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Electron-transfer processes in the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with carbazole: unexpected formation of metallic potassium

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Abstract

Transfer of one electron from K^- to the aromatic ring occurs in the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with carbazole giving K° and a radical anion. The latter rapidly decomposes with the liberation of hydrogen and formation of carbazylpotassium. It can also undergo an intramolecular proton-exchange reaction followed by a transfer of the second electron from the part of K° product. That leads to a dianion which then reacts with another carbazole molecule. Finally, carbazylpotassium and 1,4-dihydrocarbazylpotassium are formed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbazole; Potassium anions; Electron transfer; Intramolecular proton transfer

1. Introduction

Alkali metals are soluble in some organic solvents in the presence of crown ethers, giving dark blue solutions in which the negative species are metal anions [1]. In the case of Na, K, Rb or Cs solutions, metal anions and cations complexed by the ligand are formed. When solubilizing bimetallic systems, e.g. Na-containing alloys, sodium anions and cations of the other alkali metal are obtained [2]. These systems have been employed as novel reagents especially for the metallation, enolization and selective ring-opening reactions of heterocyclic compounds [3–8] and also as the reducing agents of acetylene derivatives or aromatic hydrocarbons [9] and ethers [10,11]. However, the literature concerning the reaction with a compound containing acidic hydrogen atoms is scanty [12].

In the present work, carbazole ($pK_a = 19.9$ [13]) was selected for the study in this field and its reaction with K^-, $K^+(15\text{-crown-}5)_2$ solution in tetrahydrofuran (THF) was examined.

2. Results and discussion

When a solution of carbazole in THF was slowly dropped into the blue K^-, $K^+(15\text{-crown-}5)_2$ solution, discoloration of the reaction mixture resulting from the K^- decay was observed at about 20 mol% excess of carbazole relative to potassium anions. After that, no potassium anions or carbazole remained in the system as determined by ^{39}K-NMR and GC–MS methods, respectively. Hydrogen was observed to evolve, and a yellow–white product was precipitated during the reaction. A piece of solid substance of metallic color was also found in the liquid phase.

Part of the latter substance was isolated from the mixture. It dissolved rapidly in *n*-butanol with liberation of hydrogen. Benzylation of the resulting solution allowed us to identify *n*-butyl benzyl ether in the mixture using the GC–MS method. Another part of the solid substance was introduced into the solution of 15-crown-5 in THF. The substance dissolved giving a deep blue color for the solution. In this solution K^- and $K^+(15\text{-crown-}5)_2$ ions were detected by ^{39}K-NMR. The experiments clearly showed that metallic potassium was one of the reaction products.

When the metallic potassium had been removed, methyl iodide was added to the reaction mixture and

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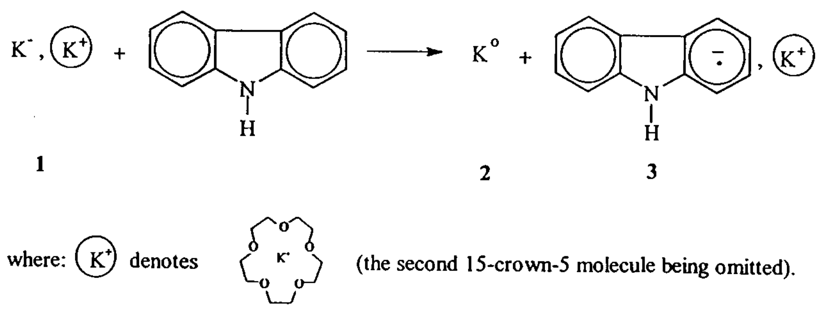


Scheme 1.

the liquid phase was analyzed by GC–MS. The chromatogram showed two signals of methylated products. The first one was identified as 9-methylcarbazole in 70% yield. The mass spectrum of this product was identical to the spectrum of original compound with a molecular ion at 181. The mass spectrum of the second product (26% as calculated from the signal intensities of both reaction products) was very similar; a molecular ion of 183 was found in this case.

