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The Reaction Mechanism Between Tetraarylammonium Salts and Hydroxide

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Abstract: The mechanism of the reaction between tetraaryl ammonium salts and hydroxide is studied experimentally for different N,N-diaryl carbazolium salts. The N,N-diarylcarbazolium salts are designed, synthesized, characterized, and reacted with hydroxide under different conditions. The products of the reactions were directly characterized or isolated when possible and, using different substituents, the reaction mechanisms were compared. An unexpected H/D exchange observed in these salts helped to discard the classical S_NAr mechanisms, supporting instead a radical mechanism initiated by a single-electron transfer from the hydroxide. By understanding the preferred reaction pathways, better quaternary ammonium salts can be designed to withstand aggressive alkaline environments, critical for many practical applications such as anion-exchange membrane fuel cells.

Introduction

Quaternary ammonium (QAs) salts are of foremost importance for the chemical industry, as they are used in a very wide spectrum of applications including surfactants, disinfectants, antistatic agents, phase transfer catalysts, and more.^[1–4] In recent years, the synthesis of new QA salts has burst, given their potential use in anion-exchange membrane fuel cells (AEMFCs).^[5] AEMFC is a promising technology for affordable and efficient energy conversion but is currently limited by the chemical stability of the cationic functional groups that decompose under fuel cell operation.^{[6][7]} Currently, no organic cation has proved to be stable enough to withstand the harsh combined alkaline and low hydration environment for the required lifetime of an AEMFC.^[8] Yet, among organic cations, QAs have shown the most promising results.^[9]

QAs are typically prepared by the alkylation of a tertiary amine, and as a consequence, most QAs have at least one alkyl substituent.^[10] As a general rule, the presence of β -hydrogens leads to fast degradation through Hofmann elimination (E2

mechanism - Scheme 1a).^[11] In this case, hydroxide acts as a base, abstracting the β proton while a tertiary amine is formed as a good leaving group (LG), neutralizing the molecules' positive charges, thus ceasing anion conductance. In the absence of β hydrogens, the positive charge distributed at the carbons connected to the nitrogen, leads to classical nucleophilic attack at an α carbon, with the amine again acting as a good LG (S_N2, Scheme 1b), again, producing neutral molecules.^[12,13]

Recently, some QAs have been produced that showed remarkable stability in highly alkaline aqueous conditions even at high temperatures, including substituted imidazolium salts,^[14-16] spirocyclic ammonium salts,^[12,17-19] and others. Still, when tested under strictly dry alkaline conditions, in which hydroxide microsolvation is limited,^[20] these ammonium salts decomposed very rapidly by the expected mechanisms.^[21] This is another example in which solvation environment, and particularly water molecules, can affect reaction mechanisms heterogeneously.^[22–24] Therefore, new paradigms of QAs which may decompose through different reaction mechanisms is of supreme importance, as it opens new avenues for the development of more stable cations.





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A reasonable strategy to suppress both E2 and S_N2 mechanisms is to change the α carbons hybridization from sp³ to sp^{2,[25]} However, the fact that the intermolecular arylation of triarylamines has not yet been demonstrated^[10,26] hampers the testing of simple tetraphenyl ammonium (TPA) salts. TPA salts, in the presence of hydroxide, could still decompose through known decomposition mechanisms, but these typically require harsher reaction conditions for the same nucleophile. Hydroxide could still attack the electrophilic α carbon leading to S_NAr mechanism through addition-elimination. However, recently, this pathway has been shown to be much more rarer than described in organic chemistry textbooks (Scheme 2a).^[27] A concerted S_N2like mechanism is still possible, but compared to aliphatic S_N2, it is kinetically sluggish due to steric hindrance imposed by the aromatic ring on the nucleophile. In addition, carbon-LG bonds are shorter as a result of the higher s-character of the carbon (Scheme 2b). Finally, TPA can decompose through β hydrogen abstraction, producing a strained benzyne intermediate (Scheme 2c). While intermolecular arylation of triarylamines has not yet been demonstrated, the intramolecular arvlation using diazonium salts^[28,29] or C-F activation by sillyl cation^[30] to produce N,Ndiarylcarbazolium salts has proven possible, generating QAs with a similar general structure compared to TPA salts, given all the nitrogen substituents are aromatic carbons.



