact that the rate of reaction of the biphenyl radical-anion with this substance in DEE is much higher than in diglyme (Table 11).

In general, in solvents with a comparatively low solvating capacity the rate of metallation directly by the radical-anion or dianion of biphenyl is ultimately determined by the reactivity of the dihydrobiphenyl carbanions [58,106,107]. At the same time, in all the instances where the reactions of aliphatic-aromatic compounds with the carbanions of dihydronaphthalene and dihydroanthracene were investigated, the reactions are faster than those with the corresponding radical-anions but slower than with the dianions [57,106]. Thus smaller rate constants have been obtained for the metallation of diphenylmethane by dihydronaphthalene carbanions [106] (with Li^+ cations), $k = 2.3 \times 10^{-5}$ s^{-1} in THF and 2.5×10^{-4} s^{-1} in DEE, than for the

naphthalene dianions (9.5×10^{-3} and 6×10^{-4} s^{-1} respectively). The higher reactivity of the dihydroanthracene carbanion compared with the anthracene radical-anion in protonation by water has also been noted [34]. It was explained by the fact that the electron density in the 9-position of the radical-anion is smaller by a factor of two than in the carbanions. Deuterium exchange with dihydroanthracene carbanions [114] is slower than with anthracene dianions, which also indicates more marked protophilic properties of the latter. As far as one can judge from the data in Table 11, an increase of the degree of solvation of the cation tends to increase the protophilic properties of the carbanions of the dihydro-derivatives.

Table 11. Rate constants for the metallation (litre $mole^{-1}$ s^{-1}) of triphenylmethane and 9-phenylxanthene by biphenyl radical-anions (k_1) and dihydrobiphenyl carbanions (k_2). [106]

Hydrocarbon	Cation	Solvent	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$
Triphenylmethane	K^+	DG	55	>1000
"	K^+	DME	25	11
"	K^+	DEE	10	5
9-Phenylxanthene	Na^+	DG	16	>1000
"	Na^+	DEE	200	11

As already stated (Section I), the position of equilibrium in the reactions of such carbanions with aliphatic-aromatic compounds is determined primarily by the strength of the CH acids involved in them. Dihydrobiphenyl and dihydronaphthalene are apparently very weak CH acids ($pK > 33$), while the equilibrium acidity of dihydroanthracene, determined in cyclohexylamine [115] by the transmetallation method, is somewhat higher than that of triphenylmethane [116] (the respective pK values are 30.4 and 31.5).

Table 12. Equilibrium constants for the reactions of dihydroanthracene carbanions with triphenylmethane at 25°C. [115]

Cation	Solvent				
	DG	DME	DEE	DE*	CHA*
Li^+	2.3	2.8	44	125	—
Na^+	—	3.0	17	—	—
K^+	3.0	4.8	17	30	12
Cs^+	5.1	11	11	—	12

*DE = diethyl ether; CHA = cyclohexylamine.

Therefore the reactions of the anthracene radical-anions or dianions with triphenylmethane [57,106] do not go to completion and equilibrium is established in the last stage. Its position depends significantly on the cation and solvent [115] (Table 12). The observed effects have been explained by the unequal changes in the energy of the interaction of dihydroanthracene and triphenylmethane carbanions when the reaction conditions are varied, in particular by a difference in the type of ion pairs in many instances.

It is noteworthy that the elucidation of the factors governing the influence of the structure of the ion pairs of organic derivatives of alkali metals on the position of the acid–base equilibrium of the transmetallation reaction is important for the problem of estimating the strength of CH acids by the above procedure [115,117–120].

VI. COMPARISON OF THE PROTOPHILIC PROPERTIES OF METALLATING AGENTS

The combined data for the reactivities of the above three types of metallating agents lead to the conclusion that the dianions are the most protophilic among them. The carbanions of the dihydro-derivatives are less reactive. The naphthalene and anthracene radical-anions are less protophilic than the carbanions, while the biphenyl radical-anions can be more protophilic than the carbanions of dihydrobiphenyl under conditions where the degree of solvation of the cation is comparatively low. The relative reactivities of the dianions, radical-anions, and the carbanions of dihydro-derivatives established in the metallation reactions are consistent with quantum-chemical predictions, in particular with calculations by the Pariser–Parr–Pople (PPP) method of the proton localisation energies [106] (Table 13).