An attempt to separate the two compounds and to obtain them without impurities was unsuccessful. However, NMR spectroscopy was found to be useful in identification of the unknown reaction product. The ^{1}H-NMR spectrum of the methylated mixture showed (aside from the signals of 9-methylcarbazole) signals which can be ascribed, respectively, to aromatic protons (multiplets within the range of 8.05–6.97 ppm, partially overlapped with those from 9-methylcarbazole), protons of unsaturated aliphatic groups (two identical multiplets centered at 5.86 ppm), a methyl (singlet at 3.32 ppm) and methylene protons (two multiplets centered at 3.25 ppm). It is worthwhile noting that analogous signals due to CH=CH and CH_2 protons were observed earlier in the ^{1}H-NMR spectrum of 1,4-dihydronaphthalene, obtained during the reaction of naphthalene with metallic potassium [14]. The ^{13}C-NMR analysis of the product formed in the examined system seems to confirm the structure of the unknown product. Besides the signals characteristic for 9-methylcarbazole the spectrum exhibits ten signals within the range from 105 to 137 ppm, which can be ascribed to six aromatic and four olefinic carbons, a signal at 28.74 ppm due to a CH_3 group and two signals arising from CH_2 groups (at 23.4 and 23.3 ppm). The assignment was supported by analyzing the ^{13}C-DEPT-NMR spectrum of the mixture. From the NMR analysis it follows that the signal of the unknown compound observed in the chromatogram is due to 1,4-dihydro-9-methylcarbazole. No other hydrogenation products were formed as indicated by the absence of any additional signals in the GC–MS and NMR spectra. By integrating the NMR signals corresponding to the methyl protons of the two compounds, the molar ratio between 1,4-dihydro-9-methylcarbazole and 9-methylcarbazole was found to be ca. 1:2.5, being in a good agreement with the chromatographic data. A value close to that was also obtained from the gated-decoupled ^{13}C-NMR spectrum recorded with 300 s delay between successive pulses.

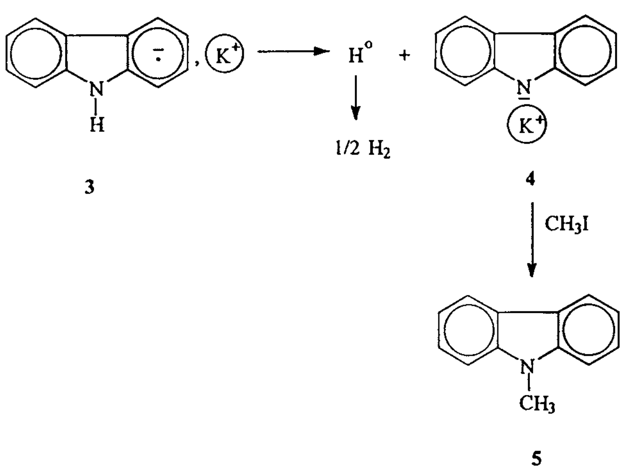
Based on the experimental results the following mechanism for the reaction between carbazole and potassium supramolecular complex is proposed. In the first step a one-electron transfer occurs from K^- of **1** to the aromatic ring of carbazole, resulting in potassium metal **2** and radical anion **3** (Scheme 1).

Then **3** decomposes with the liberation of hydrogen and formation of carbazylpotassium **4**; compound **2** remains in the system (Scheme 2).

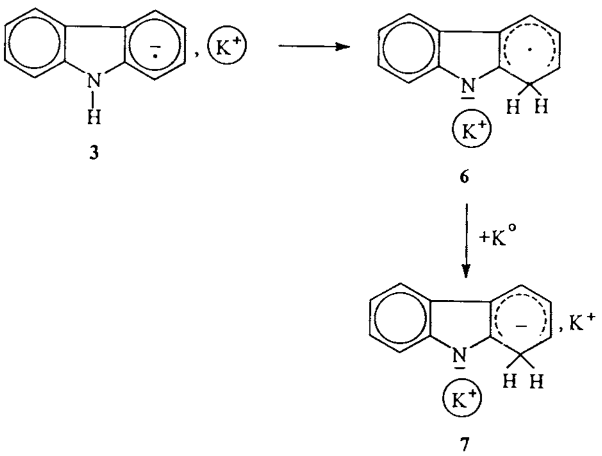
Compound **3** can also undergo an intramolecular proton exchange reaction giving **6**. Transfer of the second electron from a part of K° to **6** leads to the formation of dianion **7** (Scheme 3).