Scheme 2. Possible decomposition mechanisms of TPA hydroxide: (a) addition-elimination, (b) concerted S_N2 and (c) benzyne (c).

In his pioneering work, Nesmeyanov et al. noticed that the N,N diphenyl carbazolium salt was quite stable and decomposed only upon heating with 50% aqueous KOH.^[29] In their study, it was proposed that hydroxide preferably attacks the freely rotating phenyl rings and not the carbazole ring, given they identified the reaction products as N-phenyl carbazole, phenol and diphenyl ether; yet, the prevailing reaction mechanism was not described. A few years later, Hellwinkel, [31,32] in an attempt to make pentacoordinated nitrogen species, added strong carbon nucleophiles to a 9,9-spiro-biscarbazolium salt. In his manuscript, decomposition through benzyne mechanism was suggested, but given the analytical limitations at the time, this proposed mechanism could not be supported by experimental evidence. Our group has been interested in the synthesis^[26,28] and decomposition^[21,33–35] of QAs in order to try to open new directions in the development of stable cations for AEMFCs. We have recently developed an improved procedure for the synthesis of N,N-diaryl carbazolium salts, which allows for the synthesis of a variety of derivatives with different substituents in very few synthetic steps and significantly better yields.^[28] Driven by previous studies that were able to better simulate AEMFCs conditions by creating non-aqueous alkaline and low hydration conditions,^[21,33,36] we expected that making such molecules and testing them under such conditions would open new pathways to developing more stable QAs, needed for durable AEMFCs.^[7] Importantly, by changing the mechanism of reaction with hydroxide, different molecular optimization can be used to further tackle the stability of transition states and intermediates, towards the production of kinetically stable QAs which will be able to survive the aggressive conditions present in AEMFC for the lifetime of the fuel cell.

Nansi Gjineci obtained her degree in Chemical Engineering from National Technical University of Athens, Greece. She receives a M.Sc. after investigating the effect of ionic liquids on the separation of azeotropic mixtures under the supervision of Professor Epaminondas Voutsas in 2015. In October 2016, Nansi joined the Technion-Israel Institute of Technology under the supervision of Professor Charles Diesendruck in Schulich Faculty of



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Chemistry and Dario Dekel in Wolfson Department of Chemical Engineering in a joint project as a PhD student. Nansi works on the development and testing of novel functional groups and ionomers for alkaline fuel cell applications.

Sinai Aharonovich studied Chemical Engineering at the Wolfson Department of Chemical Engineering at the Technion -Israel Institute of Technology, graduating in 1997. After working as process engineer, he joined the group of Professor Moris S.Eisen at the Schulich Faculty of Chemistry, where he got a Ph.D. in 2010. He then did a postdoc with Prof. Robert M. Waymouth at Stanford University, working on homogenous Ziegler-Natta catalysis. In



2012, he returned to Israel to serve as CSO in the development of organocatalytic oxidation of sulfur and nitrogen oxides. Since 2016, he returned to the Technion and joined the group of Prof. Diesendruck where he works as a senior researcher, focusing on polymer chemistry, organic and organometallic syntheses.

