kcal/mol for X = F, Cl, and Br, respectively; the simple curve crossing model, however, is certainly a rather crude approximation (see the above-mentioned VB analysis[28]).

This discussion shows that it is not possible at present to verify our predictions quantitatively by comparison with experimental information, except for the finding that all three reactions should have positive barriers ΔE^{B} of a few kilocalories per mole.

IV. Conclusions

From the present study the following main findings should be accentuated:

(1) The inclusion of electronic correlation effects is a prerequisite for a reliable description of the potential energy profile for S_N2 rearrangements in the systems $(XCH_3X)^-$ with X = F, Cl, and Br. For the potential well depths the correlation contributions are very small (a few tenths of a kilocalorie per mole) whereas for the activation barriers they amount to several kilocalories per mole. To determine the latter quantities accurately, advanced methods beyond the Hartree–Fock level and extended basis sets of at least DZDP quality are necessary.

(2) The geometrical parameters of the ion–dipole complexes correspond to a face-centered structure with C_{3v} symmetry.

(3) The ion–dipole complex stabilities are rather reliably obtained to lie in the ranges 11–13 kcal/mol for X = F and 8–9 kcal/mol for X = Cl and Br, for the latter in good accordance with experimental (HPMS) data.

(4) The geometrical structure of the transition configuration is trigonal-bipyramidal (D_{3h} symmetry).

(5) The uncertainties of the calculated barrier heights are much larger; cautious estimates should be 1–3 kcal/mol for X = F, 6–8 kcal/mol for X = Cl, and 2–4 kcal/mol for X = Br (relative to the reactants).

The correlation part is negative for X = F but positive for X = Cl and Br. Thus in the sequence F–Cl–Br a nonmonotonous change is obtained: $\Delta E^{\mathrm{B}}(\mathrm{Cl}) > \Delta E^{\mathrm{B}}(\mathrm{Br}) \gtrsim \Delta E^{\mathrm{B}}(\mathrm{F})$ for the barriers, $\Delta E^{\mathrm{IB}}(\mathrm{Cl}) > \Delta E^{\mathrm{IB}}(\mathrm{F}) > \Delta E^{\mathrm{IB}}(\mathrm{Br})$ for the intrinsic barriers, in the latter case with somewhat smaller gradation between Cl and F systems.

At present, no conclusive comparison with experimental data is possible.

(6) For X = F and Cl at the Hartree–Fock SCF and CI levels, as well as for X = Br at the Hartree–Fock SCF level, the pseudo-potential results agree reasonably well with all-electron results. For the ion–dipole complex stabilities the correspondence is almost perfect; for the barrier heights, there are increasing differences in the sequence F–Cl–Br but retaining the trend.

Summarizing, the results of the present study should stimulate further experimental work to provide more complete and reliable data on rate constants and complex stabilities but also theoretical investigations for analyzing measured quantities, as well as predicting more accurate potential energy characteristics and possibly kinetic parameters.

Acknowledgment. We are indebted to Prof. S. D. Peyerimhoff (Bonn) for placing at our disposal the MRD-CI program package and for giving advice on computational aspects. Many thanks are also due to Dr. J. P. Daudey (Toulouse) for providing us with his PSHONDO program and to Dr. P. C. Hiberty (Orsay) for useful discussions. The services and computer time made generously available by the Rechenzentrum des Zentralinstituts für Astrophysik der AdW der DDR (Potsdam) are gratefully acknowledged.

Note Added in Proof. After submission of the manuscript, two recent theoretical papers came to our knowledge in which, at the Hartree–Fock and MP2 levels with basis sets not too different in quality from ours, ion–dipole complexes and transition configurations of S_N2 systems, eqs 1 and 2, are investigated. Z. Shi and R. J. Boyd (*J. Am. Chem. Soc.* **1989**, *111*, 1575) report mainly on geometrical and charge distribution characteristics of an extended series of systems; the structural parameters obtained for $F^- + CH_3F$ and $Cl^- + CH_3Cl$ in Hartree–Fock approximation are in close agreement with our results. Geometries, energies, and vibrational frequencies for the $Cl^- + CH_3Cl$ system are calculated by S. C. Tucker and D. G. Truhlar (*J. Phys. Chem.* **1989**, *93*, 8138). These authors conclude that electron correlation (MP2 level) has a noticeable effect on the optimized geometries and on vibrational frequencies; nevertheless their data are still qualitatively in accordance with ours. The complex stabilization energy is somewhat larger compared with our values; the barrier height, however, is significantly smaller ("best" result ~4.5 kcal/mol), not unexpected for the MP2 approximation.

