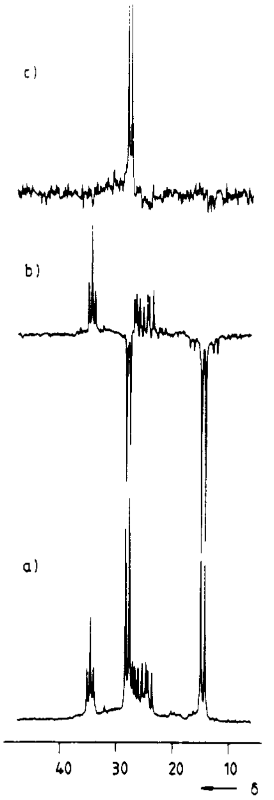

Figure 1. Identification of the resonance of the quaternary carbon C_q of t-$BuP(CH_2CH_2CH_2PMe_2)_2$ using the attached proton test (APT) pulse sequence:[16] (a) 20.15-MHz $^{13}C\{^1H\}$ NMR spectrum; (b) APT experiment (pulse width 45°, relaxation delay 2 s, τ = 8 ms) showing the CH_3 signals with inverted amplitudes (note the decrease in intensity of the doublet at δ 27.9 superimposed by the (positive) signal of C_q); (c) APT pulse sequence (τ = 4 ms) solely displaying the C_q doublet.

Note that apart from $\delta(t\text{-BuP})$ the $\delta(^{31}P)$ values are predictable with a high degree of confidence using Grim's alkyl group contributions to ^{31}P chemical shifts.[35]

^{13}C NMR Spectra. ^{13}C NMR shifts and carbon-phosphorus coupling constants of bis- and tris(phosphines) containing $-CH_2CH_2CH_2-$backbones have previously been reported by McAuliffe, Hill, and Dyer[36] as well as by ourselves.[5,9] Thus, the ^{13}C spectra of the compounds described herein were readily assigned by comparison with the data from the cited papers; cf. Table I.

Similar to the methyl and ethyl carbon resonances of the phosphines studied earlier,[5,9,36] the CH_3 and CH_2 carbons of the alkyl substituents attached to the terminal phosphorus atoms gave rise to doublets well upfield from the trimethylene region. Within the C_3 linkages the signals of the central carbons occurred at higher field than those of the ^{13}C nuclei directly linked to phosphorus although there remained some ambiguity concerning the assignment of the respective CH_2 resonances in the spectrum of t-$BuP(CH_2CH_2CH_2PMe_2)_2$. Most of the trimethylene ^{13}C multiplets exhibited the ABX pseudotriplet splitting frequently found for P_ACCCP_B moieties;[5,9,36] in some cases a four-line spectral pattern was observed, indicating a somewhat more pronounced difference between $^1J(PC)$, $^2J(PC)$, and $^3J(PC)$ than is usual.[5,9,36-38]

A rather curious situation was met with the quaternary carbon atom of t-$BuP(CH_2CH_2CH_2PMe_2)_2$, which could not be identified from the routine $^{13}C\{^1H\}$ spectrum. However, an attached proton test experiment[16] did unambiguously reveal the resonance of this unique carbon as a doublet precisely coincident with the signal originating from the adjecent methyl ^{13}C nuclei (Figure 1).

Mass Spectra. The major mass spectral fragmentation pathways are shown in Scheme I.

$R_2P(CH_2)_3\cdot$, $R_2P(CH_2)_2\cdot$, and t-$C_4H_9\cdot$ radicals are readily lost from the parent ions, which have not been observed for any of the alkylated oligo(phosphines) described in this paper. The stability of the $R_2P(CH_2)_3PR^+$ fragments generated according to the scheme is ascribed to the formation of heterocyclic onium ions containing P-alkylated five-membered ring structures of the 1,2-diphospholane type. As reported earlier,[5,9] facile generation of stable $R^2\overline{P(CH_2)_3P}R^+$ fragment ions is also a common feature of the mass spectra of trimethylene-bridged tris(phosphines) bearing phenyl groups at the donor atoms. The smooth formation of the 1,2-diphospholane system from $P(CH_2)_3P$ precursors is further demonstrated by an observation of Issleib and Thorausch[39] who reported the facile elimination of dihydrogen from the lithio derivative of 1,3-propanediylbis(phosphine) according to $H_2P(CH_2)_3P(Li)H \rightarrow H\overline{P(CH_2)_3P}PLi + H_2$.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Bonn) for financial support of this research (Grant Da 123/4-1) and to Hoechst AG (Frankfurt) for a generous gift of $MePCl_2$. Thanks are also expressed to Dr. E. Haupt for carrying out the APT NMR experiments and to Prof. W. A. König and his group for taking the mass spectra.