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Dario R. Dekel received his BSc in Chemical engineering in the National Technology University in Argentina. He immigrated to Israel in 1990, and joined the Technion – Israel Institute of Technology, from where he received his M.Sc. in Chemical Engineering, Ph.D. in the field of Membrane Science, and his M.B.A. After managing a power source unit in Rafael Ltd., he co-found CellEra Technologies Ltd. where he led the development of the Anion-Exchange



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Charles E. Diesendruck immigrated to Israel in 1999 from Brazil. He carried out all his studies in Chemistry at Ben-Gurion University, receiving his Ph.D. working under Prof. N. Gabriel Lemcoff in 2011. He then carried out post-doctoral studies with Prof. Jeffrey S. Moore at the University of Illinois at Urbana-Champaign. Since 2014, he is part of the Schulich Faculty of Chemistry in the Technion – Israel Institute of Technology, where he recently became



Associate Professor. His research interests include Polymer Chemistry, Self-healing polymers, Mechanochemistry, Materials for Energy Applications, and Physical-Organic Chemistry.

Results and Discussion

Our recently developed synthesis of N,N-diarylcarbazolium was initially used to synthesize large quantities of N,Ndiphenylcarbazolium hexafluorophosphate,^[28] which was tested under the most aggressive media following the protocol previously developed in our group, in which dry KOH is prepared in molten 18-crown-6-ether (CE) by titration of potassium metal by water.^[21] After dissolution in dry DMSO, dry hydroxide solution has in average ca. 0.1 water molecules per hydroxide and therefore, acts as a superbase/supernucleophile.[37] In fact, we have shown that by using dry hydroxide, the rate constant for S_N2 and E2 reactions is increased by a few orders of magnitude.^[21] Unfortunately, the NMR spectrum of N,N-diphenylcarbazolium hexafluorophosphate and CE/KOH (0.5 M) with mesitylene as an internal standard in DMSO-d₆ showed complete decomposition of the QA happens almost immediately. The products were isolated by extraction and as previously shown, the main decomposition product observed was N-phenyl carbazole^[29] (see the Supporting Information). This result supports the hypothesis that hydroxide attacks occur more rapidly at the freely rotating aryls and not at the carbazole system. However, it does not allow identification of the reaction mechanism, which can allow tuning design parameters to improve the stability of these QAs, at least kinetically. Therefore, we synthesized a new carbazolium salt containing substituents in the phenyl rings, which would reveal the regioselectivity of the hydroxide attack, in order to understand the dominating decomposition mechanism.



Scheme 3. Synthesis of 9,9-di-*p*-tolylcarbazolium acetate.

N, N di(*p*-tolyl) carbazolium salt was synthesized similarly to its phenyl congener, following the synthetic strategy previously developed by us, using 4-iodotoluene instead of iodobenzene (Scheme 3).^[28] The synthesis begins with the hydrogenation of the 2,2-dinitrobiphenyl (1) using zinc under acidic conditions. Then, a Cul catalyzed Ullman reaction of diamine 2 with 2 equivalents of 4-iodotoluene provides amine (3) in 35% isolated yield. This Ullman reaction is regioselective and no additional isomers were observed by NMR (remaining product is the monoarylated 2, which can be recycled in the next batch). The final step is the formation and decomposition of the diazonium salt leading to cyclization, which forms the desired carbazolium salt (4). The QA salt in the acetate form was purified and single crystals were successfully grown after anion exchange to hexafluorophosphate (Figure 1).



Figure 1. X-ray structure of 9,9-di-p-tolylcarbazolium hexafluorophosphate.

In the solid state, the addition of para methyl groups did not significantly change the structural features, with the C-N bond being comparable to those distances of the N.Nhexafluorophosphate,[28] diphenylcarbazolium and still significantly longer than those in common arylammoniums salts.^[38] The longest C-N bonds are to the carbon of the freely rotating phenyl rings (1.516 Å), possibly indicating the cause of the selectivity of the hydroxide attack. In the carbazole moiety, the C-N distances are shorter (1.512 Å and 1.508 Å).