In the last step of the process, dianion **7** reacts with carbazole to give carbazylpotassium **4′** and 1,4-dihydrocarbazylpotassium **8** (Scheme 4).

The scheme proposed above is consistent with the literature data. For example, during reduction of benzene by lithium in NH_3–Et_2O with ethanol, 1,4-dihydrobenzene is formed via an intermediate radical anion and radical [15]. The radical anion with acidic hydro-

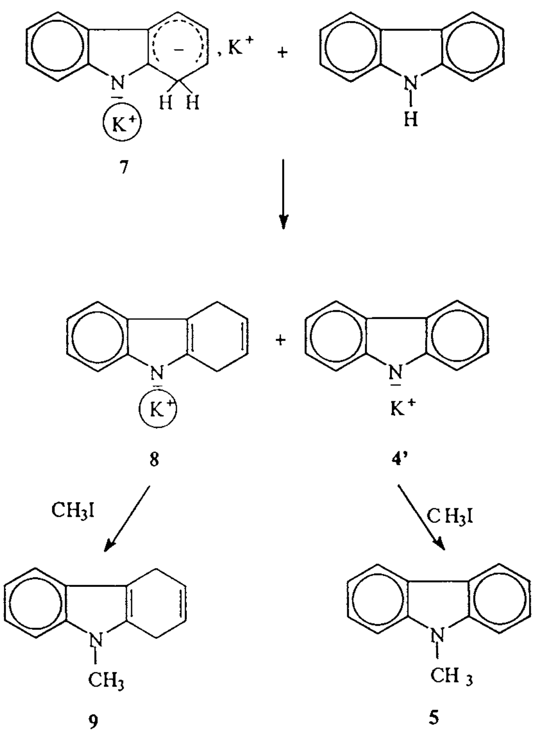


Scheme 2.



Scheme 3.

gen, formed in the reaction of potassium with triphenylmethane, can undergo decomposition with the liberation of hydrogen [16]. A stable dinegative ion can be formed when naphthalene is metallated by potassium in THF [14]. In the case of β-ethylnaphthalene possessing a labile hydrogen in the substituent, the initial aromatic dianion is isomerized into a dihydronaphthalene monoanion as a result of an intramolecular proton exchange reaction.



Scheme 4.

The mechanism of the process studied in the present work assumed the existence of paramagnetic species. However, the electron spin resonance (ESR) analysis did not indicate their presence in the reaction mixture. It could be explained by their short lifetime. All the reactions were very fast, and therefore, the methylated derivatives of **3**, **6** and **7** were not found in the mixture after quenching by CH_3I.

The experiments were repeated several times to check their reproducibility, and the same results were obtained. However, the real novelty of this work concerns the fact that metallic potassium was one of the reaction products. That is a new observation in the chemistry of metal anions.

Until now, the potassium anion has been known as a double electron donor [17]. It reacted in two steps. Initially, a single electron transfer took place from K^- to the acceptor molecule, resulting in the radical anion and K°. Then K° transferred the second electron to either the radical anion, giving dianion, or to the other acceptor molecule, converting it into the next radical anion. Jedliński [18] studied the mechanism of these processes. It was found that K^- reacted with β-lactone in the molar ratio of 1:1 [6]. The single-electron transfer from the metal anion to the lactone molecule resulted in the formation of K° and the lactone radical anion. The latter formed enolate radical after C–C bond cleavage. This radical reacted with potassium, giving the corresponding enolate carbanion with K^+ as a counterion. The reaction between K^- and benzophenone was carried out at the molar ratio of 1:2 [19]. The single-electron transfer from the potassium anion to the ketone molecule resulted in the ketyl radical anion and K°. The latter reacted with another benzophenone molecule giving the next radical anion and a potassium cation. Finally, K^+ was formed from K^- in these experiments as well as in others reported in the literature [2–12]. According to our knowledge, only in the present work was K° found as the final reaction product of K^-.