Registry No. CH_3F, 593-53-3; CH_3Cl, 74-87-3; CH_3Br, 74-83-9; $(FCH_3F)^-$, 56448-24-9; $(ClCH_3Cl)^-$, 127182-89-2; $(BrCH_3Br)^-$, 127182-90-5.

On the Determination of Redox Potentials of Highly Reactive Aromatic Mono- and Multications

Michael Dietrich and Jürgen Heinze*

Contribution from the Institut für Physikalische Chemie der Universität Freiburg, Albertstrasse 21, D-7800 Freiburg, Federal Republic of Germany. *Received October 31, 1989. Revised Manuscript Received March 12, 1990*

Abstract: Thermodynamic redox potentials of reactive mono- and multiple charged cations of aromatic systems can be accurately determined by cyclic voltammetry by using solvents such as SO_2 or CH_2Cl_2, a sophisticated sample preparation technique, low temperatures, and an appropriate time scale in the experiment. These conditions allow inter alia the measurement, for the first time, of the redox potentials (vs Ag/AgCl) of the reversible mono-, dication (tri- or tetracation) formation of naphthalene (1.67 V), fluoranthene (1.46 V), triphenylene ([di] 2.49 V), α,α-binaphthyl ([mono] 1.58 V, [di] 1.86 V), benzo[*c*]benzo-[3,4]cinnolino[1,2-*a*]cinnoline ([tri] 2.75 V), hexamethoxytriphenylene ([tetra] 2.27 V), 5,5′-dimethyl-2,2′-bithienyl ([mono] 1.08 V, [di] 1.68 V), and 3,3′-dimethoxy-2,2′-bithienyl (0.79 V).

The thermodynamic oxidation potentials of many aromatic systems, obtained either by polarographic or by voltammetric techniques, have been reported several times in the literature.[1]

In recent years new exciting fields of research have been de-

Table I. Redox Potentials and Peak Current Ratios of Various Arenes in Liquid SO_2

arene	T, °C	v, V/s	$E_1°$, V	i_{pc}/i_{pa}	$E_2°$, V	i_{pc}/i_{pa}	$E_3°$, V	i_{pc}/i_{pa}	$E_4°$, V	i_{pc}/i_{pa}
benzo[*c*]benzo[3,4]cinnolino[1,2-*a*]cinnoline	−50	0.2	0.56	1.00	1.17	1.00	2.75	0.73		
tetraphenylhydrazine	−20	0.2	0.80	1.00	1.55	1.00				
anthracene	−50	0.2	1.25	0.92	2.02	0.90				
9,10-diphenylanthracene	−40	0.2	1.20	1.00	1.74	1.00				
9,9′-dianthryl	−50	0.5	1.27	1.00	1.48	1.00	2.17	1.00	2.35	0.65
naphthalene	−40	0.05	1.67	0.60						
pyrene	−52	0.2	1.22	1.00	2.20[c]					
perylene[b]	−40	0.2	0.94	1.00	1.64	0.85				
fluoranthene[b]	−40	0.2	1.46	<0.3						
triphenylene	−50	0.2	1.73	0.3	2.49	<0.5				
α,α'-binaphthyl	−50	50.0	1.58	0.97	1.86	0.91				
β,β'-binaphthyl	−50	50.0	1.40	1.00	2.00	0.90				
2,3,6,7,10,11-hexamethoxytriphenylene	−50	0.05	1.13	1.00	1.48	1.00	1.79	1.00	2.27	1.00
2,3,6,7,10,11-hexapentoxytriphenylene[d]	−50	0.2	1.0		1.5		1.7		2.15	1.00
2,3,6,7-tetrapentoxytriphenylene-10,11-dicarbonic acid dimethyl ester[d]	−40	5.0	1.23		1.53		2.34		2.62[c]	
hexakis(dimethylamino)benzene[b]	−50	100.0	0.66	1.00	0.91	1.00	1.99	0.9		
5,5′-dimethyl-2,2′-dithienyl	−50	1.0	1.08	*a*	1.68	0.65				
4,4′,5,5′-tetramethyl-2,2′-dithienyl	−50	1.0	0.99	*a*	1.48	0.77				
3,3′,4,4′,5,5′-hexamethyl-2,2′-bithienyl	−50	1.0	1.00	*a*	1.37	0.89				
3,3′-dimethoxy-2,2′-bithienyl	−40	100.0	0.79	<0.5						