As with the N,N-diphenylcarbazolium salt, the addition of the unsolvated hydroxide leads to rapid degradation. However, in this case, through the identification of the isomeric phenol decomposition products, the dominating S_NAr mechanism could be differentiated (Scheme 4). If the main mechanism is hydroxide attack on the α carbon to the nitrogen, we expect to obtain only 9-*p*-tolyl carbazole and *para*-cresol as products (Scheme 4a). If, on the other hand, the hydroxide abstracts the β hydrogen, then the decomposition would follow a benzyne formation, which leads to

three expected degradation products: 9-*p*-tolyl carbazole, and a mixture of *para*- and *meta*-cresols (Scheme 4b).

The NMR spectrum of the reaction can be directly compared to the spectra of the possible products, after their dissolution in a similar solution (DMSO in the presence of 0.5 M CE/KOH). As seen in Figure 2, the signals of 9-tolyl carbazole are quite easily identified, but the resolution was not good enough to distinguish between the cresol isomers.



Scheme 4. The two possible reaction pathways for 9,9-di-*p*-tolylcarbazolium with hydroxide: (a) concerted S_N2 and (b) benzyne mechanism.



Figure 2. ¹H-NMR in DMSO-d₆ of (a) decomposition product from 9,9-di-*p*-tolylcarbazolium acetate after addition of CE/KOH, (b) 9-*p*-tolyl-carbazole, (c) *meta* and (d) *para* cresol with CE/KOH, and (e) 9,9-di-*p*-tolylcarbazolium acetate. The aromatic protons of 9-*p*-tolyl carbazole are shown in the green box. The aromatic peaks of *p*-cresol and *m*-cresol are shown in the black box.

Therefore, we decided to analyze the reaction mixture and the two isomeric phenols by GC-MS. To that end, the content of the NMR tube after the reaction was acidified by concentrated sulfuric acid which neutralized the strong base and turns the phenoxides into phenols. A few mL of water were then added and the organic decomposition products were extracted using CH₂Cl₂, which was dried and injected into the more sensitive GC-MS (Figure 3). We also injected a mixture of *para* and *meta* cresols as references, given their EI fingerprint in standard conditions can be misleading.



As seen in Figure 3a good separation and clear peaks were

obtained, with meta cresol coming at ca. 7 min whereas para

cresol presents a retention time of ca. 8 min. The injected extract

(Figure 3b) showed a complete dominance of the para cresol as

a product (also identified by comparison to the NIST library),

together with a very small peak of the meta cresol.

Figure 3. Chromatogram of (a) mixture of para and meta cresol and (b) CH_2CI_2 extract from the reaction mixture after work-up.

The GC analysis clearly indicates that the predominant mechanism seems, unexpectedly, to be a direct attack on the ipso carbon by an S_N2 -like mechanism (or addition-elimination) (Scheme 4a), both of which seemed unlikely for the reasons described above. Additional experiments further lead us to question these mechanisms. Given that the hydroxide reacts selectively with the freely rotating phenyls, we decided to prepare a spiro-biscarbazolium salt, without any such rings. The 9,9-spirobiscarbazolium acetate was synthesized following a similar synthetic strategy (Scheme 5), but in this case, 2,2'-diiodobiphenyl was used instead of iodobenzene, providing amine 5 in 20% yield after column chromatography. This arylation reaction was quite challenging due to steric hindrance at the *ortho* position of the iodine, as reflected in the 7 days (as opposed to 3.5 hours) needed for its completion.



Scheme 5. Synthesis of 9,9-spiro-biscarbazolium acetate.

The final cyclization was obtained through the formation of the diazonium salt in acetic acid followed by addition of urea and heating to 40 °C for 1 h. The spiro-biscarbazolium **6** was obtained as a pure compound and single crystals could be obtained after a salt metathesis with ammonium hexafluorophosphate (Figure 4).