It is worth noting that potassium anions also react with N-substituted carbazole, e.g. methylcarbazole and vinylcarbazole. In contrast to unsubstituted carbazole, stable radical anions were formed in these systems, their concentration being of the order of 10^{-5} M as revealed by ESR. The blue color of the metal solution changed to dark red in this case. Metallic potassium was not observed in the reaction mixture.

Therefore, it may be concluded that the mechanism of the metal anion reaction depends on the presence of acidic hydrogen atom in the reagent molecule. The K^- acts as the electron transfer agent, whereas typical nucleophilic ions, e.g. RO^-, cause deprotonation of carbazole giving the carbazole anion in a one-step process [20].

3. Experimental

3.1. Materials

THF (POCH) was purified by the method described earlier [21]. Carbazole (Aldrich) and 9-methylcarbazole (Aldrich) were purified by recrystallization from xylene. 15-Crown-5 (Aldrich) was dried under vacuum at 50°C for several hours. The 0.1 M K^-, K^+(15-crown-5)$_2$ dark blue solution was prepared by dissolving metallic potassium in the 0.2 M 15-crown-5 THF solution at 20°C. The contact time was 25 min. The details of the experimental procedures are described elsewhere [22].

3.2. General procedure

A 0.1 M K^-, K^+(15-crown-5)$_2$ (10 cm^3) solution was slowly titrated by 12 cm^3 of a 0.1 M solution of carbazole in THF under a dry argon atmosphere. During this time the reaction mixture became colorless. The reaction was carried out at 20°C with stirring and 4 cm^3 of hydrogen was found to evolve during the reaction. A titration time of 10 min was required to obtain metallic potassium in the form of a solid piece, weighing 0.021 g after washing in THF. At considerably shorter periods of time, the metal was usually dispersed. After isolation of the metal, the reaction mixture was quenched by CH_3I and analyzed by GC–MS. The mass of the methylated reaction products was equal to 0.19 g.

GC–MC analyses were performed on a 30 m long fused silica capillary column DB-1701 using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. Diethylene glycol dimethyl ether was used as an internal standard for the yield determination.

Analysis of hydrogen was conducted by the GC technique on a 2.4 m long stainless steel column packed with Al_2O_3 (0.02–0.03 mm) and deactivated with 5% K_2CO_3, using an INCO 505 gas chromatograph with flame ionization detector.

^{1}H-, ^{13}C- and ^{39}K-NMR spectra were recorded at 20°C on a Varian VXR-300 multinuclear spectrometer at the ^{1}H resonance frequency of 300 MHz, ^{13}C resonance frequency of 75 MHz, and ^{39}K resonance frequency of 14 MHz. $CDCl_3$ was used as the solvent for ^{1}H- and ^{13}C-NMR analysis. Chemical shifts were referenced to tetramethylsilane (TMS) serving as an internal standard in this case.

ESR measurements were carried out with an ESR 300 Bruker X-band spectrometer employing 100 kHz field modulation and a microwave frequency of ca. 9.4 GHz. In order to determine the concentration of paramagnetic species a double rectangular cavity was used and a solution of 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH) served as a reference.

3.2.1. 9-Methylcarbazole (**5**)

^{1}H-NMR $CDCl_3$: δ 8.05–7.09 (m, 8H, Ar); 3.53 (s, 3H, CH_3). ^{13}C-NMR $CDCl_3$: δ 140.8, 125.5, 122.6, 120.1, 118.7, 108.3; (C_{Ar}, six signals); 28.66 (CH_3). Mass spectrum (*m*/*e*): 181 [M^+, 100]; 180 (60); 167 (6); 152 (14); 140 (6); 90 (4); 39 (1).