[a] Cyclic voltammetry was performed at a Pt electrode (ϕ = 1 mm) with solution 10^{-4}–10^{-3} M in substrate. All redox potentials were determined from the average of the cathodic and anodic peak potentials and are expressed in V vs Ag/AgCl (calibrated by using an internal ferrocene standard); T between −20 °C and −50 °C. [b] The standard potentials were determined in CH_2Cl_2. [c] Irreversible. [d] Signals are disturbed by adsorption effects.

veloped dealing with unconventional materials such as radical cation salts,[2] conducting polymers,[3] and organic ferromagnetics.[4] In numerous cases these materials are prepared by chemical or electrochemical oxidation of aromatic hydrocarbons or heterocycles and develop their unusual properties in the oxidized state.

Thus, the oxidation of aromatic systems to their respective dications or higher charged states and the formation of other highly reactive cations have attracted increasing interest. Their study provides information about the thermodynamics and kinetics of charged π-systems, which may increase our knowledge about advanced materials and improve strategies for the development of new properties. Heinze et al. used the results of their cyclic voltammetric studies on the anodic redox properties of monomeric and oligomeric systems to develop a model for the charge storage mechanism of conducting polymers[5] and to improve their electropolymerization.[6]

The reduction of aromatic hydrocarbons to their respective dianions or more highly charged states in alkylamine solutions has recently been described by Meerholz and Heinze.[7]

The proper choice and purification of the solvent are even more crucial for anodic oxidation than for the cathodic reduction, because highly charged cations react very easily with nucleophilic impurities or, as is usually the case, with the nucleophilic solvent itself. Moreover, many cations undergo fast dimerization reactions, which render the measurement of thermodynamic oxidation potentials extremely difficult.

In the past, a standard solvent for anodic oxidation studies was acetonitrile; however, due to its nucleophilicity it is less suitable for the detection of reactive intermediates. In 1979 Tinker and Bard showed that liquid SO_2 is an excellent solvent for the reversible generation of reactive cations because of its low nucleophilicity and its ability to solvate ionic compounds as well as covalent substrates.[8] Dietrich, Heinze, and Mortensen were able to electrochemically oxidize 9,9′-dianthryl in four reversible redox steps to its tetracation in liquid SO_2.[9] Its average lifetime was estimated to be about 1 s. Another suitable solvent for the study of highly reactive cations is CH_2Cl_2. In 1972 L. Byrd et al. described the anodic oxidation of several arenes in CH_2Cl_2 and observed the formation of the dication of rubrene, which was stable within the experimental time scale.[10]

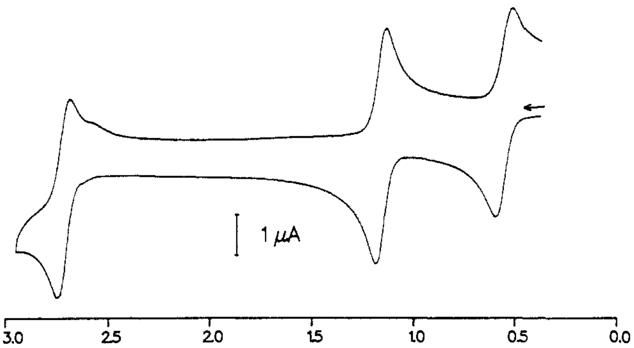

Figure 1. Cyclic voltammogram for the oxidation of benzo[*c*]benzo[3,4]cinnolino[1,2-*a*]cinnoline in liquid SO_2/0.1 M $TBAPF_6$ ($c = 1 \times 10^{-3}$ M, v = 200 mV/s, T = −50 °C).