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The C-N bonds in **6** are slightly shorter than in **4**, with values ranging from 1.498 Å to 1.506 Å. Interestingly, **6**-acetate was soluble in water, which motivated us to test its stability in aqueous (D₂O) KOH first. As expected, the molecule seemed perfectly stable in these conditions. To accelerate the decomposition reaction, we increased the temperature to 60°C. Surprisingly, the most upfield aromatic hydrogen signals, which correspond to the *ortho* hydrogens started to disappear, while the other hydrogens remained almost unchanged (Figure 5). After 7 days, this hydrogen signal completely disappeared, as did its splitting of the meta carbon, but surprisingly, the compound remains pure – no additional peaks were observed.



Figure 4. X-ray structure of 9,9-spiro-biscarbazolium hexafluorophosphate (6).



Figure 5. ¹H-NMR in D₂O of (a) pure 9,9-spiro-biscarbazolium acetate, (b) after addition of 0.5 M KOH, (c) after 16 h at room temperature, (d) after additional 24 h at 60° C, (e) after 4 days at 60° C, and (f) after 7 days at 60° C.

The crude reaction mixture was sent to mass spectrometry and returned showing a mass gain of 4 mass units (see the Supporting Information), indicating that the *ortho* hydrogens exchanged with deuterium, without any decomposition of the molecule. H/D exchange of acidic hydrogens under harsh alkaline conditions has been mentioned in the literature for other QAs. It is known that the benzylic hydrogen position in benzyl trimethylammonium rapidly is deuterated when the salts are exposed to alkaline environment in MeOD or D₂O^[39–41]. This same effect has been more recently observed also in imidazolium cations.^[16] While the hydroxide is fully hydrated in this case, this H/D exchange, which typically has a high energy barrier, should not occur if the hydroxide preferably attacks the ipso carbon, as this would lead to irreversible C-N bond scission. We, therefore, went to the literature to look for an alternative mechanism that would agree with all the experimental observations.

An interesting possibility described in many literature examples, is the reactivity of hydroxide as a reducing agent. Based on previous fundamental studies carried out by Sawyer,^[42] Schreiner et al. have shown that hydroxide, especially with low water microsolvation, is capable of triggering radical halogenations^[43] through single-electron transfer (SET) reactions. SET to carbazolium molecules would provide similar products as a nucleophilic attack on the ipso carbon, following a mechanism similar to a Birch reduction (Scheme 6).^[44]



Scheme 6. Proposed Birch-like single-electron transfer (SET) reaction between hydroxide and 9,9-di-p-tolylcarbazolium.

To further support this SET reaction mechanism, we carried out cyclic voltammetry studies on N,N-diphenylcarbazolium acetate in acetonitrile using Ag/AgNO₃ as the reference electrode. The cyclic voltammetry was performed in the absence of supporting electrolyte at a sweep rate of 10 mV/s (Figure 6) and the potential scale was fixed based on literature data, against Normal Hydrogen Electrode (NHE).^[45] The diphenyl carbazolium shows a clear reduction peak at -0.882 V. However, combined with the +0.92 V of the OH⁻/HO[•] redox couple potential,^[42] the SET shown here is 1.80 V endergonic. Therefore, a discrete SET reaction between diphenyl carbazolium with OH⁻ is improbable. Actually, considering the many examples of radical organic transformations using OH⁻ for SET, it is quite interesting that most of them, when looking only at the initial steps, are quite inaccessible. The reason these reactions do occur was nicely discussed by Sawyer:^[42] "The redox potentials for the electron acceptors that react with HO⁻ are such that a pure outersphere SET step would be endergonic. Hence, the observed net reactions must be driven by coupled chemical reactions, particularly bond formation by the HO[•] to the electrophilic atom of the acceptor molecule, that accompany a single-electron shift."

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Figure 6. Cyclic voltammogram of N,N-diphenylcarbazolium acetate in $\ensuremath{\mathsf{CH}_3\mathsf{CN}}$.

Therefore, based on our results and the literature, we propose that a plausible reaction mechanism between the carbazolium salt and hydroxide consists of an inner sphere single electron transfer in the ion pair followed by radical coupling.^[46] The zwitterionic sigma complex intermediate undergoes spontaneous elimination of the carbazole group, restoring aromaticity. The formation of the bond between the radicals provides the driving force to make the reaction exergonic (Scheme 7).



