J. Am. Chem. Soc. **1981**, *103*, 5265-5267

Phosphonium Fluoride Salts

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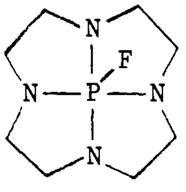
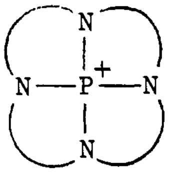
Received April 9, 1981

We wish to report the characterization of compounds that we believe represent the first examples of phosphonium salts containing *ionic fluoride*.[2] Phosphonium salts with complexed fluoride ion (e.g., PF_6^-) have been reported.[3]

In previous communications in this series we reported the synthesis of cyclenfluorophosphorane (**1**)[4] and the chloride salts of the cyclic phosphonium ions represented by structure **2**.[5]



1



2

Table I. Physical and Spectrosopic Properties of the Chloro and Fluoro Derivatives of **2**

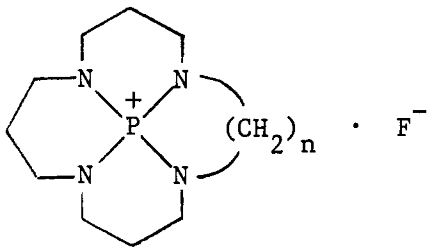
		fluoro derivatives					chloro derivative[b]
compd[a]	peripheral ring size	$\delta\ {}^{31}P$	$\delta\ {}^{19}F$	J_{PF}, Hz	mp, °C	bp, °C (pressure, torr)	$\delta\ {}^{31}P$
2,2,2,2 (**1**)[c]	12	−14.2	−75.4	793	87–92	100 (0.1)	
3,2,2,2	13	−32.2	−82.6	872	liq.	70–80/0.05	+65.6
3,3,2,2	14	−42.8	−67.2	872	51.5–53.5	80/0.05	+43.2
3,2,3,2	14	−46.3	−93.3	927	63.5–66.5	80/0.1	+31.4
3,3,3,2 (**3**)	15	+25.2	−126.7	0	97–105	*d*	+25.4
3,3,3,3 (**4**)	16	+15.1	−127.4	0	120–128	*e*	+15.0

[a] Numbers represent the bridging sequences in structure **2**. [b] In $CDCl_3$ solution.[5] [c] Reference 4. [d] An extremely weak molecular ion of 3 (covalent) was observed in the mass spectrum only at ca. 300 °C. [e] Not volatile.

(Curved lines in structure **2** represent ethylene or trimethylene bridges.) The chloride salts of **2** show increasing stability as the periphery is expanded. Models suggest that with a 16-membered periphery (four trimethylene bridges) the phosphonium center in **2** can achieve a tetrahedral geometry buried within the macrocyclic shell.[6] We have prepared the fluoro derivatives of **2** with the expectation that the larger members of this series would also be ionic. This expectation has been realized.

The original synthesis of **1** involved the reaction of PF_5 with the silylated derivatives of cyclen (the peripheral ring of **1**).[4] Attempts to extend this synthesis to higher homologues of **1** have not succeeded. However, ion exchange of the chloride salts of **2** by stirring overnight with AgF in anhydrous acetonitrile produces the fluoro compounds in good yields. Filtration or centrifugation of the resulting slurries followed by vacuum removal of the solvent gives about a 50% yield of the hygroscopic fluoro derivatives (see Table I).[7]

The spectroscopic data in Table I offer convincing evidence that in acetonitrile solution both **3** and **4** exist as ionic salts.



