

tometer equipped with a locally modified LT-1 low-temperature device. No decay in the intensity of standard reflections was observed during the data collection.

The structure was solved by direct methods in the space group $P2_1/n$. All computing was carried out by using SHELXTL Version 5 programs installed in a Data General Eclipse computer. Atomic scattering factors and anomalous dispersion corrections were from common sources.²⁷ An absorption correction was applied,²⁸ and the structure refinement pro-

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ceeded smoothly. All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were refined by using a riding model in which an idealized C-H vector, 0.96 Å in length, was recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded atom.

Further details are in Table I. Atom coordinates are given in Table II. Selected bond distances and angles are given in Table III.

Acknowledgment. We thank the NATO Scientific Affairs Division for financial support; a scholarship from the "Studienstiftung des Deutschen Volkes" for M.M. is gratefully acknowledged.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (6 pages); listings of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

Spontaneous Oxidation of Xenon to Xe(II) by Cationic Ag(II) in Anhydrous Hydrogen Fluoride Solutions

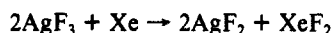
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Contribution from the Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720, and "Jožef Stefan" Institute, "Edvard Kardelj" University, 61000 Ljubljana, Yugoslavia.

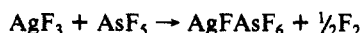
Received January 3, 1990

Abstract: Blue solutions, prepared by dissolving AgF_2 in anhydrous hydrogen fluoride (AHF) with BF_3 or AsF_5 , oxidize Xe, at $\sim 20^\circ\text{C}$, to produce nearly colorless solids. Overall reactions (all in AHF) are as follows: $2\text{AgF}_2 + 2\text{BF}_3 + \text{Xe} \rightarrow \text{XeF}_2 + 2\text{AgBF}_4$; $4\text{AgF}_2 + 5\text{AsF}_5 + 2\text{Xe} \rightarrow \text{Xe}_2\text{F}_3\text{AsF}_6 + 4\text{AgAsF}_6$. Solid AgF_2 does not interact, at $\sim 20^\circ\text{C}$, with Xe. Ag(I) in AHF is catalytic to the interaction of Xe with F_2 ($\text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2$), but XeF_2 precipitates AgF_2 from Ag(II) AHF solutions (e.g. $\text{AgFAsF}_6 + 2\text{XeF}_2 \rightarrow \text{Xe}_2\text{F}_3\text{AsF}_6 + \text{AgF}_2$). To maintain the Ag(I/II) catalyst the fluoride-ion donor, XeF_2 , must be neutralized with acid, e.g. $2\text{Xe} + 2\text{F}_2 + \text{AsF}_5 \rightarrow \text{Xe}_2\text{F}_3\text{AsF}_6$.

A new approach to the synthesis of polymeric binary fluorides¹ has provided AgF_3 as a diamagnetic red solid, isostructural with AuF_3 . This fluoride² was found to oxidize xenon gas spontaneously at $\sim 20^\circ\text{C}$ according to the equation



In liquid anhydrous hydrogen fluoride (AHF), together with the strong fluoride ion acceptor AsF_5 , the AgF_3 reacted to form a blue solution with elimination of F_2 . From this solution the previously described Ag(II) salt,³ AgFAsF_6 , was isolated, the overall reaction being



When the oxidation of xenon was carried out with the AgF_3 , in AHF, in the presence of AsF_5 , it was observed that the silver was reduced to Ag(I) (i.e. AgAsF_6). This implied that cationic Ag(II) species were capable of oxidizing xenon and, therefore, that AgF_2 , in AHF, in the presence of strong fluoroacids should also do so. This has proved to be the case not only with $\text{AgF}_2/\text{AHF}/\text{AsF}_5$ but also with $\text{AgF}_2/\text{AHF}/\text{BF}_3$. In addition Ag(I/II) in AHF has been shown to catalyze the combination of Xe with F_2 in the presence of AsF_5 to yield $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$.

