

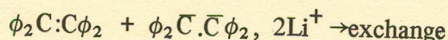
## DOES A SIMULTANEOUS TWO-ELECTRON TRANSFER OCCUR IN THE SYSTEM TETRAPHENYLETHYLENE AND ITS DIANION

Mahboob Mohammad

*Electrochemistry Group, Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan*

(Received March 1, 1982; revised August 16, 1982)

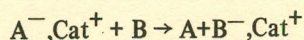
The  $^{13}\text{C}$  NMR spectrum of tetraphenylethylene ( $\phi_2\text{C}:\text{C}\phi_2$ ), of its dilithium salt ( $\phi_2\text{C}:\text{C}\phi_2 \cdot 2\text{Li}^+$ ), and of their mixtures in  $\text{C}_6\text{D}_6$  were recorded. The spectra of the mixture consist of two sets of the hydrocarbon and the lithium salt lines each. This demonstrates that the exchange.



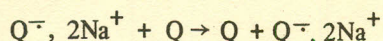
is very slow, even on NMR scale, and its bimolecular rate constant has, therefore, to be smaller than  $100\text{M}^{-1}\text{sec}^{-1}$

### INTRODUCTION

One-electron transfer processes involving organic or inorganic substrates have been extensively investigated [1,2]. When a process involves ionic aggregates the electron transfer is accompanied by a counter-ion transfer, e.g.,

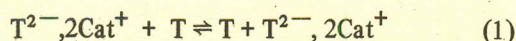


and at least one example is known [3] where the transfer of electron is associated with a transfer of two counter-ions, namely,

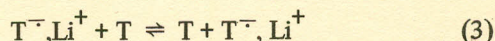
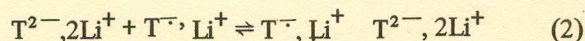


Where Q denotes duroquinone. Investigation of organic systems undergoing a simultaneous two-electron transfer has not been reported so far in the literature, although there are claims that such reactions have been observed in some inorganic systems [4].

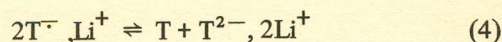
In the course of our studies of tetraphenylethylene dianions [5] we attempted to investigate the feasibility of a two-electron transfer process, namely,



Where T denotes tetraphenylethylene and  $\text{T}^{2-}$  its dianion. The lithium salt was chosen for this study since its solubility in solvents used in our investigation is relatively high. In order to eliminate the two one-electron transfer steps, viz.,



Where  $\text{T}^-$  denotes the radical anion of T, we had to use solvents in which the disproportionation constant of equilibrium



is very large. Benzene and diethylether fulfill these requirements. In neither of them was it possible to detect the presence of tetraphenylethylene radical anion by ESR technique when the concentrations of T and of  $\text{T}^{2-}, 2\text{Li}^+$  were in the range  $5 \times 10^{-2}$  to  $2 \times 10^{-1}\text{M}$ . These observations imply that the concentration of  $\text{T}^-, \text{Li}^+$  in those solutions is smaller than  $10^{-7}\text{M}$ , although it could be perhaps as high as  $10^{-6}\text{M}$  because the exchange of radical anions with the parent hydrocarbon broadens the ESR lines and, therefore, reduces the sensitivity of the ESR detection.

### RESULTS AND DISCUSSION

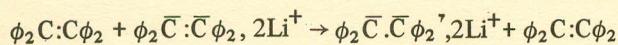
The results of our studies transpire from the  $^{13}\text{C}$  NMR spectra of the parent hydrocarbon,  $\phi_2\text{C}:\text{C}\phi_2$ , its dilithium salt,  $\text{Li}^+\phi_2\text{C}:\text{C}\phi_2\text{Li}^+$  and their mixtures in deuterated benzene (Fig.1) and diethyl ether [5]. The concentrations of the reagents in the investigated solutions are given in the captions under the appropriate fig.