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Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Trifluoramine Oxide with Nitric Oxide: A Facile in Situ Source of Nitrosyl Fluoride

SCOTT A. KINKEAD and JEAN'NE M. SHREEVE*

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Trifluoramine oxide (NF_3O) has been found to react rapidly with nitric oxide to give nitrosyl fluoride (FNO). A free-radical reaction involving the known difluoronitryl ($F_2NO\cdot$) radical is proposed as a plausible mechanism. This reaction has been used as an in situ source of nitrosyl fluoride to synthesize the previously unknown nitroso compounds $R_f(CF_3)CFNO$ (R_f = n-C_5H_{11}, SF_5, OC_2F_5).

Nitrosyl fluoride, first synthesized by Ruff in 1905 from AgF_2 and NOCl,[1] has been prepared by a variety of methods, including the reaction of fluoride ion with nitrosyl salts[2-4] or N_2O_4[5] and the direct reaction of nitric oxide with F_2.[6] In

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addition, FNO has been used as a starting material in a convenient synthesis of trifluoramine oxide, NF_3O:[7]

$$FNO + F_2 \xrightarrow{h\nu,\ 25\ ^\circ C,\ 1\ atm} F_3NO\ (50\%)$$

This reaction probably proceeds via the fluorination of FNO to form the difluoronitryl radical, followed by rapid reaction of the radical in the presence of elemental and atomic fluorine to give trifluoramine oxide. The $F_2NO\cdot$ radical has been characterized by its ESR spectrum[8] at low temperature.

$$FNO + F_2 \rightarrow F_2NO\cdot + F\cdot$$

$$F_2NO\cdot + F_2 \rightarrow F_3NO + F\cdot$$

$$\text{or}\quad F_2NO\cdot + F\cdot \rightarrow F_3NO$$

During our investigation of trifluoramine oxide addition to fluoro olefins,[9] we observed the occasional formation of small amounts of intensely blue nitroso compounds, particularly at elevated reaction temperatures. Although the decomposition of NF_3O had been alluded to earlier,[10] we investigated this reaction as a potentially useful synthetic reaction for the preparation of nitroso compounds.

Results and Discussion

In an attempt to form $(CF_3)R_fCFONF_2$, via a thermally induced, free-radical addition of NF_3O to a fluoro olefin, only perfluoronitrosoalkanes and perfluoroalkanes were observed:

$$F_2C{=}CFR_f + NF_3O \xrightarrow{250\ ^\circ C,\ 12\ h} CF_3CF_2R_f + CF_3CF(NO)R_f$$

Even when the reaction mixture was heated for extended periods of time at 250 °C, conversion of the olefin was low. This reactivity at elevated temperature is in stark contrast to the reported thermal stability of NF_3O at 300 °C.[8] From these data, we propose that the first step of this reaction is a free-radical abstraction of fluorine from NF_3O by the olefin:

$$\dot{C}F_2\text{-}\dot{C}FR_f + F_3NO \rightleftarrows CF_3\text{-}\dot{C}FR_f + F_2\dot{N}O$$

Subsequent decomposition of the difluoronitryl radical affords both fluoroalkane and nitrosyl fluoride in a chain-quenching step:

$$F_2NO\cdot + CF_3\text{-}\dot{C}FR_f \rightarrow FNO + CF_3CF_2R_f$$

Alternately, the chain reaction may be propagated by fluorine atom transfer to the olefin:

$$F_2NO\cdot + CF_2{=}CFR_f \rightarrow FNO + CF_3{-}\dot{C}FR_f$$

Nitrosyl fluoride may then add either to a fluorocarbon radical or to an olefin molecule to give the product nitroso compound:

$$FNO + CF_3{-}\dot{C}FR_f \rightarrow CF_3CF(NO)R_f + F\cdot$$

$$FNO + CF_2{=}CFR_f \rightarrow CF_3CF(NO)R_f$$

In another experiment, trifluoramine oxide and 2 equiv of nitric oxide were warmed together to ambient temperature from −196 °C. Owing to the reactive nature of FNO toward glass, no FNO was observed in the infrared spectrum; however, no trace of the starting trifluoramine oxide was seen after only 1 h at room temperature. In the infrared spectrum, only decomposition products of FNO and glass, e.g. NO_2 and SiF_4, were observed.