3, n = 2

4, n = 3

The ^{31}P NMR spectra of the fluoro derivatives of **2** with 12- to 14-membered peripheries show doublets that exhibit a monotonic shift to higher field as ring size increases. Table I shows a similar effect for ring expansion on the ^{31}P chemical shifts of the tetravalent phosphonium chloride salts.[8] The ^{31}P chemical shifts of both **3** and **4** fall completely out of the sequence shown by the lower homologues and agree with the ionic chloride salts. The ^{19}F NMR spectra of **2** also show doublets for the covalent PF compounds but singlets for the ionic compounds **3** and **4** at a chemical shift characteristic of ionic fluoride.[9]

Weakly solvated ionic fluoride compounds are of interest as sources of nucleophilic and basic fluoride ion. Addition of benzyl bromide to a dilute solution (ca. 0.1 M) of **3** in acetonitrile at ambient temperature cleanly produced benzyl fluoride. The rate of this reaction followed by ^{19}F NMR is estimated to be approximately 100 times that for the reaction of "naked" fluoride[10] (KF·18-crown-6 in acetonitrile) with benzyl bromide. This observation supports the ionic nature of **3** and suggests that there is only a weak interaction of the phosphonium center with the fluoride ion.

Other tests of the reactivity of the fluoride ion in **3** and **4** are under way. A report on the structures of the oxides derived by hydrolysis of **2** is forthcoming.[11]

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(2) Kloditz (Kloditz, L. *Z. Anorg. Allg. Chem.* **1956**, *286*, 307–316) has previously reported the ionic phosphonium fluoride $PCl_4^+F^-$. The structure of this salt is questionable; $PFCl_3^+Cl^-$ would appear more likely.

(3) For closely related examples, see: (a) Schlak, O.; Schmutzler, R.; Schiebel, H.-M.; Wazeer, M. I. M.; Harris, R. K. *J. Chem. Soc., Dalton Trans.* **1974**, 2153–2157. (b) Peake, S. C.; Fild, M.; Hewson, M. J. C.; Schmutzler, R. *Inorg. Chem.* **1971**, *10*, 2723–2727. (c) Jeanneaux, F.; Riess, J. G. *Nouv. J. Chim.* **1979**, *3*, 263–268.

(4) Richman, J. E. *Tetrahedron Lett.* **1977**, 559–562.

(5) Richman, J. E.; Gupta, O. D.; Flay, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1291–1292.

(6) The faces of the P^+ center not covered by the bridges are protected by the lone pair electrons of the four sp^3 hybridized nitrogens.

(7) The fluoro derivatives of **2** all give acceptable C, H, and N elemental analyses. The volatile fluoro derivatives show molecular ions in their mass spectra.

(8) A similar relationship between phosphorus chemical shifts and O–P–O bond angles in phosphate esters has been reported by: Gorenstein, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 898–900.

(9) Connick, R. E.; Poulson, R. E. *J. Phys. Chem.* **1959**, *63*, 568–569.

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Gas-Phase Nitration of Aromatic Radical Cations

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Received April 6, 1981

The possibility that radical cations may be intermediates in aromatic nitrations is a subject of current debate. For aromatics

0002-7863/81/1503-5265$01.25/0

which are more easily oxidized than toluene, Perrin[1] has suggested that an initial electron transfer takes place in the reaction of nitronium ion with the aromatic, followed by recombination of the resulting $NO_2\cdot/ArH^{+}\cdot$ pair. Perrin studied the nitration of naphthalene in acetonitrile solvent in the anodic compartment of an electrochemical cell and found the same ratio of α- and β-nitronaphthalene products as that produced by nitric acid nitration in acetonitrile.[1] However, Eberson et al. question this result and suggest that the electrochemical nitration observed by Perrin was a homogeneous, acid-catalyzed process mediated by traces of protic substances in the acetonitrile.[2] Further questions were raised by Draper and Ridd when they found that the radical cation of mesitylene generated by Ce(IV) was nitrated on both the ring and the methyl carbons, in contrast to the pure ring nitration by nitric acid under the same conditions.[3]