The  $^{13}\text{C}$  NMR spectrum of  $\phi_2\text{C}:\text{C}\phi_2$  consists of 5

lines corresponding to the quaternary carbons of the phenyl groups (1), the ethylenic carbons (2), and the *meta*, *ortho* and *para* carbons (3, 4, and 5, respectively). The assignment of the lines to the pertinent carbon atoms is discussed in [5]. The observed pattern is virtually independent of solvent, being the same in THF<sup>5</sup>, benzene and diethyl ether [5] although the position of its center depends on the solvent's nature.

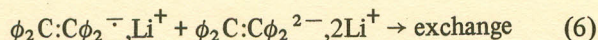
The spectrum of the dilithium salt consists again of 5 lines, their assignment has been also discussed by Lundgren and others [5]. The line of the quaternary carbons of the phenyl groups (1) is slightly shifted downfield, while the line corresponding to the ethylenic carbons [2] is substantially shifted upfield (Fig.1). The chemical shift of the *meta* carbons (3) in the salt is essentially the same as in the hydrocarbon, while the lines pertaining to the *ortho* and *meta* carbons (4 and 5) are shifted slightly upfield.

Both sets of lines appear in the spectra of mixtures of  $\phi_2C:C\phi_2 + \phi_2\bar{C}:\bar{C}\phi_2, 2Li^+$  and this proves that the exchange,

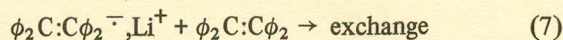


is very slow even on NMR scale. The lines of the salt remain as sharp in the spectrum of the mixture as in the spectrum of the pure salt solution, with less than 10 Hertz width. Hence, the bimolecular rate constant of two-electron exchange in those solvents has to be smaller than  $100M^{-1}sec^{-1}$  because the concentration of the hydrocarbon was about  $10^{-1}M$ .

Interestingly, the lines of the hydrocarbon, excluding those of the salt, are substantially broader in the mixture than in the pure solution of  $\phi_2C:C\phi_2$ . We, therefore, conclude, that the radical anions,  $\phi_2C:C\phi_2, Li^+$ , present in a concentration too low to be detected by the ESR technique, exchange with the hydrocarbon causing broadening of its NMR lines, whereas the exchange,



apparently is substantially slower than



A 1:1 mixture of  $\phi_2C:C\phi_2$  and  $\phi_2\bar{C}:\bar{C}\phi_2, 2Na^+$  in THF contains about 5% of  $\phi_2C:C\phi_2^-, Na^+$  radical anions as the disproportionation constant is only 400 [6] in that solvent.

The  $^{13}C$  NMR spectrum of such a solution shows only the greatly broadened lines of the salt (Fig.2). The lines of the hydrocarbon could not be recorded, presumably because

their degree of broadening is too great. This observation confirms again the slowness of the exchange (Eq[6]) between the radical anion and the dianion when compared with exchange (Eq[7]).

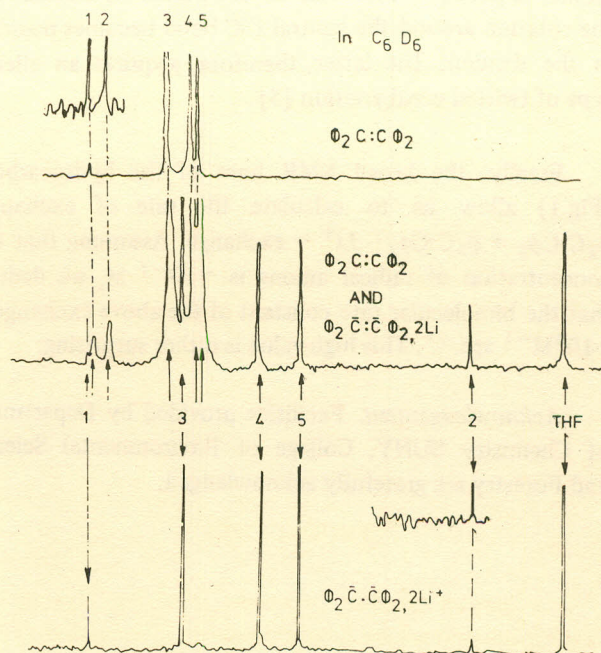


Fig. 1. The  $^{13}C$  NMR spectra of  $\phi_2C:C\phi_2$  (0.14 M), of a mixture of  $\phi_2C:C\phi_2$  (0.14 M) and its dilithium salt,  $\phi_2\bar{C}:\bar{C}\phi_2, 2Li^+$  (0.04 M), and of the dilithium salt only (0.04M) in deuterated benzene.