Because of the thermal stability of NF_3O, fluorine atom abstraction by NO must be the first step in this reaction:

$$NO\cdot + F_3NO \rightarrow FNO + F_2\dot{N}O$$

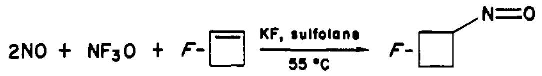
The short-lived difluoronitryl radical then further reacts with nitric oxide to produce two more molecules of FNO:

$$F_2\dot{N}O + NO\cdot \rightarrow 2FNO$$

or

$$F_2\dot{N}O \rightarrow FNO + F\cdot$$

Since the manipulation of nitrosyl fluoride in all-glass vacuum systems usually results in significant quantities of nitrogen oxide and SiF_4 impurities, the use of this reagent normally mandates the use of all-metal vacuum lines or its in situ generation in a suitable apparatus. As a final check, a 2:1 mixture of NO and NF_3O gave comparable yields of perfluoronitrosocyclobutane in an adaptation of the literature procedure:[11,12]



It should be noted that when the reactants were heated for longer than 6–8 h, significant degradation of the product was observed in the form of ring-opened nitroso compounds.

Previously, nitroso compounds have been synthesized by a variety of routes. In addition to the already mentioned reaction of fluoro olefins with nitrosyl fluoride[11]

$$F_2C{=}C(CF_3)_2 + FNO \xrightarrow{KF} (CF_3)_3CNO$$

which generally gives quite good yields of nitroso compounds, such materials may also be prepared by the free-radical reaction of perfluoroaliphatics with NO:[13-16]

$$R_fI + NO \xrightarrow{h\nu,\ Hg} R_fNO + HgI_2$$

Yields by this method vary from excellent for fluoroalkyl iodides to very low for iodotrifluoroethylene,[17] a reflection of the stability of $R_f\cdot$. The thermal decarboxylation of acyl nitrites[18-20] is another useful source of nitroso compounds, despite the risk of explosion.

$$R_fC({=}O){-}O{-}NO \xrightarrow{\Delta} R_fNO + CO_2$$

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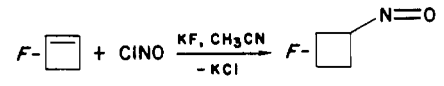
Nitrosyl chloride, KF, and fluoro olefins will also react to give nitroso compounds:[12,21]



In the first step of this reaction, FNO is formed from KF and ClNO, as adduced by the rapid decoloration of the brown ClNO prior to any blue nitroso compound formation.

Other synthetic routes to nitrosoperfluoroalkanes, including the reaction of nitrogen oxides and fluoro olefins,[22-24] are reviewed elsewhere.[25]

The suitability of trifluoramine oxide as a useful source of nitrosyl fluoride in the synthesis of fluoroaliphatic nitroso derivatives was demonstrated by the fact that the yields achieved with this method in the preparation of the new nitroso derivative $CF_3CF(NO)(n\text{-}C_5F_{11})$ were comparable to those obtained by traditional nitroso synthesis techniques.[11] These reactions proceed at ambient temperature with only mild agitation.

$$3F_2C{=}CF(n\text{-}C_5F_{11}) + 2NO + NF_3O \xrightarrow[CH_3CN]{KF,\ 4\ days} 3(CF_3)(n\text{-}C_5F_{11})CFNO\ (78\%)$$

$$F_2C{=}CF(n\text{-}C_5F_{11}) + 2NO_2 \xrightarrow[4\ days]{KF,\ CH_3CN,} (CF_3)(n\text{-}C_5F_{11})CFNO\ (80\%)\quad (+KNO_3)$$

In an identical series of reactions, (trifluorovinyl)sulfur pentafluoride and perfluoro(ethyl vinyl ether) are converted in high yields to the corresponding nitroso derivatives:

$$3F_2C{=}CFSF_5 + 2NO + NF_3O \xrightarrow[4\ days]{KF,\ CH_3CN} 3(CF_3)(SF_5)CFNO\ (77\%)$$

$$3F_2C{=}CFOC_2F_5 + 2NO + NF_3O \xrightarrow[2\ days]{CsF,\ CH_3CN} 3(CF_3)(C_2F_5O)CFNO\ (58\%)$$

These new nitroso compounds are deep blue liquids and gases that attack glass slowly at room temperature. The ^{19}F NMR data indicate that, in each case, only Markovnikov-type addition products are formed. It is noteworthy that, while the perfluoro(ethyl vinyl ether) did react with FNO in the presence of KF, the reaction was slow and only trace amounts of the nitroso product were found. Substantially better yields were obtained with cesium fluoride.