In this paper, we report the first direct observation of the reaction of an aromatic radical cation with NO_2 and the formation of a σ-bonded intermediate product. Our research was performed by using a new high-pressure mass spectrometer to study the gas-phase reactions of the odd-electron species $NO_2\cdot$ and benzene radical cation. Earlier gas-phase work was done by Ausloos and Lias, who studied the even–even NO_2^+/ArH systems and observed only charge transfer and oxygen atom transfer.[4]

$$NO_2^+ + ArH \rightarrow NO_2 + ArH^{+}\cdot \qquad (1a)$$

$$NO_2^+ + ArH \rightarrow NO\cdot + ArHO^{+}\cdot \qquad (1b)$$

Their studies were performed at pressures of about 10^{-5} torr in an ion cyclotron resonance spectrometer. In agreement with earlier work,[5] they were able to form the "nitration" product $ArHNO_2^+$ only by transfer of NO_2^+ from species such as $CH_2ONO_2^+$, but no information on the structure of the product was obtained.[6,7] Moreover, under these conditions, the formation of the $ArHNO_2^+$ product was favored for aromatic systems containing electron-withdrawing substituents, in distinct contrast to the common experience in condensed phase nitrations.

Our work uses a flow discharge mass spectrometer of a unique design. Reactions are run in a 1.27-cm i.d. × 17-cm stainless seel tube with 10 torr of helium and 0.5 torr of argon as the buffer gas. Ions are generated by a pulsed discharge in a flowing argon atmosphere that functions as an argon flash lamp. The lamp is isolated from the helium and all reactive neutrals by an open-ended glass tube through which the flow of argon enters the ion source. The argon resonance radiation ionizes species with an ionization potential of less than 12 eV down the full length of the flow tube. The ion source is sampled by a pinhole orifice; the ions are then mass analyzed by an extranuclear quadrupole mass filter and pulse counted by an electron multipler. This lamp is pulsed at about 100 Hz. Ion concentration vs. time data are recorded by using a Digital Equipment Corporation LSI 11/2 processor in a VT103 terminal. The buffer gas concentration is about 4×10^{17} molecules/cm^3, reactive neutral concentrations are about 10^{13} molecules/cm^3, and the ion concentration is about 10^8 ions/cm^3. The gas velocity is about 2000 cm/s, and the helium flow rate is about 15 atm cm^3/s.[8]

We find that when a mixture of benzene, NO_2, helium, and argon is ionized, rapid electron transfers during the first 0.25 ms yield the aromatic radical cation.[9] Equilibrium 2 is then established, giving predominantly the dimer. The product ion

$$C_6H_6^{+}\cdot + C_6H_6 \rightleftharpoons (C_6H_6)_2^{+}\cdot \qquad (2)$$

$C_6H_6NO_2^+$ readily forms from the reaction of the dimer with NO_2 (eq 3).

$$(C_6H_6)_2^{+}\cdot + NO_2 \rightarrow C_6H_6NO_2^+ + C_6H_6 \qquad (3)$$

$$k = 2.4 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

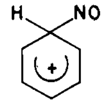
Also observed are two other primary products, $C_6H_6NO^+$ and $C_6H_6O^+$. The former arises from the reaction of NO, present as an impurity, with the radical cation dimer (eq 4). The $C_6H_6O^{+}\cdot$

$$(C_6H_6)_2^{+}\cdot + NO \rightarrow C_6H_6NO^+ + C_6H_6 \qquad (4)$$

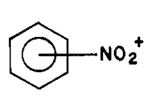
$$k = 2.0 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

ion is formed only at short times by the reaction 1b, consistent with the earlier ICR results.[4]

In order to probe the structure of the nitration product $C_6H_6NO_2^+$, we studied a mixture of benzene-d_6, NO_2, and tetrahydrofuran (THF). Because the proton affinity (PA) of THF (PA = 196.4 kcal/mol) is greater than that of nitrobenzene (PA = 191.6 kcal/mol)[10] and assuredly greater than the PA of any σ-bonded intermediate that might be formed, deuteron transfer from $C_6D_6NO_2^+$ to THF would establish that the reaction of the aromatic radical cation with NO_2 gives a σ-bonded product (structure I or O-protonated nitrobenzene). However, a π complex (II) would not be able to transfer a deuteron (proton) to THF because this structure lacks acidic protons. Benzene-d_6 was used to eliminate any possible confusion about the source of the proton (deuteron) transferred in the reaction. Neither $C_6D_6^{+}\cdot$ nor $(C_6D_6)_2^{+}\cdot$ transferred a deuteron to THF in control experiments (eq 5 and 6). The proton transfer (7) readily took place, demonstrating the σ-bonded character of the product. Similar results were found with pyridine (PA = 218 kcal/mol) as the base.