Results and Discussion

Although solid AgF_2 does not oxidize xenon at ordinary temperatures and pressures, the blue solutions, prepared by the interaction of AgF_2 with fluoride ion acceptors such as AsF_5 or BF_3 in AHF, quickly do so at $\sim 20^\circ\text{C}$. That the strongly oxidizing character of these blue solutions is associated with cationic Ag(II) is indicated by the structures of the deep blue solids, AgFAsF_6 , and $\text{Ag(SbF}_6)_2$ first prepared and described^{3,4} by Gantar et al.

In the AgFAsF_6 structure,³ fluorine ligands symmetrically bridge the Ag(II) in $(\text{AgF})_n^{n+}$ chains. It is probable that such chains also occur in the dark blue solid of composition AgFBF_4 isolated in the course of this work (see Table I). Perhaps the AHF solutions, of these 1:1 compounds of AgF_2 with fluoride ion acceptors, contain solvated AgF^+ species. These 1:1 compounds are not highly soluble in AHF, however, and the interactions of these solutions with Xe are sluggish in comparison with the Ag(II) solutions obtained when additional BF_3 or AsF_5 is used. Two moles of fluoride ion acceptor to one mole of Ag(II) appears to be optimal. This stoichiometry suggests that the oxidizing species

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[†] Institut Jožef Stefan, Ljubljana.

[‡] University of California.

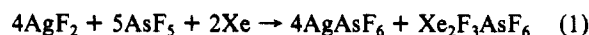
Table I. X-ray Powder Data for AgBF₄^a (CuK α Ni Filter)

I/I ₀	1/d ² × 10 ⁴		hkl	I/I ₀	1/d ² × 10 ⁴		hkl	I/I ₀	1/d ² × 10 ⁴		hkl
	obsd	calcd			obsd	calcd			obsd	calcd	
s	442	446	110	m	6221	6205	501, 150	w	10110	10078	423, 243
m	623	624	001			6205	431, 341			10085	532, 352
vs	845	847	101, 011	w	6300	6290	412, 142	m	10202	10203	104, 014
vs	889	893	200, 020			6427	511, 151			10425	114
		1070	111	m	6522	6507	203, 023			10530	602, 062
w	1520	1517	201, 021			6513	332			10668	631, 361
s	1738	1740	211, 121	w	6723	6730	213, 123	w	10747	10755	612, 162
m	1792	1786	220	mb	6988	6960	422, 242			10871	204, 042
vs	2239	2232	310, 130			7097	521, 251	m	11089	11096	214, 124
vw	2427	2410	221	mb	7144	7143	440	m	11144	11162	710, 170
m	2506	2495	002	wb	7411	7400	223			11162	550
s	2637	2633	301, 031	mb	7615	7590	530, 350			11193	503, 053
m	2718	2718	102, 012			7623	303, 033			11193	433, 343
w	2871	2856	311, 131			7766	441			11416	513, 153
m	2944	2941	112	mb	7847	7846	313, 133			11423	622, 262
m	3393	3388	202, 022			8036	600, 060			11561	701, 071
sb	3532	3526	321, 231	wb	8077	8076	502, 052	mvb	11632	11608	640, 460
wb	3604	3572	400, 040			8076	432, 342			11648	542, 452
		3611	212, 122			8213	531, 351			11764	224
w	4036	4018	330	wb	8317	8299	512, 152			11784	711, 171
		4195	401, 041	vw	8534	8516	323, 233			11784	551
w	4304	4281	222			8659	601, 061	m	11995 α_1	11989	304, 034
mb	4441	4419	141, 411	m	8891	8883	611, 161		11984 α_2	11989	
		4465	420, 240	m	8961	8929	620, 260			12086	523, 253
mb	4508	4504	302, 032			8969	522, 252			12211	314, 134
		4641	331			9184	403, 043			12231	641, 461
s	4730	4727	312, 132			9408	413, 143	w	12508 α_1	12455	721, 271
vw	5098	5088	421, 241			9552	621, 261		12503 α_2	12540	632, 362
s	5399	5397	322, 232	w	9654	9632	333			12756	443
vw	5613	5614	003			9637	442	m	12902 α_1	12882	324, 234
mb	5822	5804	510, 150	w	9794	9776	541, 451		12913 α_2	12948	730, 370
		5837	103, 013			9979	004	w	13207 α_1	13204	533, 353
m	6068	6060	113						13194 α_2	13204	
		6067	402, 042								

