Review Article

Two-Electron Transfers. Are they Simultaneous?[†]

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Equilibria and rates of electron transfer reactions involving anions as the electron donors are affected by the nature of counter-ions and solvents as exemplified by the work of Ramme *et al.* [*Proc. R. Soc. A 327* (1972) 467]. The striking effect of counter-ions upon the electron-transfer equilibria is demonstrated by the systems shown in eqn (i) and the mechanism of these effects is discussed.

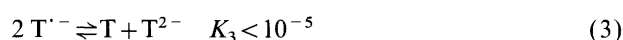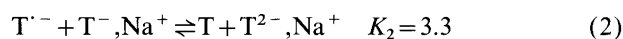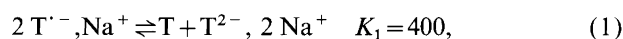$$2\,(A^-,Cat^+) \rightleftharpoons A + (A^{2-},\,2\,Cat^+) \tag{i}$$

The formation and nature of the negative alkali-metal ions is outlined. The negative alkali ions act as two-electron donors yielding under suitable conditions dianions. The problem of 'simultaneity' of such two-electron transfers is elaborated. The interaction of K^- with styrene leading to formation of a dianion demonstrates that the time interval between the transfers of the two electrons of K^- to styrene is shorter than 10^{-8} s (duration of encounters in liquids). The contemplated experiments involving acyl peroxide may provide evidence for even shorter interval between the two transfers.

The rates and equilibria of electron transfers involving anions as the donors are affected by the nature of cations and solvents. For example, we found the rate constant of electron transfer from the sodium salt of biphenyl radical-anion, Na^+, $B^{\cdot-}$ to pyrene π, i.e., Na^+, $B^{\cdot-} + \pi \rightarrow B + Na^+$, $\pi^{\cdot-}$ to be 0.6×10^{10} M^{-1} s^{-1} in THF at ambient temperature, whereas under the same conditions the rate is six times faster when the free anion is the donor.[1] The kinetics of this transfer were investigated by a flash photolytic technique, and in the course of these studies we succeeded in determining the rate of collapse of the electron–sodium cation pair into sodium atom,[2] i.e., Na^+, $e^- \rightarrow Na^0$, to be 4×10^3 s^{-1}.

Disproportionation of radical anions. The effects of counter-ions and solvents on the equilibria and rates of the disproportionation of radical-anions, i.e., 2 radical anions $\rightleftharpoons$ dianion + parent molecule, are astonishing. The equilibrium constant of the disproportionation of radical anions derived from the same electron acceptor may vary from as low as 10^{-5}, or even less, to as high as 10^6, depending on the nature of the cation and solvent.

Three equilibria are involved in the disproportionation. Taking tetraphenylethylene, T, as an example the follow-

ing data have been reported[3] for THF solutions of this donor at 20 °C [eqns. (1)–(3)].

$$2\,T^{\cdot-},Na^+ \rightleftharpoons T + T^{2-},\,2\,Na^+ \quad K_1 = 400, \tag{1}$$

$$T^{\cdot-} + T^{\cdot-},Na^+ \rightleftharpoons T + T^{2-},Na^+ \quad K_2 = 3.3 \tag{2}$$

$$2\,T^{\cdot-} \rightleftharpoons T + T^{2-} \quad K_3 < 10^{-5} \tag{3}$$

The kinetics of the above disproportionation were investigated, again by flash-photolytis.[4] A flash of light ($\lambda > 300$ nm) ejects electrons from the irradiated radical-anions and dianions. In systems rich in the parent hydrocarbons the electrons ejected from the dianions are captured mainly by the neutral species. Thus the concentration of radical anions increases and that of the dianions decreases after the flash. In systems rich in radical-anions the electron ejected from the radical-anions are captured by other radical-anions increasing therefore the concentration of the dianions and decreasing that of the radical-anions. In either case the equilibrium is upset and the system returns to its equilibrium state during the dark period following the flash. Let it be mentioned that the extent of the photo-bleaching *is* affected by the nature of solvent and counter-ion. For example, dioxane solutions of K^+ or Cs^+ salts of tetracene radical-anions are not bleached by a flash that strongly bleaches a solution of its Li^+ and Na^+ salts. Apparently the former aggregates are too tight and the ejected electron cannot escape from the Coulombic field of the cation.

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In the tetraphenylethylene system the return of the flash-irradiated solution to its equilibrium is relatively slow (few seconds), simplifying therefore its kinetic studies because the dissociative–associative equilibrium between the free ions and their aggregates is maintained in the course of this reaction. The results demonstrate that the reaction of eqn. (2) ($k_2 = 10^7$ M^{-1} s^{-1}) accounts for the observed rate. The step of eqn. (3) is too slow to be observed, presumably due to the Coulombic repulsion between the colliding free radical-anions, while the exceedingly low concentration of the free T^{2-} dianions renders the reverse step also to be slow. Eqn. (1) is again too slow to be observed, most probably because it demands transfer of Na$^+$ cation and not only electron transfer.