These compounds have characteristic absorption bands in the infrared spectrum at approximately 1600 cm^{-1} due to the N=O stretch, which are of medium intensity. Molecular ions in the mass spectra are weak (<1%); an intense fragment is usually found at $(M - NO)^+$. In the fluorine NMR spectra, the signal due to the fluorine geminal to the nitroso group is far upfield; for example, in perfluoroaliphatic nitroso derivatives, it is at ϕ −160 to −170. In the case of $(CF_3)(SF_5)CFNO$ and $(CF_3)(C_2F_5O)CFNO$, the signals due to the geminal fluorine atoms are observed at ϕ −141.0 and −129.3, respectively.

Experimental Section

Materials. C_7F_{14} (PCR) and $F_2C{=}CFOC_2F_5$ (Du Pont) were used as received. The literature method was used to prepare $F_2C{=}CFSF_5$.[26] Trifluoramine oxide (Allied Chemical Corp.) was passed through two traps cooled to −78 °C to remove NO_2. Nitric oxide (Matheson) was passed through a trap that contained silica gel cooled to −78 °C to remove any NO_2. Potassium fluoride (Baker) and cesium fluoride (Aldrich) were dried in an oven maintained at 160 °C and were ground repeatedly prior to use. Acetonitrile (Baker) was first dried over CaH_2 for 18 h, then distilled from P_2O_5 under argon, and stored over activated molecular sieves (3A).

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube gauge. Most of the starting materials and products were measured quantitatively by using *PVT* techniques. Products were purified by fractional condensation (trap-to-trap distillation) and, when necessary, on a Hewlett-Packard Model 5712A gas chromatography equipped with a Valco gas sample injection valve. The products were separated on 4- or 24-ft columns fashioned from $^1/_4$-in. copper tubing and containing 25% w/w Kel-F No. 3 oil on Chromosorb P. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer by using a 10-cm cell fitted with KBr windows. ^{19}F NMR spectra were obtained on either a JEOL FX-90Q FT NMR spectrometer or a Varian EM360L NMR spectrometer, with CCl_3F as an internal reference. Chemical shifts upfield of the reference are assigned negative values. Mass spectra were recorded with either a Hitachi Perkin-Elmer RMU-6E or a VG 7070HS mass spectrometer operating at 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

$CF_3{}^aCF^b(NO)CF^cF^dCF_2{}^eCF_2{}^fCF_2{}^gCF_3{}^h$. A stainless-steel Hoke vessel was charged with 2–3 g (34–50 mmol) of anhydrous KF, 5 mmol of $CF_2{=}CF(CF_2)_4CF_3$, 5 mmol of NO, 2.5 mmol of NF_3O, and about 3 mL of CH_3CN at −196 °C and then warmed to room temperature over a period of 1 h. After mild shaking for 4 days, the mixture was trap-to-trap distilled and the traps held at −116 and −78 °C contained a deep blue liquid. Purification by gas chromatography (4-ft column; Kel-F No. 3 oil (30%) on Chromosorb P) gave approximately 80% overall yield of $CF_3CF(NO)(CF_2)_4CF_3$. This new nitroso compound has a vapor pressure of 68 torr at room temperature. Gas-phase infrared spectrum: 1629 m, 1332 s, 1241 vs, 1162 vs, 1064 m, 1033 m, 952 w, 916 s, 846 vs, 820 m, 784 w, 755 s, 744 s, 727 s, 678 s, 542 w cm^{-1}. The ^{19}F NMR spectrum displays a multiplet at ϕ −167.5 (F^b) typical for methine fluorine atoms geminal to a nitroso group, in additon to a pair of multiplets at ϕ −116.9 and −119.1 due to the magnetically inequivalent fluorine atoms F^c and F^d attached to the carbon adjacent to the nitroso-bearing carbon. The remainder of the ^{19}F NMR consists of a doublet of triplets of triplets at ϕ −74.9 ($CF_3{}^a$), with $^3J_{FF} = 5.5$ Hz, $^4J_{FF} = 9.5$ Hz, and $^5J_{FF} = 8.5$ Hz, a triplet of triplets at ϕ −83.8 ($CF_2{}^h$), with $^3J_{FF} = 2.2$ Hz and $^4J_{FF} = 10.5$ Hz, and multiplets at ϕ −122.7 ($CF_2{}^e$), −124.2 ($CF_2{}^f$), and −128.0 ($CF_2{}^g$). The mass spectrum shows a weak molecular ion at *m/e* 399 (less than 1% of base peak). Intense fragments are observed at *m/e* 300 ($C_6F_{12}{}^+$), 219 ($C_4F_9{}^+$), 169 ($C_3F_7{}^+$), and 119 ($C_2F_5{}^+$) and the base peak is found at *m/e* 69 ($CF_3{}^+$).