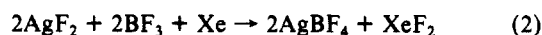
^a Tetragonal unit cell with (20 °C) $a_0 = 6.693$ (3) Å, $c_0 = 4.004$ (3) Å; $V = 179.4$ Å³; $z = 2$; possible space group, $P4/n$. If ...AgF₄AgF... chains exist in this structure they are constrained to run parallel to c_0 because the Ag–Ag distance in such a chain³ could not greatly exceed 4.0 Å and the number of Ag atoms in the unit cell is 2.

in AHF could be solvated Ag²⁺. Discrete Ag(II) occur in the structure⁴ of Ag(SbF₆)₂ and lie in elongated octahedral holes of a CdCl₂ type arrangement of Ag and SbF₆ species, the distortion being appropriate for a d⁹ electron configuration of Ag²⁺.

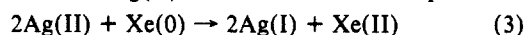
In the case of the AgF₂·2AsF₅ stoichiometry in AHF, the concentration of Ag(II) can exceed 0.8 mol per 1000 g of AHF. Such a solution, when well mixed with xenon, will interact completely within 30 min at 20 °C, the blue solution rapidly becoming paler and finally colorless. Simultaneously, colorless AgAsF₆ precipitates. The overall reaction in this case is



Because of the low solubility of BF₃ in AHF at 20 °C and its weakness as an acid relative to AsF₅, the impact of excess acid on the solubility of Ag(II) is less marked than in the AsF₅ case. Lower temperatures, however, enhance the solubility of the BF₃ in the solvent and perhaps thereby increase the concentration of Ag(II). But the rapid oxidation of the xenon is favored by higher temperatures; therefore for faster interaction of the Ag(II) and xenon in the AHF/BF₃ system at ambient pressures, thermal cycling of the mixture proves to be advantageous. Because of the relatively weak acidity⁵ of the BF₃, however, this oxidation of xenon by Ag(II) gives XeF₂ directly. Again, the dark blue Ag(II) system [this time containing much undissolved Ag(II)] interacts to yield colorless products, from which XeF₂ is recovered in high yield by vacuum sublimation. The overall reaction is

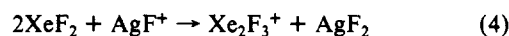


Precipitates of AgAsF₆ or AgBF₄ sometimes appear when AgF₂ is dissolved in the acidified AHF in apparatus that has not been fully dried under high-vacuum conditions. No such Ag(I) salts appear when all is scrupulously dry. Because of the formation of small quantities of Ag(I) salts at the outset, the yields of Xe(II) based on AgF₂ are, as a consequence, lower than indicated by eq 1 and 2. When the product of the AgF₂ dissolution in acidified AHF is fluorinated, to oxidize any Ag(I) formed to Ag(II) (and to destroy any water remaining in the system) the oxidation of xenon by the cationic Ag(II) is in accord with the requirement



All of the silver in the product is Ag(I) and all of the xenon is Xe(II). Attempts to oxidize Xe(II) to Xe(IV), or higher, with cationic Ag(II) have failed. This failure is probably a consequence of all of the Xe(II) in the solutions being in cationic forms, such as Xe₂F₃⁺ or XeF₂⁺, as a result of the required acidic conditions. Cationic Ag(II) would not attack cationic Xe(II).

Since each of AgBF₄ and AgAsF₆ in AHF is rapidly oxidized by elemental fluorine, at 20 °C, to the corresponding Ag(II) salt, which in turn can oxidize xenon, it was anticipated that Ag(I) would catalyze the combination of Xe with F₂ in AHF solution. This has proved to be so, but the superior basicity of XeF₂, relative to AgF₂, results in the precipitation of the latter fluoride as the XeF₂ concentration builds up.⁶



Therefore, in order to sustain the catalytic action of the Ag(I/II) species, it is necessary to add sufficient fluoride ion acceptor (A, e.g. BF₃ or AsF₅) to the 1:1 Xe/F₂ mixture to meet the neu-

(4) Gantar, D.; Leban, I.; Frlč, B.; Holloway, J. H. *J. Chem. Soc., Dalton Trans.* 1987, 2379.