As important as the proper choice of solvents is its purification. Careful purification together with a standard sample preparation technique produces a solvent–electrolyte system known in electrochemical jargon as "waterfree". However, it is impossible to remove all traces of water from the walls of the cell and the supporting electrolyte. Thus, the available potential range is smaller than theoretically possible, and the produced cations are not as stable as they would be in the absence of the water. To avoid this problem Hammerich and Parker added superactive alumina to the voltammetric cell,[11] but this method cannot be used with sensitive substances or for quantitative measurements. To avert contamination during the voltammetric experiment, we use special electrochemical cells that enable drying of the solvent–electrolyte system with superactive alumina.[12,13]

---

(1) Weinberg, N. L.; Weinberg, H. R. *Chem. Rev.* **1968**, *68*, 449–523. Marcoux, L. S.; Fritsch, J. M.; Adams, R. N. *J. Am. Chem. Soc.* **1967**, *89*, 5766–5769. Peover, M. E.; White, B. S. *J. Electroanal. Chem. Interfac. Electrochem.* **1967**, *13*, 93–99.

(2) Fritz, H. P.; Gebauer, H.; Friedrich, P.; Ecker, P.; Artes, R.; Schubert, U. *Z. Naturforsch.* **1978**, *B33*, 498–506. Wegner, G.; Kröhnke Ch.; Enkelmann, V. *Angew. Chem.* **1980**, *92*, 941–942; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 912–913. Enkelmann, V.; Morra, B. S.; Kröhnke, Ch.; Wegner, G.; Heinze, J. *Chem. Phys.* **1982**, *66*, 303–313.

(3) Heinze, J. *Top. Curr. Chem.* **1989**, *152*, 1–48.

(4) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927–938. Thomaides, J.; Maslak, P.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 3970–3979.

(5) Heinze, J.; Störzbach, M.; Mortensen, J. *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 960–967.

(6) Heinze, J.; Hinkelmann, K.; Land, M. *DECHEMA-Monographie* **1988**, *112*, 75–87.

(7) Meerholz, K.; Heinze, J. *J. Am. Chem. Soc.* **1989**, *111*, 2325–2326.

(8) Tinker, L. A.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 2316–2319.

(9) Dietrich, M.; Mortensen, J.; Heinze, J. *Angew. Chem.* **1985**, *97*, 502–503; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1225–1226.

(10) Byrd, L.; Miller, L. L.; Pletcher, D. *Tetrahedron Lett.* **1972**, 2419–2422.

(11) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 519–522.

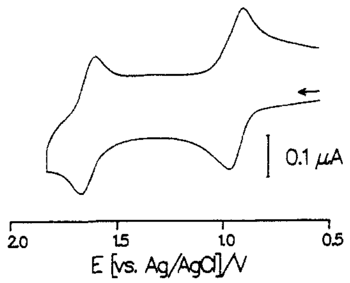

Figure 2. Cyclic voltammogram for the oxidation of perylene in liquid SO_2/0.1 M $TBAPF_6$ ($c = 3 \times 10^{-4}$ M, v = 500 mV/s, T = -20 °C).

In the following we will report on the determination of reversible oxidation potentials of highly reactive cations achieved with optimal solvents, a special sample preparation technique, low temperatures, and an appropriate time scale in the voltammetric experiment. A sizeable number of redox data were determined for the first time or could be accurately measured.

Results and Discussion

The redox potentials of all systems studied were determined from cyclic voltammetric data. They are summarized in Table I. As already mentioned there are two classes of electrogenerated cations. In the first, the species are in principle stable and react only with nucleophilic impurities in the solvent-electrolyte system. In the second, the cations themselves undergo dimerization or decay reactions. It is obvious that for systems belonging to the first class a "perfectly" purified solvent is sufficient for the reversible generation of cationic species. As long as no solubility problems arise, the solvent of choice is alumina-dried SO_2 because its anodic potential limit with $TBAPF_6$ as supporting electrolyte exceeds a value of +3.6 V vs Ag/AgCl.