3.2.2. 1,4-Dihydro-9-methylcarbazole (**9**)

^{1}H-NMR $CDCl_3$: δ 8.05–6.97 (m, 4H, Ar); 5.86 (dm, 2H, =CH); 3.25 (dm, 4H, CH_2); 3.32 (s, 3H, CH_3). ^{13}C-NMR $CDCl_3$: δ 136.7, 132.6, 126.6, 125.6, 122.1, 120.6, 118.6, 117.8, 108.4, 105.8; (C_{Ar}, six signals + CH=, four signals); 28.74 (CH_3), 23.4, 23.3 (CH_2, two signals). Mass spectrum (*m*/*e*): 183 [M^+, 100]; 182 (94); 167 (56); 152 (9); 140 (6); 90 (5); 39 (1).

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References

[1] J.L. Dye, in: R.M. Izatt, J.J. Christensen (Eds.), Progress in Macrocyclic Chemistry, vol. 1, Wiley–Interscience, New York, 1979, p. 63.
[2] M. Sokół, Z. Grobelny, A. Stolarzewicz, J. Phys. Chem. 99 (1995) 12670.
[3] Z. Jedliński, M. Kowalczuk, P. Kurcok, M. Grzegorzek, J. Ermel, J. Org. Chem. 52 (1987) 4601.
[4] Z. Jedliński, A. Misiołek, W. Główkowski, Synlett (1990) 211.
[5] Z. Jedliński, A. Misiołek, A. Jankowski, H. Janeczek, J. Chem. Soc. Chem. Commun. (1991) 1513.
[6] Z. Jedliński, A. Misiołek, P. Kurcok, J. Org. Chem. 54 (1989) 1500.
[7] Z. Jedliński, M. Kowalczuk, A. Misiołek, J. Chem. Soc. Chem. Commun. (1988) 1261.
[8] A. Stolarzewicz, Z. Grobelny, Makromol. Chem. 193 (1992) 531.
[9] D.J. Mathre, W.C. Guida, Tetrahedron Lett. 21 (1980) 4773.
[10] R.H. Fish, J.W. Dupon, J. Org. Chem. 53 (1988) 5230.
[11] Z. Grobelny, A. Stolarzewicz, A. Maercker, W. Demuth, J. Organomet. Chem., in press.
[12] R.R. Dewald, S.R. Jones, B.S. Schwartz, J. Chem. Soc. Chem. Commun. (1980) 272.
[13] F.G. Bordwell, X. Zhang, J.-P. Cheng, J. Org. Chem. 56 (1991) 3216.
[14] Huynh-Ba-Gia, R. Jérôme, Ph. Teyssié, J. Organomet. Chem. 190 (1980) 107.
[15] (a) A.P. Krapcho, A.A. Bothner-By, J. Am. Chem. Soc. 81 (1959) 3658. (b) A.P. Krapcho, A.A. Bothner-By, J. Am. Chem. Soc. 82 (1960) 751.
[16] K.K. Brandes, R. Suhrman, R.J. Gerdes, J. Org. Chem. 32 (1967) 741.
[17] Z. Jedliński, Acc. Chem. Res. 31 (1998) 55.
[18] Z. Jedliński, Makromol. Chem. Macromol. Symp. 73 (1993) 65.
[19] Z. Jedliński, A. Misiołek, W. Główkowski, H. Janeczek, Bull. Pol. Acad. Sci. Ser. Sci. Chem. 39 (1991) 195.
[20] K. Gregory, M. Bremer, P.R. Schleyer, P.A.A. Klusener, L. Brandsma, Angew. Chem. Int. Ed. Engl. 28 (1989) 1224.
[21] Z. Grobelny, A. Stolarzewicz, Pol. J. Chem. 33 (1981) 1933.
[22] Z. Grobelny, A. Stolarzewicz, M. Sokół, J. Grobelny, H. Janeczek, J. Phys. Chem. 96 (1992) 5193.