

Unusual Electron Transfer to Styrene and α -Methylstyrene Mediated by Potassium Supramolecular Complex with 18-Crown-6

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Received April 17, 1995

Revised Manuscript Received July 5, 1995

Single electron transfer processes (SET) are very common in chemistry;^{1,2} however, transfer of two electrons to an acceptor molecule is very unusual. The discovery of macrocyclic ligands as crown ethers and cryptands^{3,4} which are able to complex alkali metal cations provided the possibility of alkali metal solubilization in aprotic solvents.^{5,6} The resulting alkali metal solutions contain complexed metal cations, solvated electrons, and metal anions. If the process of metal solubilization is performed according to the results of kinetic studies^{7,8} and contact time between a metal surface and a crown ether solution is prolonged to 15 min, the amount of electrons in the solution is negligible and metal complexes $M^+/crown$, M^- (where $M = K$ or Na) are the main products formed in aprotic solvents.^{7,8}

It has been revealed now that the reaction of styrene with an 18-crown-6 (18C6) complex of potassium, carried out in THF solvent, produces after protonation ethylbenzene, 1,3-diphenylbutane, and oligomers. The yield of 1,4-diphenylbutane, which is the main product in the case of single electron transfer,^{9,10} is small (Table 1). The ¹H NMR spectrum of styrene oligomers obtained in the reaction of styrene with potassium complex, molar ratio 4:1, indicates the presence of a methyl group, which can be formed as the end group only by two-electron transfer to styrene (Figure 1).

It means that the reaction of styrene with a potassium supramolecular complex with 18-crown-6 proceeds differently from that published previously by M. Szwarc,⁹ who used sodium naphthalenide as a one-electron donor. In the latter case the transfer of only one electron is possible, resulting in the formation of a radical anion. The recombination of two radical anions by coupling yields a dimeric dianion. If a supramolecular complex of potassium is used, the direct formation of a unique dianion of styrene is possible (Scheme 1). Similar two-electron transfer, mediated by potassium supramolecular complex to α -methylstyrene (1:1), has been demonstrated and evidenced by GC-MS analysis (Table 1). Products of single electron transfer as, e.g., dimer 2,5-diphenylhexane, were not present in the reaction mixture.

The final product evidence provided by GC-MS and ¹H NMR spectroscopy (Table 1, Figure 1) can be considered as direct proof of two-electron transfer and formation of styrene dianion (or α -methylstyrene dianion respectively).

Another evidence of transfer of two electrons was provided also by ³⁹K NMR (Varian VXR-300) spectroscopy. It turned

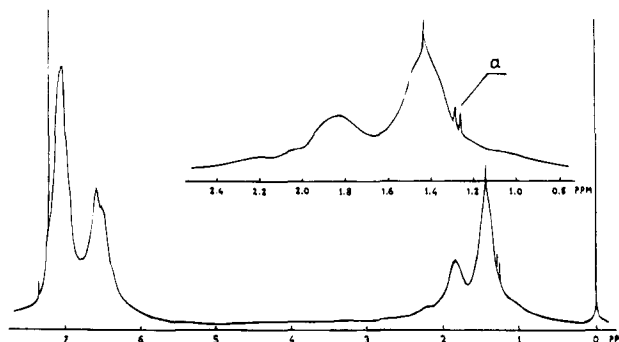
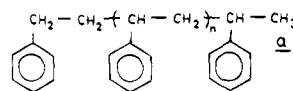
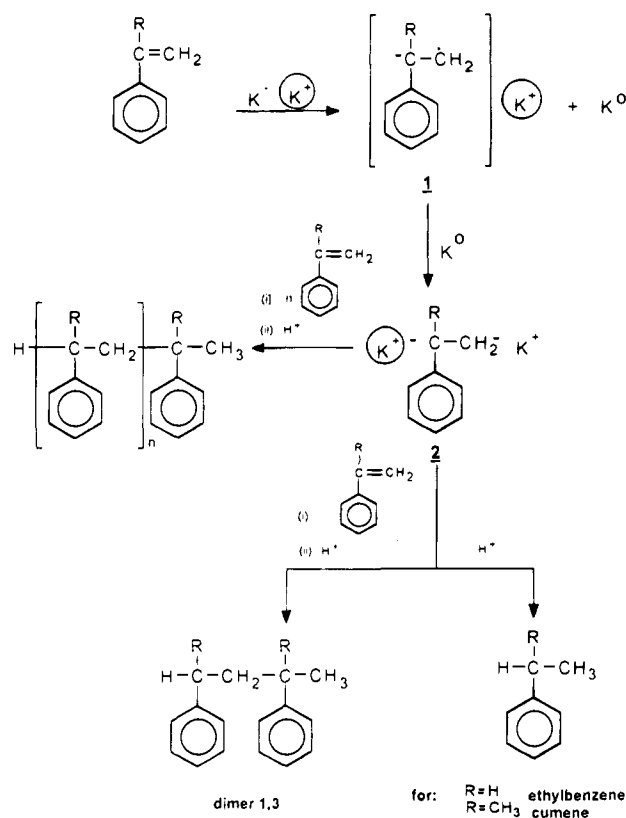