Cyclic voltammetry of benzo[*c*]benzo[3,4]cinnolino[1,2-*a*]cinnoline in $SO_2/TBAPF_6$ at a sweep rate of 200 mV/s indicates the reversible formation of a trication at +2.75 V (Figure 1). The life time of this species is about 1 s. This experiment documents that even redox states with $E°$ values near 3 V can be measured, provided that the nucleophilicity of the solvent is weak and that dimerization or decay reactions of the electrophore are slow. We were also able to reversibly generate the dication of tetraphenylhydrazine in liquid SO_2 at -20 °C, which is stable far beyond the time scale of the voltammetric experiment. In agreement with expectations, the mono- and dications of anthracene show also a very high stability. By contrast, in acetonitrile already the monocation of anthracene reacts with the solvent via a nucleophilic addition.[14] The high sensitivity of these cations to nucleophilic impurities is documented by the fact that, in SO_2 dried with P_2O_5, all (tri-) dications react via irreversible follow-up steps.

The cations of the aromatic hydrocarbons naphthalene, pyrene, perylene, fluoroanthene, and triphenylene are sensitive to nucleophiles in the solvent-electrolyte system and as electrophiles usually tend to attack the neutral hydrocarbons forming charge-transfer complexes or react with each other producing covalently bonded dimers or higher oligomers[2,3] (eqs 1 and 2).

$$ArH_2 \rightleftarrows ArH_2^{\bullet+} + e \qquad (1a)$$

$$ArH_2^{\bullet+} + ArH_2 \rightleftarrows (ArH_2)_2^{\bullet+} \qquad (1b)$$

$$(n + 2)ArH_2 \rightarrow HAr(Ar)_nArH^{(nx)+} + (2n + 2)H^+ + (2n + 2 + nx)e^- \qquad (2)$$

Thus, the redox potentials for the first and second oxidation steps of these arenes could only be determined at low concentrations, temperatures below -40 °C, and high sweep rates. It was possible to generate anodically the extremely reactive dications of pyrene and perylene and to characterize them by cyclic voltammetry. Figure 2 shows the cyclic voltammogram of perylene at -40 °C and a sweep rate of 200 mV/s. Owing to the high reactivity of the perylene dication, only quasi-reversible voltammograms for the second electron-transfer step have been observed. The generation of the dications of fluoranthene and triphenylene are completely irreversible, while no dication formation within the accessible potential range could be observed in the case of naphthalene.

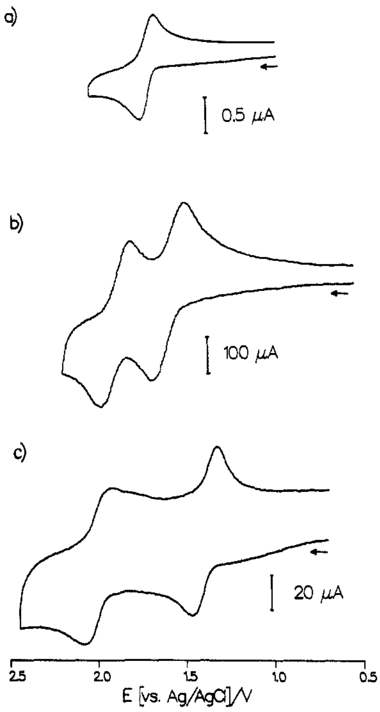

Figure 3. Cyclic voltammograms for the oxidation of (a) naphthalene (T = -50 °C, v = 400 mV/s), (b) α,α'-binaphthyl (T = -20 °C, v = 50 V/s, $c = 10^{-3}$ M), and (c) β,β'-binaphthyl (T = -50 °C, v = 50 V/s, $c = 10^{-3}$ M) in liquid SO_2/0.1 M $TBAPF_6$.