The long arrows point to the hydrocarbon lines and the short ones to the lines of the salt.

The numbers refer to the quaternary carbons of phenyl groups (1), the ethylenic carbons (2), and the *meta*, *ortho* and *para* carbons (3, 4, and 5, respectively). The triplet of the deuterated benzene coincides with the *meta* carbons and is deleted in the drawing for the sake of clarity.

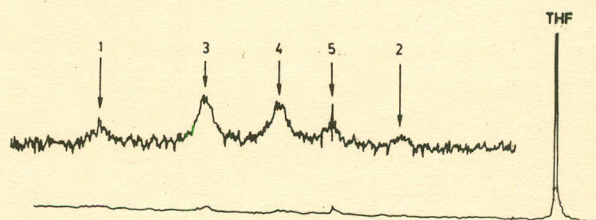


Fig. 2. The  $^{13}C$  NMR spectrum of a 1:1 mixture of  $\phi_2C:C\phi_2$  (0.05M) and its disodium salt,  $\phi_2\bar{C}:\bar{C}\phi_2, 2Na^+$  (0.05M) in THF. The solution contains the radical anions,  $\phi_2C:C\phi_2^-, Na^+$ , at their equilibrium concentration ( $N = 0.025 M$ ).

The broadened lines correspond to those observed in the solution of the disodium salt only (ref.5) as marked by the arrows.

The hydrocarbon lines could not be detected, presumably their broadening caused by the radical anions is too large to allow their detection. The numbers refer again to the respective carbon atoms in which the sharp spectrum of  $\phi_2C:C\phi_2^{2-}, 2Na^+$  in THF is depicted.

The slowness of the exchange between the radical anion and the dianion seems to be caused by the different geometry of these species. While the C=C structure of the former is planar, like that of the parent hydrocarbon, the rotation around the central C-C bond becomes possible in the dianion. The latter, therefore, acquires an allenic type of twisted configuration [5].

Finally, the broad NMR lines of the hydrocarbon, (Fig.1) allow us to calculate the rate of exchange,  $\phi_2\text{C}:\text{C}\phi_2 + \phi_2\text{C}:\text{C}\phi_2^-, \text{Li}^+ \rightarrow \text{exchange}$ . Assuming that the concentration of radical anions is  $\sim 10^{-7}$  M, we deduce that the bimolecular rate constant of the above exchange is  $\sim 10^8 \text{M}^{-1} \text{sec}^{-1}$ . This high value is rather surprising.

*Acknowledgement.* Facilities provided by Department of Chemistry SUNY, College of Environmental Science and Forestry are gratefully acknowledged.

## REFERENCES

1. M. Szwarc and J. Jagur-Grodzinski *Ions and Ion Pairs in Organic Reactions*. (John Wiley 1974).
- 2(a) H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*. (Academic Press, 1972).  
(b) J. Halpern; *Quart. Rev.*, **15**, 207(1961).  
(c) F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, (John Wiley 1967).
3. R.F. Adams, T.L. Staples and M. Szwarc; *Chem. Phys. Lett.*, **5**, 474 (1970).
4. B. Felcinella, P.D. Felgate and G.S. Laurence, *J. Chem. Soc. (Dalton)*, 1974, p. 1367.
5. B. Lundgren, M. Mohammad, G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, **98**, 1461 (1976).
6. B. Lundgren, G. Levin, S. Claesson and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 262 (1975).