σ complex
I



π complex
II

$$C_6D_6^{+}\cdot + \text{THF} \qquad (5)$$

$$(C_6D_6)_2^{+}\cdot + \text{THF} \qquad (6)$$

$$C_6D_6NO_2^+ + \text{THF} \rightarrow \text{THFD}^+ + C_6D_5NO_2 \qquad (7)$$

We have also studied the nitration of the toluene and *p*-xylene radical cations (eq 8 and 9). Both of these reactions occur via

$$C_6H_5CH_3^{+}\cdot + NO_2 \rightarrow C_6H_5CH_3NO_2^+ \qquad (8)$$

$$p\text{-}C_6H_6(CH_3)_2^{+}\cdot + NO_2 \rightarrow C_6H_4(CH_3)_2NO_2^+ \qquad (9)$$

$$k = 1.2 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

the monomer of the aromatic cation unlike the benzene reaction (eq 3) which goes only by the dimer of the radical cation. Thus, we are not observing a simple exchange of ligands in the reaction complex, but rather a direct reaction between an aromatic radical cation and NO_2.

While the present results prove that the nitration product contains a σ bond between the NO_2 and the aromatics, they cannot distinguish between structure I and O-protonated nitrobenzene. No evidence has been found for formation of a π complex in this study. This is in contrast to nitrosation reactions, either Frieser and Reents' work on $C_6H_6 + CH_2ONO^+$ or our own studies of

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[8] As a test of the establishment of thermal equilibrium within the ion source, the equilibrium constant was measured as a function of temperature for the dimerization (eq 2). Values of ΔG = 14.7 kcal/mol and ΔS = 22.5 eu were obtained, which are in good agreement with the literature values of ΔG = 15.06 kcal/mol and ΔS = 23.18 eu. (a) Jasinski, J. M.; Rosenfeld, R. N.; Golden, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 2259–2265. (b) Anicich, V. G.; Bowers, M. T. *Ibid.* **1974**, *96*, 1279–1286. (c) Field, F. H.; Hamlet, P.; Libby, V. F. *Ibid.* **1969**, *91*, 2839–2842.

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$C_6H_6^{+\cdot}$ + NO,[11] where only a π complex is formed with no evidence for a σ complex.

We believe this to be the first clear example of a reaction of an aromatic radical cation with NO_2 to produce a nitroaromatic species. We have also observed similar reactions for other aromatic radical cations. While solvation effects may change, in some cases, the relative stabilities of the radical cation and NO_2^+, these results show that further consideration is warranted of the aromatic radical cation as an intermediate in nitration reactions.

Acknowledgment. We acknowledge the support of the Army Research Office (Contract DAA629-80-C0046).

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(11) Unpublished results.

On the Reversibility of η^4-Cyclobutadiene–Metal Formation from Complexed Alkynes: Unimolecular Isomerization of Labeled Racemic and Enantiomerically Enriched η^5-Cyclopentadienyl-η^4-cyclobutadiene–Cobalt Complexes

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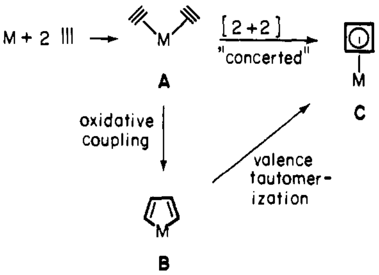
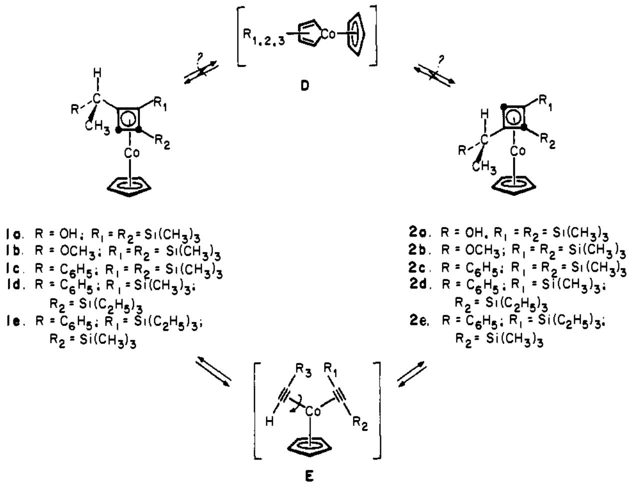
Received June 16, 1980
Revised Manuscript Received April 28, 1981