Table 13. Protonation localisation energies for the dianions (L_1) and radical-anions (L_2) of aromatic hydrocarbons and the carbanions of their dihydro-derivatives (L_3) (in eV). [106]

Hydrocarbon	L_1	L_2	L_3
Biphenyl	0.34	—4.6	—5.1
Naphthalene	1.4	—5.2	—4.2
Anthracene	0.3	—5.4	—4.5

The protonation of the dianions entails an energy gain by the π-electron system, while the protonation of the radical-anions and the carbanions of the dihydro-derivatives is accompanied by a decrease of the π-conjugation energy. This implies that the dianions must be more protophilic than the other two types of agents, as in fact has been observed experimentally. Also in agreement with experiment, theory predicts a higher reactivity of the dihydronaphthalene and dihydroanthracene carbanions than that of the corresponding radical-anions ($L_3 > L_2$). On the other hand, according to theory, the protophilic properties of the biphenyl radical-anions should be more marked than those of the dihydro-biphenyl carbanions ($L_3 < L_2$). The opposite relation between the protophilic properties of the above two species observed in many cases is due to the effects of the medium and the counterions, which are so far difficult to take into account quantitatively in quantum-chemical calculations.

The absence of a correlation between the rate constant k for the protonation by water of the radical-anions of aromatic hydrocarbons and the localisation energies ($L_{r.a.}$) calculated for the protonation of the radical-anions by the simple Hückel method (Table 14) has been noted [30]. It is assumed that $L_{r.a.} = L + m_{m+1}$, where L is the localisation energy for the hydrocarbon and m_{m+1} the energy of

the lowest non-bonding hydrocarbon orbital in β units. For example, the rate of reaction falls on passing from the biphenyl to the anthracene radical-anion, despite the decrease of $L_{r.a.}$. At the same time, the authors noted a satisfactory agreement between the values of k and $L + 2m_{m+1}$ (or, what amounts to the same thing, between k and the sum $L_{r.a.} + m_{m+1}$). In their view, this is evidence that charge transfer from the radical-anion to the proton-donor molecule plays an important role in the mechanism of the protonation of the radical-anions (m_{m+1} characterises the electron affinity of the hydrocarbon and hence also the ionisation potential of the radical-anion).

Table 14. Rate constants for the protonation by water (k, litre mole^{-1} s^{-1}) of the radical-anions of aromatic-hydrocarbons and the localisation energies L calculated by the simple LCAO-MO method [30].

Hydrocarbon	$k \cdot 10^3$	L	$-m_{m+1}$	$L_{r.a}$	$L+2m_{m+1}$
Biphenyl	18	2.447	0.705	1.742	1.037
Naphthalene	4.6	2.299	0.618	1.681	1.063
Phenanthrene	1.0	2.299	0.605	1.694	1.089
Anthracene	0.2	2.015	0.414	1.599	1.185
1,2-Benzanthracene	0.055	2.049	0.452	1.597	1.145
Pyrene	0.012	2.190	0.445	1.745	1.300

Moreover, calculation by the more sophisticated PPP method yields values of $L_{r.a.}$ (Terekhova et al.[106]), the variation of which in the series of hydrocarbons (L_2 in Table 13) is consistent with the variation of the rates of the metallation (Tables 1 and 2) and protonation (Tables 4 and 14) [30,57,58] reactions. We may also note that the sum $L + 2m_{m+1}$ essentially defines the localisation energy for the protonation of the dianions (in terms of Hückel's approximation), the protophilic properties of which decrease in the same direction as in the radical-anions judging from the available qualitative data [106].

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The data presented in this review reveal certain characteristics of the metallation reactions involving the radical-anions and dianions of aromatic hydrocarbons. Metallation by radical-anions includes, together with their protonation, an electron transfer stage. The dianions react with proton donors as diacidic bases. However, in consequence of the high reduction potential of the dianions, there is a possibility of a side reaction involving electron transfer to the proton donor. The products of the protonation of the radical-anions and dianions (the carbanions of the dihydro-derivatives) are also highly reactive metallating agents. In the course of studies on metallation by radical-anions, an unusual feature was observed—an increase of their reactivity (protophilic properties) in the case of a strong interaction with the counterion. The details of the structure of the reactants, which determine the structure or the activated complex incorporating the cation, play an important role under these conditions.

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