Figure 1. ¹H NMR spectrum of styrene oligomers produced via two-electron transfer.

Scheme 1



(K^+) - complexed cation; $R = H, CH_3$; $n = 3$

out that the signal of the potassium anion in the ³⁹K NMR spectrum of the metal complex disappeared completely after the reaction with α -methylstyrene (or styrene), the resonance signal of cation becoming more intensive. It means that in this reaction the metal anion, after the transfer of two electrons to the α -methylstyrene (or styrene) molecule, is converted into the respective cation (Figure 2).

The experimental results¹¹ indicate that the potassium supramolecular complex with 18C6 acts as a donor of two

(11) Experimental procedure: The 0.2 M THF solution of 18C6 was kept in contact with potassium mirror for 15 min at 20 °C under an inert gas atmosphere. Then, to the blue metal solution filtered through a glass frit was added a corresponding amount of styrene (or α -methylstyrene) in THF solution. The blue color of the solution changed to red. After 10 min in the experiment with styrene (4 h in the experiment with α -methylstyrene), the protonation was performed by the addition of a methanol/THF solution, and the colorless solution was analyzed.

- (1) Baumgarten, M.; Müllen, K. *Top. Curr. Chem.* **1994**, *169*, 1–103.
- (2) Kaim, W. *Top. Curr. Chem.* **1994**, *169*, 232–251.
- (3) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 386–391.
- (4) Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1–69.
- (5) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327–441.
- (6) Edwards, P. P.; Ellaboudy, A. S.; Holton, D. M. *Nature* **1985**, *317*, 242–243.
- (7) Jedliński, Z.; Stolarzewicz, A.; Grobelny, Z.; Szwarc, M. *J. Phys. Chem.* **1984**, *88*, 6094–6095.
- (8) (a) Jedliński, Z.; Sokół, M.; Grobelny, J. *J. Phys.* **1991**, *C5*, 291–296. (b) Jedliński, Z.; Sokół, M. *Pure Appl. Chem.* **1995**, *67*, 587–592.
- (9) Szwarc, M. *Nature* **1956**, *178*, 1168–1169.
- (10) Richards, D. H.; Williams, R. L. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 89–104.