Sceme 7. SET reaction pathway including all the reaction potentials and estimated free energies. $^{[42,47]}$

Naturally, given the reaction is done in DMSO, there is also a considerable amount of dimsyl anions, which are slightly better reducing agents than dry OH⁻ (by ca. 0.3 mV).^[46] Therefore, this full mechanism may also be occurring with dimsyl counter anions instead of OH⁻, but the innersphere process is still a requirement in this case.

Conclusion

Using our new approach for the synthesis of N,N-diaryl carbazolium salts, we were able to study the reaction mechanism between tetraarylammonium salts and hydroxide. Given their possible use in ionic polymers for AEMFCs, we studied their reactions with hydroxide under different severe alkaline conditions. Identification of N-aryl carbazole as the major decomposition product confirmed that degradation occurs through the attack on the freely rotating phenyl rings, while the carbazole remains intact. The classical nucleophilic reaction mechanisms were put forward and, in order to decide on the reaction pathway, tetraarylammonium salts having para methyl substituents were used to look at the reaction regioselectivity, leading to observations which did not fit with the classical S_NAr mechanisms. Therefore, inspired by previous work with dry hydroxide, a radical decomposition mechanism was proposed. However, cyclic voltammetry measurements revealed that the reduction potential of the N,N diphenylcarbazolium acetate, in combination with that of hydroxide, could not support a discrete, outer sphere single-electron transfer (SET) mechanism. Therefore, inspired by Sawyer's seminar work,^[42] we proposed the inner sphere coupling of SET with a polar group transfer reaction as a major operative mechanism. The free radical pair generated from the SET reaction is followed by the elimination of the leaving group and the energy of the formed C-O bond provides sufficient driving force to overcome the unfavorable electron transfer reaction. This SET mechanism is not seen in other QAs used in AEMs, which typically show a good electrochemical range and decompose through classical S_N2 and E2 mechanisms. Still, with this knowledge at hand, new tetraarylammonium salts can be judiciously designed to address this radical mechanism reaction pathway, in order to increase their stability to match the harsh conditions of ultra-dry hydroxide, providing a new pathway for the development of highly stable ionic polymers for AEMFCs and other applications.

Experimental Section

Materials and General Methods

Commercially available materials were used as received unless noted. Xylene used for synthesis was dried before use by filtration through an alumina column. The complex of 18-crown-6/KOH was prepared as previously described,^[33] stored and handled in a glovebox. For thin-layer chromatography, silica gel GF254 plates were used and visualized with a UV lamp (254nm). Silica gel 60 (230-400 mesh) from Merck was used in column chromatography. NMR spectra were recorded in a Bruker Avance III 400 MHz or Bruker Avance 300 MHz spectrometer. The chemical shifts are referenced to signal at δ 0.00 (TMS) or partially undeuterated solvent peaks. The coupling constants (J) are reported in Hz. Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (double triplet), br (broad) and m (multiplet). Highresolution mass spectrometry was performed in a Waters LCT Premier Mass Spectrometer (ESI) and a Bruker maxis impact with APCI solid probe. Gas chromatography data were obtained using an Agilent 6850 GC equipped with an Agilent 5973 MSD working under standard conditions and an Agilent HP5-MS (30*0.25*0.25) column. X-ray diffraction data was collected on a Nonius Kappa CCD diffractometer with monochromated Mo Kα radiation (λ=0.71073 Å). Accurate cell parameters were acquired by analyzing the amount of indicated reflections. The diffraction image was processed by software Mercury. The structure was solved by direct methods (SHELXS-97) and refined against F² by full-matrix least squares methods (SHELXL-97). All non-hydrogen atoms were refined

anisotropically. Hydrogen atoms were refined isotropically on calculated positions using a riding model. The isotropic displacement parameters $U_{\rm iso}$ were constrained to 1.5 times the $U_{\rm eq}$ value of their pivot atoms for terminal sp³ carbon atoms, and 1.2 times for all other carbon atoms.