Scheme I



Scheme II



1a. R = OH; $R_1 = R_2 = Si(CH_3)_3$
1b. R = OCH_3; $R_1 = R_2 = Si(CH_3)_3$
1c. R = C_6H_5; $R_1 = R_2 = Si(CH_3)_3$
1d. R = C_6H_5; $R_1 = Si(CH_3)_3$; $R_2 = Si(C_2H_5)_3$
1e. R = C_6H_5; $R_1 = Si(C_2H_5)_3$; $R_2 = Si(CH_3)_3$

2a. R = OH, $R_1 = R_2 = Si(CH_3)_3$
2b. R = OCH_3; $R_1 = R_2 = Si(CH_3)_3$
2c. R = C_6H_5; $R_1 = R_2 = Si(CH_3)_3$
2d. R = C_6H_5; $R_1 = Si(CH_3)_3$; $R_2 = Si(C_2H_5)_3$
2e. R = C_6H_5; $R_1 = Si(C_2H_5)_3$; $R_2 = Si(CH_3)_3$

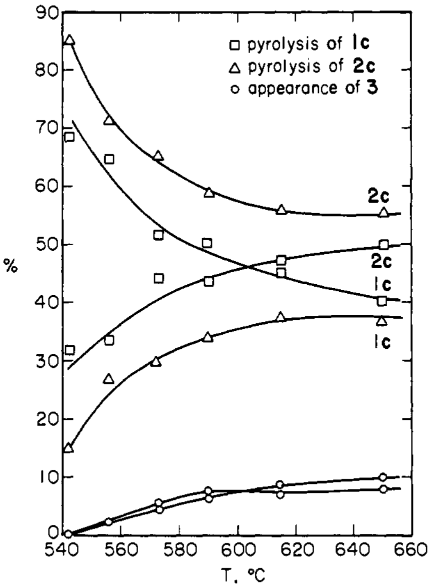


Figure 1. Flash vacuum pyrolysis results of diastereomers **1c** (squares) and **2c** (triangles). Percentages of the cyclobutadiene isomers are normalized to sum to 100%.

The interaction of transition-metal complexes with alkynes frequently results in the formation of η^4-cyclobutadiene–metal complexes.[1] However, the mechanism of their formation has never been elucidated. Two obvious pathways are illustrated in Scheme I. The first involves a concerted one-step [2 + 2] cycloaddition in the coordination sphere of the metal (A → C). This reaction, when occurring in the neighborhood of only one metal, is postulated to be unfavorable on theoretical grounds,[2,3] although its symmetry-dictated "forbiddenness" is removed for binuclear metal catalysis. The second, currently most accepted, mechanistic possibility is a stepwise process comprising initial oxidative coupling of the two alkynes followed by valence tautomerization (A → B → C).[1,2,4] Metallacyclopentadienes of type B have been invoked as crucial intermediates in the cyclotrimerization of alkynes to benzenes.[5a] Cyclobutadiene complexes C may be relay points in the synthesis of cyclooctatetraene from acetylene[1,5b] and in alkyne metathesis.[5c] Some isolable representatives of B thermally convert to cyclobutadiene–metal complexes,[6a] supporting the notion that they might also be intermediates en route to C. However, it is not clear whether this reaction, which appears to be forbidden,[6b] proceeds through initial retrocyclization (e.g., B → A → C). There are indications that complexes of type C may react through representatives of B.[5d] We present for the first time

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[§] SRC–NATO Postdoctoral Fellow, 1978–1980.

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