The relatively high value of the disproportionation constant of the salts of T$^{\cdot-}$ radical ions is attributed to its non-planar structure modified in the disproportionation, whereas the disproportionation constant of planar aromatic radical-anions, studied polarographically or potentiometrically by several research groups,[5] is reported to be very low. However, the above techniques measure the undoubtedly low disproportionation value of the free ions (A$^-$). Disproportionation of the Li$^+$, Na$^+$, K$^+$, and Cs$^+$ salts of the planar tetracene radical-anions has been investigated in several solvents[6] and the respective equilibrium constants are reported to vary from 6×10^{-9} to 16, depending on the nature of the cation and the solvent (see Table 1). The question arises, therefore, how these factors affect the equilibrium and the rate of disproportionation.

A model shown in Fig. 1 accounts for the observed variations. The naively calculated Coulombic interaction of the cations and anions of two radical-anion–cation pairs amounts to $2e^2/r$, but it increases to $4e^2/r$ on disproportionation due to the double charge of the dianion, favoring thus the formation of the latter. The solvation of the cations is more extensive in the radical-
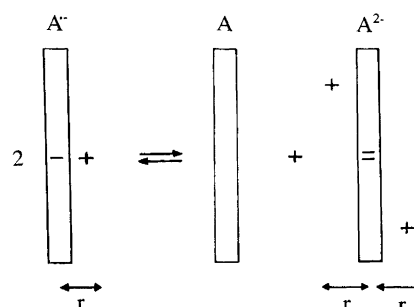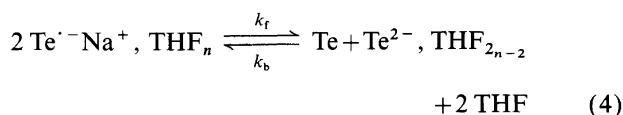

Fig. 1. Naive representation of the disproportionation equilibrium.

ions than in the dianions because the cations are less strongly bonded to the singly charged radical-anions than to doubly charged dianions. Hence, desolvation may take place in the course of the disproportionation, decreasing the r values of the dianion clusters. In other words, the conversion of the loose ion-pairs of radical-anions into the tight aggregates of the dianions favors the disproportionation on both accounts: decrease in energy and increase in entropy.

The following example illustrates this effect. The small Li$^+$ and Na$^+$ cations are strongly solvated by THF, both forming loose ion-pairs when associated with tetracene radical ions. The Li$^+$ interaction with THF seems to be sufficiently strong to permit its solvation even in the dianion aggregates. The respective disproportionation constant is therefore low ($K_{\text{disp}} = 5.8 \times 10^{-9}$ at 25 °C, see Ref. 6). However, the relatively weaker solvation of Na$^+$ seems to lead to its desolvation in the dianion aggregates, increasing therefore the disproportionation constant by decreasing r. Thus, $K_{\text{disp}} = 1 \times 10^{-5}$ for the sodium salt, i.e. is ca. 10^5 times larger than that of the Li$^+$ salt. Similar reasoning explains the other data collected in Table 1.

The participation of solvent in the disproportionation is revealed directly by the disproportionation of Na$^+$ tetracene radical-anions in benzene solution.[7] This salt is insoluble in pure benzene but becomes soluble on addition of small amounts of THF. log{[Te][Te^{2-}, 2 Na$^+$]/[Te$^{\cdot-}$, Na$^+$]^2}, determined photometrically, is proportional to log[THF], the proportionality constant 2 indicating that eqn. (4) is operative.

$$2\,\text{Te}^{\cdot-}\text{Na}^+, \text{THF}_n \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{Te} + \text{Te}^{2-}, \text{THF}_{2n-2}$$

$$+ 2\,\text{THF} \qquad (4)$$

Although the value of n is unknown, this finding shows that one THF molecule solvating the cation of the Te$^-$ radical ion-pair is desolvated in the course of the disproportionation. The kinetics of this reaction reveal that k_f decreases with increasing [THF] whereas k_b is unaffected by the THF concentration, indicating that only the desolvated radical anions disproportionate.