Table 1. Styrene and α -Methylstyrene Reaction with Supramolecular Complex $K^+/18C6, K^-$ in THF at 20 °C

substrate; molar ratio to potassium complex	products of reaction, wt %
styrene; 4:1	ethylbenzene, ^a 5.1; 1,3-diphenylbutane, ^{a,b} 7.4; 1,4-diphenylbutane, ^{a,c} 1.7; oligomers, 85.8
α -methylstyrene; 1:1	cumene, ^a 0.2; 2-methyl-2,4-diphenylpentane, ^{a,d} 55.8; 2,4-dimethyl-2,4,6-triphenylheptane, ^{a,e} 1.0; unreacted α -methylstyrene, ^a 43.0

^a Recalculated from GC areas (wt %). ^b 1,3-Styrene oligomer formed due to two-electron transfer. ^c 1,4-Styrene oligomer (reported previously by Szwarc⁹ as main products formed, due to one-electron transfer). ^d Dimer of α -methylstyrene formed due to two-electron transfer. ^e Trimer of α -methylstyrene formed by the reaction of the α -methylstyrene dimer with another α -methylstyrene molecule.

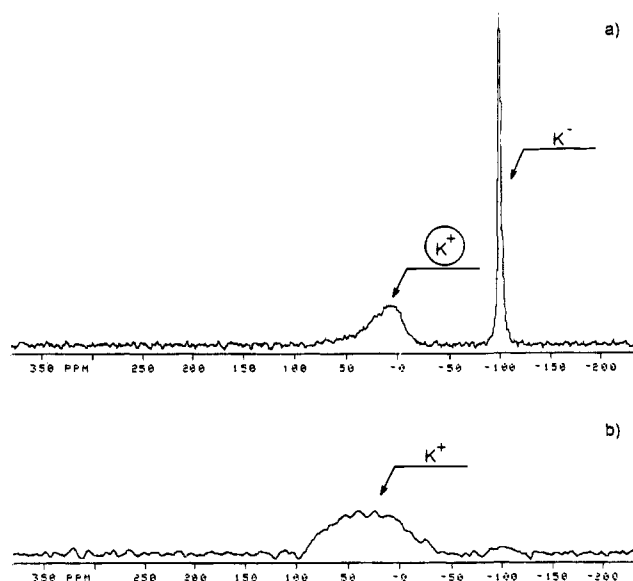


Figure 2. ^{39}K NMR of the potassium complex with 18C6 (a) before the reaction with α -methylstyrene and (b) after the reaction.

electrons being transferred to a styrene or α -methylstyrene molecule, respectively. On the basis of experimental data, the following course of two-electron transfer from alkali metal-18C6 complex and formation of styrene dianion (or of α -methylstyrene, respectively) may be proposed (Scheme 1).

According to the scheme, the transfer of two electrons from potassium complex to styrene proceeds probably in two steps. After the transfer of one electron, radical anion **1** is formed. In the next step the recombination reaction of the radical anion **1**

with potassium (K^0) yields styrene dianion **2** and potassium becomes a cation. Similar reactions of potassium with radical anions have been reported in the literature.¹² We demonstrated previously the transfer of two electrons step by step from potassium supramolecular complex to a β -lactone molecule resulting in the C-C bond scission of the β -lactone ring and generation of a carbanion.¹³ The carbanions of styrene and α -methylstyrene, demonstrated in this communication, are capable of transferring their charge to neutral molecules, thus inducing various reactions.

In summary, unusual two-electron transfer processes to styrene and α -methylstyrene, mediated by alkali metal complexes with macrocyclic ligands, are of general significance and deserve further studies.

Acknowledgment. One of the authors (Z.J.) is indebted to Professor W. D. Ollis, FRS, from the Birmingham University, U.K., and to Professor J. Dye from the Michigan State University for a fruitful discussion on the mechanistic features of two-electron transfer reactions. The financial support of this work by the NSF and M. Skłodowska-Fond (Grant PAN-NSF No. 94/195) is duly acknowledged.

Supporting Information Available: Characteristic data of protonated volatile products of the reaction of styrene with 18-crown-6 potassium complex (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951209T

(12) (a) Finnegan, R. A. *Tetrahedron Lett.* **1963**, 429. (b) Jedliński, Z.; Kowalczyk, M.; Misiołek, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1261–1262.

(13) Jedliński, Z.; Misiołek, A.; Kurcok, P. *J. Org. Chem.* **1989**, *54*, 1500–1501.