(5) For evaluation of the fluoride ion affinities of BF₃, AsF₅, and other fluoroacids see: Mallouk, T. E.; Rosenthal, G. L.; Muller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* 1984, 23, 3167.

(6) Removal of AHF from such a solution yields a tetragonal adduct, AgAsF₆·2XeF₂, in which each Ag⁺ is square coordinated by four XeF₂ molecules, each XeF₂ being coordinated (through F) to two Ag⁺.

trahzation requirement expressed in the equation



The powerful-oxidizer character of cationic Ag(II) in AHF correlates with two fundamental aspects of Ag^{2+} gaseous ion: (1) the high electron affinity of the ion and (2) the strongly antibonding character of the d^9 electron configuration (antibonding both in σ and π character). The electron affinity (eV)⁷ of $\text{Ag}^{2+}(\text{g})$ (21.49) is higher than that of the $\text{Cu}^{2+}(\text{g})$ (20.29) or $\text{Au}^{2+}(\text{g})$ (20.5) and, indeed, even exceeds that of $\text{Xe}^{2+}(\text{g})$ (21.21). The Ag^{2+} species is the most powerful electron oxidizer of the electron-rich (and therefore of antibonding d configuration) transition-metal ions routinely available. Because of the strongly antibonding character of its d electron configuration, the Ag^{2+} may solvate no more effectively than Xe^{2+} , in which case the more favorable electron affinity of Ag^{2+} could even lead to solvated Xe^{2+} . Oxidation of Xe by AHF-solvated Ag^{2+} , to form species such as Xe^+ or $(\text{XeF})^+$, is highly favorable energetically. If solvated AgF^+ is the cationic Ag(II) of the acid AHF solutions, we can expect it to be weakly bound and of high electron affinity. It would be a strongly electrophilic fluorine atom source.

Evidently cationic Ag(II) species in fluoroacid AHF solution are oxidizing and fluorinating agents of great power and should be of wide potential utility, not least because they can be derived from readily obtainable reagents and without use of elemental fluorine. They are, effectively, F-atom sources.

Experimental Section

Materials. AgF_2 was prepared by fluorination of AgNO_3 (Reagent grade) with F_2 (~ 10 atm, at 20°C) in a Monel reactor at 220°C for 3 h with occasional removal of volatiles and reintroduction of F_2 . X-ray powder photography showed the dark brown solid to be indistinguishable from authentic samples of $\text{AgF}_{2.0}$ stoichiometry (Found: Ag, 74.2; F, 25.9. AgF_2 requires: Ag, 74.0; F, 26.0). Anhydrous HF (Matheson Gas Products, Newark, CA) was distilled from $\text{O}_2\text{Sb}_2\text{F}_{11}$ to ensure removal of water from it. AsF_5 and AgF (Ozark-Mahoning, Inc., Tulsa, OK), Xe (Airco, Riverton, NJ), and BF_3 (Matheson) were used as supplied. AgAsF_6 was prepared from AgF and AsF_5 in AHF and checked by X-ray powder diffraction (cubic, $a_0 = 7.745 \text{ \AA}$).⁸ Translucent fluorocarbon polymer tubing (FEP) was obtained from CHEMPLAST Inc., Wayne NJ, 07470.

Apparatus and Technique. All interactions were carried out in 0.5 in. o.d. Teflon FEP tubes sealed at one end and fused at 0.25 in. o.d. tubing to an overall length of ~ 10 in. Such vessels were connected via a Teflon valve to a metal vacuum line for fluorine handling as previously described.⁹ The Teflon valve had a Kel F stem with a Teflon tip, the seat side of the valve always being on the reactor side. Because of the strong corrosive action of HF/AsF_5 or BF_3 mixtures on the metal system and the associated generation of hydrogen, such mixtures were as far as possible avoided in the metal system. Mixtures containing AHF were stirred magnetically by Teflon-coated stirring bars and, in case of interaction of solutions with gaseous reactants, the tubes were inclined only slightly from the horizontal to maximize the liquid surface.