Experimental Procedures

N,N-di-p-tolyl-[1,1'-biphenyl]-2,2'-diamine (3)

In an oven-dried Schlenk flask (50 mL), amine 2 (1.00 g, 5.42 mmol) and 4-iodotoluene (2.367 g, 10.84 mmol) were dissolved in xylenes (15 mL) and the flask deoxygenated using 3 freeze-pump-thaw cycles. The flask was backfilled with argon. KOtBu (1.33 g, 11.92mmol) was then added and the mixture left for 10 min stirring at room temperature. Then, Cul (0.201 g, 1.084 mmol) and 1,10-phenanthroline (0.195 g, 1.084 mmol) were added and the mixture was stirred for 3.5 h at 125°C. The mixture was allowed to cool to room temperature and was filtered. The solids were washed with chloroform and then dissolved in 25% NH₄OH (30 mL). The aqueous phase was then extracted with CHCI3. The organic phases were combined, and the solvents evaporated. The concentrated paste was redissolved in CHCl3 and extracted with NH4OH until no blue color was observed. To separate the unreacted amine 2, HCI (10 wt% in water) was added to the organic phase and extracted. The organic phase was then washed with saturated NaHCO3, dried over Na2SO4, filtered and evaporated. At this stage, the mixture could be used for the next step without further purification. Alternatively, the pure amine 3 could be isolated by column chromatography using CHCl₃ as an eluent (Rf = 0.85). In this case, it is obtained as a brown solid (695 mg, 35% yield).¹H NMR (300 MHz, CDCl₃) δ 7.39 (dd, J = 20.4, 7.7 Hz, 3H), 7.29 – 7.19 (m, 2H), 6.94 – 6.86 (m, 5H), 6.73 (d, J = 7.6 Hz, 4H), 6.58 (t, J = 7.5 Hz, 1H), 6.45 (d, J = 7.9 Hz, 1H), 3.26 (s, 2H), 2.26 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 147.16, 145.90 (2C), 144.08, 137.24 (2C), 133.13, 131.34 (2C), 130.96 (2C), 130.31, 129.75, 129.16, 128.47, 126.32, 125.49, 122.76, 122.76, 118.80, 115.99, 115.43, 21.19 (2C). HRMS (APCI Solid Probe MS+) [M+]calculated: 365.2012 . [M+]found: 365.2021. m.p.123-125°C.

9,9-di-p-tolyl carbazolium hexafluorophosphate(4)

Amine 3 (0.3g, 0.824 mmol) was dissolved in glacial acetic acid (4 mL) in an Erlenmeyer (25 mL). The solution was cooled to 0°C in an ice bath. The frozen acetic acid is crushed with a metallic spatula before NaNO₂ (0.3 q, 4.35 mmol) in water (0.4 mL) was added, and the slurry mechanically stirred for 20 min. Urea (0.23 g, 3.8 mmol) was added next, and the mixture stirred for 1 h at 40°C. The solvents were evaporated, and the residue dissolved in CHCl₃. The non-soluble part was filtered and washed with CHCl_{3.} The filtrate was concentrated in vacuo and separated using extraction with water and ether. Water and acetic acid were removed in vacuo by freeze-drying. The acetate produced is highly hygroscopic and difficult to be quantified. To quantify the reaction yield and obtain single crystals, 4 was converted to the hexafluorophosphate by addition to a saturated solution of NH₄PF₆. 4 hexafluorophosphate precipitates and the solids are filtered and washed with water and ether. The red-brown solids are then dried under vacuum (220 mg, 54% yield).¹H NMR (300 MHz, D₂O) δ 8.04 (dd, J = 7.8, 0.9 Hz, 2H), 7.71 – 7.62 (m, 2H), 7.60 – 7.42 (m, 4H), 7.08 (dt, J = 6.7, 5.8 Hz, 8H), 2.21 (s, 6H). $^{13}\mathrm{C}$ NMR (101 MHz, D_2O) δ 181.31, 149.98, 143.93, 142.09, 132.06, 130.75, 129.99, 123.00, 121.84, 121.25, 23.18, 19.90. HRMS (TOF MS ES+): [M]_{calculated}: 348.1752. [M]_{found}: 348.1793. m.p. 195-200 °C (decomp.)