Figure 3 shows the cyclic voltammograms of naphthalene, β,β'-binaphthyl, and α,α-binaphthyl. Although β,β'-binaphthyl and α,α'-binaphthyl tend to dimerize, forming charge-transfer complexes or poly(naphthalene), nevertheless at -50 °C in liquid SO_2 it was possible to generate the fully reversible monocation of β,β'-binaphthyl in the time scale of slow sweep voltammetry, whereas the oxidation steps to the monocation of the α,α'-isomer and to the dications of both systems exhibited reversible behavior only at low temperatures and high sweep rates. The different redox potentials of α,α'-binaphthyl and β,β'-binaphthyl are explained by the different torsion angles between the two naphthalene units. In the case of α,α'-binaphthyl this angle is $\Phi = 48°$, whereas β,β'-binaphthyl has a nearly planar structure ($\Phi = 0°$).[15] This allows a better conjugation of the two π-systems of β,β'-binaphthyl than of the α,α'-isomer; therefore the first reversible oxidation step of β,β'-binaphthyl occurs at lower potentials, leading to a more stable cation. The second electron is harder to remove in the case of the planar system because of the greater interaction between the two charges. Consequently, the α,α'-isomer with its higher oxidation potential has, in comparison to the β,β'-isomer, higher reactivity and dimerizes already at the monocation level, while β,β'-binaphthyl reacts only at the dication level. On the other hand, the α,α'-isomer shows a reasonable tendency to form charge-transfer complexes and to yield crystalline radical cation salts.[16]

Hexasubstituted triphenylene and benzene derivatives are model compounds of organic ferromagnetics.[4] If their dications form a ground-state triplet, a ferromagnetic interaction is expected in

---

(12) (a) Heinze, J. *Angew. Chem.* **1984**, *96*, 823-840; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831-847. (b) Hinkelmann, K.; Heinze, J.; Schacht, H.-T.; Field, J. S.; Vahrenkamp, H. *J. Am. Chem. Soc.* **1989**, *111*, 5078-5091.

(13) Kiesele, H. *Anal. Chem.* **1981**, *53*, 1952-1954.

(14) Howell, J. O.; Wightmann, R. M. *Anal. Chem.* **1984**, *56*, 524-529.

(15) Le Fèvre, J. W.; Sundaram, A.; Sundaram, K. M. S. *J. Chem. Soc.* **1963**, 3180-3188.

(16) Dietrich, M.; Heinze, J. Unpublished results.

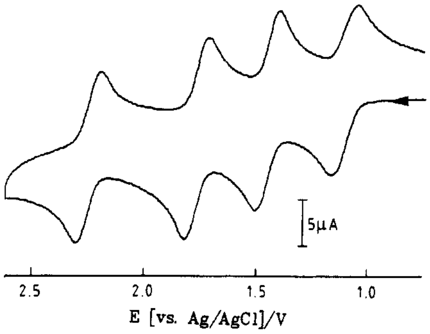

Figure 4. Cyclic voltammogram for the oxidation of 2,3,6,7,10,11-hexamethoxytriphenylene in liquid SO_2/0.1 M $TBAPF_6$ ($c = 1 \times 10^{-3}$ M, $v = 5$ V/s, $T = -40$ °C).

organic solids with an appropriate anion radical acceptor. Therefore, it is important to know if such systems have low-lying redox potentials or may easily undergo disproportionation reactions. The formation of the trication of 2,3,6,7,10,11-hexamethoxytriphenylene has been described in the literature.[17] We were able to generate the tetracation of this species with an unusually high average lifetime of 36 s at −25 °C in liquid SO_2 (Figure 4). It is interesting to note that the redox potential separation between the mono- and dication is similar to those between the di- and trication and between the tri- and tetracation. This supports the view that the excess charges are localized near the heteroatoms and that their coulombic repulsions are relatively small.

By contrast, high sweep rates are necessary to observe the reversible formation of the trication of 2,3,6,7-tetrapentoxytriphenylene-10,11-dicarbonic acid dimethyl ester. The cyclic voltammograms of the oxidation of 2,3,6,7,10,11-hexapentoxytriphenylene are disturbed by adsorption effects. Thus, it was impossible to determine the redox potentials, and the values given in Table I may differ by ±100 mV from the exact redox potentials.