X-ray powder photographs were obtained with a 45-cm-circumference G. E. camera (Straumanis loading) with $\text{Cu K}\alpha$ radiation. Samples were usually packed in 0.3 or 0.5 mm o.d. quartz capillaries (Charles Supper Co.) sealed by drawing down in a small flame. Single crystals of XeF_2 or $\text{Xe}_2\text{F}_3\text{AsF}_6$ in 0.3–0.5-mm capillaries were each grown in a suitable temperature gradient and characterized by Polaroid photography with use of a Nonius precession camera with $\text{Mo K}\alpha$ radiation.

AgF_2 with AHF, AsF_5 , and Xe. AgF_2 (1.07 mmol), AHF (3 to 4 mL), and xenon (0.7 mmol) were stirred at 20°C . No uptake of xenon nor any visible sign of interaction of these reagents occurred within 30 min. When AsF_5 gas (0.1 mmol) was admitted to the tube a pale blue green coloration of the AHF occurred, but this color faded rapidly, the AgF_2 diminished in quantity, and a colorless precipitate appeared. These events were repeated with additional AsF_5 (to a total of 1.8 mmol) until complete consumption of the xenon (by tensimetry) and of the AgF_2 had occurred and a colorless solution and precipitate remained. Volatiles were removed under a dynamic vacuum at -10°C to leave a colorless solid. The bottom of the closed evacuated tube was heated to 60°C

whereupon a colorless crystalline solid collected in the upper reaches of it. This proved from X-ray single-crystal diffraction to be $\text{Xe}_2\text{F}_3\text{AsF}_6$. The nonvolatile colorless solid yielded an X-ray powder diffraction pattern characteristic⁸ of AgAsF_6 .

AgF_2 Conversion to AgFAsF_6 and Its Interaction with Xe. AgF_2 (1.73 mmol) in AHF (3–4 mL) was treated with AsF_5 (~ 2.5 mmol) to yield a blue solution. Since a small colorless precipitate (probably AgAsF_6) appeared, this solution was treated with F_2 gas (1 mmol) to afford a clear blue solution. Removal of AHF and an excess of AsF_5 and F_2 yielded blue AgFAsF_6 (the X-ray powder data of which were indexed on the basis of the unit cell given by Gantor et al.³), the yield being 552 mg (theoretical, 546 mg). To a part of this AgFAsF_6 (274 mg, 0.87 mmol) AHF (2–3 mL) was added, which brought about a partial dissolution of the salt to a clear blue solution. Xenon was added tensimetrically to this solution (0.435 mmol). A white precipitate (AgAsF_6) formed initially, but this was eventually accompanied by a brown precipitate (probably AgF_2). The latter was dissolved by adding AsF_5 (0.22 mmol) to the solution. This restored blue color to the solution which slowly faded (~ 20 min) to pale yellow. Volatiles were removed from the reactor at -23°C . The solid residue weighed 375.3 mg (theoretical, AgAsF_6 (258.2 mg) + $\text{Xe}_2\text{F}_3\text{AsF}_6$ (111.9 mg) = 370.1 mg). The bottom of the closed evacuated reactor was heated to 60°C to separate the latter as a sublimate. X-ray powder diffraction proved⁸ the involatile residue to be AgAsF_6 , and Raman spectroscopy¹¹ proved the sublimate to be $\text{Xe}_2\text{F}_3\text{AsF}_6$.