Finally, it is interesting to report the disproportionation of the barium salt of tetracene radical-anions[8]

Table 1. Disproportionation of tetracene, Te, radical-anions at 25 °C.

$$2\,\text{Te}^-,\text{Ca}^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{Te} + \text{Te}^{2-},2\,\text{Cat}^+, \; K$$
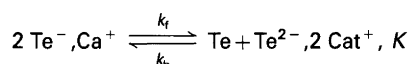
Solvent[a]	Cation	K	k_f/Ms	k_b/Ms
THF	Li$^+$	5.8×10^{-9}	3.6×10	6.3×10^9
THF	Na$^+$	1.0×10^{-5}	5.5×10^4	5.5×10^9
THF	K$^+$	4.6×10^{-6}	3.0×10^4	6.5×10^9
THF	Cs$^+$	3.2×10^{-6}	2.5×10^4	7.8×10^9
DOX	Li$^+$	6.6×10^{-2}	6.0×10^6	1.1×10^8
DOX	Na$^+$	6.5×10^{-2}	2.0×10^7	3.1×10^8
DOX	K$^+$	1.1×10^{-2}	No bleaching by flash	
DOX	Cs$^+$	0.6×10^{-2}	No bleaching by flash	
DEE	Li$^+$	2.7×10^1	7.0×10^7	2.6×10^6
DEE	Na$^+$	1.2×10^{-1}	2.4×10^8	2.0×10^9
Benzene	Ba^{2+}	ca. 10^6		

[a] THF, tetrahydrofuran; DOX, dioxane; DEE, diethyl ether.

in THF. The photometrically determined ratio [dianion][Te]/[radical anion]^2 is independent of dilution implying a large degree of dissociation of the salt Ba^{2+}, $(Te^{\cdot -})_2$ into Ba^{2+}, $Te^{\cdot -}$ and $Te^{\cdot -}$. Thus, the disproportionation equilibrium is represented by eqn. (5).

$$Ba^{2+},Te^{\cdot -} + Te^{\cdot -} \rightleftharpoons Ba^{2+},Te^{2-} + Te \tag{5}$$
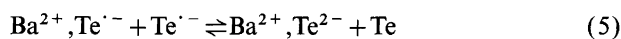
Kinetic studies of this disproportionation performed in the presence of excess of Te (the disproportionation constant is ca. 10^6) reveal a fast reaction consuming approximately half of the formed radical-anions followed by a slow reaction completing the process. Since no intermediates are observed in the spectrum of the reacting solution it is proposed that two aggregates are formed: $Te^{\cdot -}$, Ba^{2+}, $Te^{\cdot -}$ and Ba^{2+}, $Te^{\cdot -}$, $Te^{\cdot -}$. The latter aggregate is converted rapidly into dianion, whereas the slow dissociation of the former aggregate is the rate-determining step leading to completion of the conversion of the photo-formed radical anions into dianions.

Alkali anions and their reactions. In none of the previously discussed reactions was any two-electron process observed. However, two-electron transfer might take place in reactions involving alkali-metal anions, e.g., K^-, as the electron donors with suitable electron acceptors.
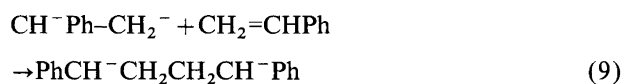
The existence of negative alkali-metal ions was first postulated by Fogel and his colleagues[9] to account for some lines observed in the spectra of nebulae. Indeed, it is plausible to expect the existence of anions resulting from the addition of an electron to the outer half-empty s orbital of an alkali-metal atom. Subsequently, Golden and his colleagues[10] proposed that the diamagnetic blue species formed in solutions of alkali metals in ethereal solvents (e.g., THF or DME) or in methylamine are the negative alkali-metal ions. This designation was confirmed by further studies, especially those of Dye and coworkers.[11] Research on alkali anions gained in reliability when more concentrated and relatively stable solutions of these species were prepared by addition of crown ethers or cryptates to the previously used solvents.[12] The stabilising effect of these agents is caused by their strong coordination with alkali-metal cations neutralizing the negative charge of alkali-metal anions.

Two conceptually feasible and clearly distinct modes of two-electron transfer may be visualized. For example, reaction of potassium anion, K^-, with a suitable electron acceptor A could lead to: (a) transfer of the two outer electrons of the K^- anion to A in the course of a single encounter eqn. (6) or alternatively (b) the formation of radical-anion, $A^{\cdot -}$, i.e., to one-electron transfer, and a neutral potassium atom K^0 [eqn. (7)]. The resulting species could diffuse out of the encounter cage, and the K^0 atoms would reduce then other A molecules, whether directly or after self-dissociation into K^+ and solvated electron.

$$K^- + A \rightarrow K^+ + A^{2-} \tag{6}$$

$$K^- + A \rightarrow K^0 + A^{\cdot -} \tag{7}$$

Reduction of styrene by K^- anions[13] allowed differentiation between these two alternatives. Addition of a slight excess of styrene to a solution of K^- in THF containing the required amount of crown ether,* followed by the addition of methanol 10 min later, led to the formation of ethylbenzene (in ca. 50% yield) and a mixture of 1,4-diphenylbutane (ca. 20%) and 1,3-diphenylbutane (ca. 30%) with a small amount of higher styrene oligomers.