The monocation of hexakis(dimethylamino)benzene is very reactive, and a reversible oxidation step could be seen only at temperatures below −40 °C and high sweep rates. Its oxidation potential is 0.66 V. This is a very high value compared to the $E° = -0.206$ V of 1,4-bis(dimethylamino)benzene and the $E° = -0.266$ V of 1,2,4,5-tetrakis(dimethylamino)benzene.[18] The explanation is that in the case of the hexasubstituted benzene steric interactions between the dimethylamino substituents cause twisting strong enough to diminish their cation-stabilizing effect.

The radical cations and dications of 5,5′-dimethyl-2,2′-bithienyl, 4,4′,5,5′-tetramethyl-2,2′-bithienyl, and hexamethyl-2,2′-bithienyl are very reactive species. Up to now, it has been impossible to detect reversible oxidation states of simple thiophenes on account of their pronounced tendency to form conducting polymers. Their reversible formation has not been observed at low temperatures and high sweep rates. The first oxidation step of the methylated bithienyls is affected not only by inductive factors but also by the sterical interaction between the methyl groups. This is demonstrated by the fact that not the highest substituted bithienyl but the tetrasubstituted one exhibits the lowest oxidation potential. The energetic separation between the first and the second transition decreases linearly with the number of substituents. Extrapolation gives a value of 700 mV for the separation in the case of the unsubstituted bithienyl. This corresponds to a repulsion energy of 70–80 kcal/mol, an important value for the discussion of charge storage in conducting polymers.[3,19] By introducing the cation-stabilizing methoxy substituent, we have succeeded in reversibly generating the cation of 3,3′-dimethoxy-2,2′-bithienyl in which the reactive 5,5′-positions are not substituted. Under normal conditions this monomer electropolymerizes to yield poly(methoxythiophene).

In conclusion by using appropriate experimental conditions it is now possible to generate reversibly highly reactive cations.

Experimental Section

Purification Procedures. Commercially available SO_2 (Messer-Griesheim) was condensed at −70 °C under nitrogen atmosphere in a glass vessel equipped with basic alumina (ICN, Super B1) and a magnetic stirrer. The vessel was then partly evacuated, and the solvent was refluxed for half an hour in the temperature range between −40 °C and −10 °C depending on the quality of the vacuum. After this procedure SO_2 was condensed under vacuum conditions in a thoroughly dried flask and stored there prior to use at −70 °C.

Technical grade CH_2Cl_2 was stirred several days with concentrated H_2SO_4. The organic phase was then washed with water until all the acid had been removed, stirred with a 1 molar aqueous Na_2CO_3 solution, and washed again with water. The solvent was then dried over $CaCl_2$, K_2CO_3, and CaH_2 and finally distilled under nitrogen atmosphere. The purified CH_2Cl_2 was stored in a thoroughly dried flask away from light at 0 °C. The anodic potential limit with $TBAPF_6$ as supporting electrolyte lies at +2.8 V (vs Ag/AgCl).

Electrochemical Measurements. All electrochemical experiments were carried out in specially constructed cells containing an internal drying column with highly activated alumina.[12,13] The working electrode was a Pt disk sealed in soft glass (1.0-mm diameter). A Pt wire, wrapped around the glass of the working electrode, was used as the counter electrode. The reference electrode was an Ag wire, on which AgCl had been deposited electrolytically, immersed in the electrolyte solution. Potentials were calibrated with ferrocene (+0.352 V vs Ag/AgCl).

The measurements were performed with an AMEL Model 553 potentiostat and a PAR 175 programmer. Data were recorded with a Philips Model PM 8131 X-Y-recorder. For the higher scan rates a Model TRC 4070 Krenz transient recorder was used.

Acknowledgment. We gratefully acknowledge support by the Stiftung Volkswagenwerk and the Fonds der Chemischen Industrie. We are indebted to J. Wolff and G. Wenz for carrying out the synthesis of hexakis(dimethylamino)benzene and substituted triphenylenes.

---

(17) Bechgaard, K.; Parker, V. D. *J. Am. Chem. Soc.* **1972**, *94*, 4749–4750.

(18) Elbl, K.; Krieger, C.; Staab, H. A. *Angew. Chem.* **1986**, *98*, 1024–1026; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1023–1025.

(19) Heinze, J.; Dietrich, M.; Mortensen, J. *Makromol. Chem. Macromol. Symp.* **1987**, *8*, 73–81.