$\text{AgF}_2 + \text{BF}_3 + \text{AHF} + \text{Xe}$. AgF_2 (2.03 mmol), AHF (~ 5 mL), and BF_3 ($\gg 4$ mmol) were mixed by occasional cooling of the mixture to ca. -100°C and thawing with vigorous stirring to room temperature (low temperature increased the BF_3 concentration in the AHF but AgF^+ salt formation was favored by higher temperatures). A light blue sediment formed within a few minutes, all AgF_2 having been consumed in forming AgF^+ salts. The AHF was colored pale blue-green. Xenon (> 2 mmol) was added to the stirred mixture (again with thermal cycling) and the blue color faded (without the thermal cycling it was necessary to leave the stirred mixture for ~ 12 h). Volatiles were removed at -45°C in a dynamic vacuum. The nonvolatile colorless residue was shown by X-ray powder photography to be identical with AgBF_4 prepared directly from AgF and BF_3 in AHF. XeF_2 , as determined by X-ray powder photography¹² and Raman spectroscopy,¹³ was removed to an FEP U trap held at -78°C and weighed: yield 113 mg, 0.667 mmol, 57.9% based on AgF_2 .

$\text{AgF} + \text{BF}_3 + \text{F}_2 + \text{Xe}$. AgF (1.37 mmol) dissolved in AHF (~ 5 mL) was treated, at $\sim 20^\circ\text{C}$, with BF_3 (~ 2 mmol) to give a colorless solution and a copious white precipitate (probably AgBF_4). On addition of F_2 gas an immediate blue coloration of the sediment occurred and in ~ 3 h this became deep blue and the supernatant solution pale blue green. Removal of volatiles yielded a deep blue solid (1.37 mmol of AgFBF_4 requires 293 mg, found 272 mg). X-ray powder data for AgFBF_4 are given in Table I. AHF (~ 5 mL) and BF_3 ($\gg 1$ mmol) together with xenon ($\gg 1$ mmol) were condensed in the reactor at ca. -100°C , and this mixture was thawed with vigorous stirring to $\sim 20^\circ\text{C}$. This thermal cycling was repeated 3 or 4 times until (in ~ 2 h) the solution and sediment were colorless. Volatiles were removed at -45°C in a dynamic vacuum (5 h). XeF_2 was removed at 40°C (15 min in dynamic vacuum) to a Teflon U trap held at -78°C and was shown to be XeF_2 by X-ray powder photography¹² and its intense Raman band¹³ at 498 cm^{-1} . The combined yield of AgBF_4 and XeF_2 was 235.3 mg (theoretical 234.3 mg): yield of XeF_2 recovered, 46.8 mg, 66%.

Catalytic Formation of $\text{Xe}_2\text{F}_3\text{AsF}_6$ by AgAsF_6 in AHF. A stirred solution of AgAsF_6 (221.2 mg, 0.75 mmol) in AHF (~ 4 mL) contained in a 0.5 in. diameter Teflon FEP tube was exposed, at $\sim 20^\circ\text{C}$, to a gaseous mixture of Xe, F_2 , and AsF_5 in molar ratio 2:2:1. The solution quickly became deep blue, which faded slowly with time. After 6 h the tube and its contents were cooled to -23°C and all volatiles were removed in a dynamic vacuum. The solid product (704.3 mg) was shown by X-ray powder photography^{8,10} to be a mixture of AgAsF_6 and $\text{Xe}_2\text{F}_3\text{AsF}_6$. The presence of $\text{Xe}_2\text{F}_3\text{AsF}_6$ was also confirmed by Raman spectroscopy.¹¹ The yield of $\text{Xe}_2\text{F}_3\text{AsF}_6$ was 483.1 mg (0.95 mmol).

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Experimental and Theoretical Aspects of the Formation of Radical Cations from Tripyrrolidinobenzenes and Their Follow-Up Reactions¹