2'-(9-carbazolyl)-[1,1'-biphenyl]-2-amine (5):

5 was prepared using the same procedure used for compound **4**. In this case, 2,2'-diiodobiphenyl (500 mg, 1.23 mmol) was reacted with **2** (225 mg, 1.22 mmol). The reaction was performed under argon, at 125 °C for 7 days. Following workup, **5** could be isolated by column chromatography using a mixture of CHCl₃/Hexane (7:3) as eluent (Rf = 0.8). Yellow solid

 $\begin{array}{l} (182 \text{ mg}, 20\% \text{ yield}).^{1}\text{H} \text{ NMR} (400 \text{ MHz}, \text{CDCI3}) \, \delta \, 7.91 \, (s, 2\text{H}), 7.63 - 7.54 \\ (m, 1\text{H}), 7.47 \, (dt, J = 9.3, 4.0 \text{ Hz}, 3\text{H}), 7.13 \, (t, J = 40.4 \text{ Hz}, 6\text{H}), 6.72 - 6.63 \\ (m, 1\text{H}), 6.57 \, (dd, J = 7.6, 1.2 \text{ Hz}, 1\text{H}), 6.33 \, (d, J = 7.9 \text{ Hz}, 1\text{H}), 6.18 \, (t, J = 7.4 \text{ Hz}, 1\text{H}). \, ^{13}\text{C} \text{ NMR} \, (101 \text{ MHz}, \text{CDCI3}) \, \delta \, 143.26, \, 138.50, \, 136.15, \\ 132.22, \, 130.39, \, 129.78, \, 129.09, \, 128.83, \, 128.72, \, 125.65, \, 123.66, \, 123.22, \\ 120.16, \, 119.61, \, 118.21, \, 115.69, \, 110.22, \, 109.70. \, \text{HRMS} \, (\text{APCI Solid Probe} \\ \text{MS+}): \, [\text{M+}]_{\text{calculated}}: \, 335.1543. \, [\text{M+}]_{\text{found}}: \, 335.1516. \, \text{m.p.} \, 156-158^{9}\text{C.}^{[49]} \end{array}$

9,9-spirobiscarbazolium acetate (6):

The compound was prepared following the procedure described in the preparation of compound **4**. The product was obtained as an off-white solid (100mg, 49% yield). ¹H NMR (400 MHz, DMSO) δ 8.53 – 8.46 (m, 4H), 7.87 (dd, J = 11.1, 4.1 Hz, 4H), 7.59 – 7.48 (m, 4H), 7.31 (d, J = 8.3 Hz, 4H), 1.72 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 159.76, 147.90, 132.71, 131.56 (d, J = 16.4 Hz), 123.88, 118.57, 23.66. HRMS (TOF MS ES+): [M]_{calculated}: 318.1283. [M]_{found}: 318.1295. m.p. (I⁻ form) 285-288°C (decomp.)^[49]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: fuel cell • quaternary ammonium • nucleophilic substitution • single electron transfer • tetraaryl ammonium

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Entry for the Table of Contents Reaction Mechanism

The reaction between different N,N-diarylcarbazolium salts and hydroxide are probed to understand the reaction mechanism. The regioselectivity of the reaction and an unexpected H/D exchange, indicate the reaction does not follow expected S_NAr , but follows a radical pathway.