Eqn. (8) accounts for these results. A single encounter between K^- and a styrene molecule leads to the formation of the dianion, which is rapidly protonated by THF, to yield CH_3CH^-Ph carbanion. The latter is eventually protonated by the added methanol and thus yields ethylbenzene. In fact, two reagents compete for the dianions: THF protonating it and the available excess of styrene reacting with the dianion according eqn. (9).

$$K^- + CH_2 = CHPh \rightarrow K^+, CH_2^- - CH^- Ph \tag{8}$$

$$CH^- Ph - CH_2^- + CH_2 = CHPh$$
$$\rightarrow PhCH^- CH_2 CH_2 CH^- Ph \tag{9}$$

Protonation of the latter by methanol yields the reported 1,4-diphenylbutane. On the other hand, the protonation by methanol of $CH_3CHPhCH_2CH^-Ph$, resulting from the well known reaction of the CH_3CH^-Ph carbanion with styrene, accounts for the formation of the 1,3-diphenylbutane.

It may be remarked that the distribution of the negative charge in the dianion makes the CH_2^- group highly basic and therefore liable to rapid protonation even by an acid as weak as THF, whereas the delocalization of charge into the benzene ring prevents the protonation of the $-CH^-Ph$ carbanion by THF. Indeed, quantum mechanical calculations,[15] using the HyperChem computer program, assign a charge density of -0.663 to the α carbon of the dianion, but only -0.207 to its β carbon.

Results of experiments in which CH_3OD was used instead of methanol support the proposed scheme.[15] The resulting ethylbenzene was found to be deuteriated in the benzylic group (CH_3CHDPh), and the 1,3-diphenylbutane was monodeuterated $[CH_3CH(Ph)-CH_2CHDPh]$, whereas the 1,4-diphenylbutane was dideuteriated $[CHD(Ph)CH_2CH_2CHDPh]$.

One could argue that one-electron transfer from K^- to styrene led to its radical-anion which diffused out from its encounter cage. Dimerization of the resulting styrene radical-anions would then lead to the formation of 1,4-diphenylbutane. Although this mode of formation of 1,4-diphenylbutane cannot be refuted, it seems unlikely.

In conclusion, the transfer of both electrons from K^- to styrene in the course of a single encounter is demonstrated. In other words, both electrons are transferred in

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* The crown ether concentration determines the concentration of K^-. Their proportion is 1:1 since each K^+ cation neutralizing K^- anion is coordinated with one crown ether molecule.

a time shorter than 10^{-8} s (duration of an encounter collision). Could we limit further the duration period of this event?

The following experiment is contemplated. Addition of a solution of diacetyl peroxide to a K^- solution should lead to electron transfer as depicted in eqn. (10).

$$K^- + CH_3COO\text{-}OCOCH_3 \longrightarrow CH_3CO_2{}^-K^0, CH_3C\overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}} \cdot$$

$$(10)$$
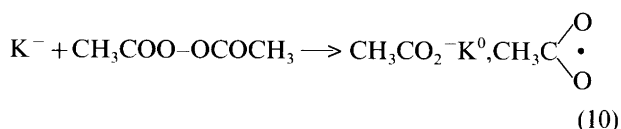
As has been shown elsewhere,[14] the CH_3–CO_2 bond-dissociation energy of the acetate radical is negative $(-17$ kcal mol$^{-1})$. A vibration converts in less than 10^{-12} s the bent CO_2 moiety into a linear CO_2 molecule simultaneously with ejection of CH_3 radical. Provided that the second electron is transferred in a still shorter time, two acetate anions would be the products of the reaction. Otherwise, the second electron would be transferred to the resulting methyl radical and the protonation of thus formed $CH_3{}^-$ anion would lead to methane. Hopefully, the results of this experiment will be available shortly.

The reaction of potassium anion with peroxide derived from phenylacetic acid, i.e., $PhCH_2C(O)O\text{-}OCOCH_2Ph$, would be even more significant. This peroxide was synthesized by Bartlett and Leffler[16] who investigated the kinetics of its decomposition indicating a simultaneous rupture of two or more bonds. Transfer of the first electron should yield $PhCH_2CO_2{}^-$ anion and, presumably, the fragments benzyl radical and CO_2. Had the second electron been transferred simultaneously with the first one, another $PhCH_2CO_2{}^-$ anion would be formed. Otherwise, toluene, resulting from protonation of benzyl carbanion would be produced. The absence of toluene

in the products would indicate, therefore, a nearly simultaneous transfer of both electrons from K^- anion to the above peroxide.

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