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Abstract: Tripyrrolidinobenzene radical cations ($1^{+\bullet}$), obtained from the corresponding arenes by oxidation with silver nitrate, are specially stabilized and thus allow specific reaction pathways of arene radical cations to be investigated separately and individually. Radical cations $1^{+\bullet}$, for instance, generated under exclusion of oxygen, undergo dimerization to **2**, or they abstract hydrogen from the solvent to form **3**. In a pure oxygen atmosphere, the O_2 reaction products **6** and **7** are formed, respectively, either exclusively or together with **2** and **3**. Kinetic measurements give the following order of reactivity for these individual processes: reaction with O_2 > dimerization (initial $[1^{+\bullet}]$ being ca. 10^{-4} M under flash photolysis conditions) > H-abstraction from solvent. The changes in the product spectrum upon modification of the reaction conditions are in accord with the kinetic results. The dimeric σ complexes **2** show surprisingly facile dissociation into two radical cations, two ($1^{+\bullet}$), with a much higher dissociation rate for the alkyl derivatives **2b–d** than for **2a**. Dissociation is enhanced substantially by light or in the presence of π donors. Individual product formation, rate of reactions of the radical cations $1^{+\bullet}$, and photochemical cleavage of the dimeric σ complexes **2** can be rationalized, by qualitative and quantitative MO considerations, in terms of their relative frontier orbital energies.

The yield of dimeric σ complexes **2** from the oxidation of 1,3,5-tripyrrolidin-1-ylbenzenes **1** is extremely dependent upon the effective reaction conditions.¹ Alkyl-substituted tripyrrolidinobenzenes, especially, have to be oxidized under absolute exclusion of light, and the reaction mixtures have to be worked up very quickly to obtain reproducible results and satisfactory yields of defined products.¹ This is due to different reaction pathways open to the intermediate radical cations $1^{+\bullet}$ which themselves may be formed either directly by oxidation of the triaminobenzenes **1** or by dissociation of the dimeric σ complexes **2** (see Scheme I). In the present paper, we report a detailed study of the electronic structure, physical properties, and chemical reactions of tripyrrolidinobenzene radical cations which allow the "preparation" of individual pathways from the manifold of secondary reactions, typical and/or feasible for aromatic radical cations in general.²

Oxidation of 1,3,5-Tripyrrolidin-1-ylbenzene (**1**) with Silver Nitrate under Various Conditions

In contrast to our earlier report,¹ oxidation of **1a–d** by silver nitrate was now carried out in the dark, at ambient temperature, with painstaking exclusion of oxygen. In one extreme, the oxidant (in CH_3CN/CH_2Cl_2 solution) was added, within 10 s, to a CH_2Cl_2 solution of **1**, and workup was initiated after 10 min. In the other extreme, addition of the oxidant was spread over 6 h, under otherwise identical conditions, with rapid workup of the reaction mixtures in each case. A mixture of the respective monomeric and dimeric σ complexes **2** and **3** was obtained for both extreme

conditions, although with varying percentages (see Scheme I, Table I). Due to the kinetic lability of the products (vide infra), the composition of the crude crystalline mixtures was determined by ¹H NMR. Oxidation of 1-methyl-2,4,6-tripyrrolidin-1-ylbenzene (**1b**) gave, besides **2b** and **3b**, an additional 10% of the 1-methylene-2,4,6-tripyrrolidin-1-ylcyclohexadienylum complex **5** by deprotonation of the radical cation $1b^{+\bullet}$ and further oxidation of the benzyl radical thus formed.³

Deprotonation by methoxide of the crude product mixtures gave mixtures of **1** and the respective biphenyls **4**; the combined yield of **1** and **4** corresponds to the amount of **1** employed in oxidation. One may conclude, then, that the only reaction channels open to the radical cations $1^{+\bullet}$ in the absence of oxygen are dimerization and hydrogen abstraction from the solvent (with the exception of the 10% side reaction of **1b** mentioned above).

Slow oxidation of **1a–d** (2–6 h, see above) in a pure oxygen atmosphere afforded, under otherwise identical conditions, only products derived from an initial reaction of $1^{+\bullet}$ with molecular oxygen. Thus, the 1-oxo-2,4,6-tripyrrolidin-1-ylcyclohexadienylum complex **6a** was obtained from **1a**, and the 1,1'-dialkyl-2,2',4,4',6,6'-hexapyrrolidin-1-ylcyclohexadienylum

(1) Aminobenzenes **20**. For part 19 see: Effenberger, F.; Mack, K. E.; Niess, R.; Reisinger, F.; Steinbach, A.; Stohrer, W.-D.; Stezowski, J. J.; Rommel, I.; Maier, A. *J. Org. Chem.* **1988**, *53*, 4379.

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