Anal. Calcd for $CF_3CF(NO)(CF_2)_4CF_3$: N, 3.51; F, 71.4. Found: N, 3.09; F, 71.8.

$CF_3{}^aCF^b(NO)SF_4{}^cF^d$. Into a 75-mL stainless-steel Hoke vessel, fitted with a stainless-steel Hoke valve and containing 2–3 g (34–50 mmol) of anhydrous KF, were condensed $CF_2{=}CFSF_5$ (5 mmol), NO (5 mmol), NF_3O (2.5 mmol), and CH_3CN (approximately 3 mL) at −196 °C. After warming to ambient temperature over a period of 1 h, the bomb was shaken for 4 days. Upon distillation the trap held at −98 °C contained 4 mmol of an intensely blue liquid, which when passed through a 24-ft Kel-F on Chromosorb P column gave an overall yield of 77% $CF_3CF(NO)SF_5$. This new nitroso compound has a vapor pressure of approximately 75 torr at room temperature and attacks glass slowly. Vapor-phase infrared spectrum: 1616 m, 1311 w, 1245 s, 1220 s, 1200 sh, 1160 m, 1033 w, 943 m, 905 vs, 867 m, 835 m, 739 m, 697 w, 619 m, 585 w cm^{-1}. The ^{19}F NMR spectrum, recorded at ambient temperature, consists of an AM_4 pattern at ϕ +62.7 due to F^d and a doublet at ϕ +55.8 due to the equatorial fluorines F^c, with a value for $^2J_{F_{ax}/F_{eq}}$ of 136.7 Hz. Other signals include

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ϕ −74.5 (d-p) for $CF_3{}^a$ ($^3J_{FF}$ = 5.4 Hz and $^4J_{FF_{eq}}$ = 9.3 Hz) and ϕ −141.0 (mult) for CF^b. The mass spectrum shows a molecular ion at *m/e* 257 (less than 1% of base peak), with other fragments of *m/e* 127 ($SF_5{}^+$, 62%), 100 (CF_3CF^+, 100%), 89 ($SF_3{}^+$, 43%), 69 ($CF_3{}^+$, 58%), and 30 (NO^+, 58%).

Anal. Calcd for $CF_3CF(NO)SF_5$: N, 5.45; F, 66.52. Found: N, 6.51; F, 66.2.

$CF_3{}^aCF^b(NO)OCF_2{}^cCF_3{}^d$. A stainless-steel 75-mL Hoke vessel, fitted with a stainless-steel Hoke valve and containing 2–3 g (13–19 mmol) of anhydrous CsF and several $^5/_{32}$-in stainless-steel balls, was loaded with $CF_2{=}CFOCF_2CF_3$ (4.25 mmol), NO (5 mmol), NF_3O (2.5 mmol), and CH_3CN (3 mL) at −196 °C. After warming to ambient temperature, the bomb was shaken mechanically for 5 days. Upon distillation, the trap held at −116 °C contained 2.7 mmol of an intensly blue liquid. The liquid was greater than 91% pure (overall yield 58%) as determined by gas chromatographic methods (24-ft column; Kel-F No. 3 oil on Chromosorb P). This new nitroso compound, a deep blue liquid and gas, has a vapor pressure of 314 mm at 0 °C. Vapor-phase infrared spectrum: 1606 m, 1384 m, 1346 s, 1248 vs, 1253 s, 1179 vs, 1142 s, 1099 s, 1056 m, 967 w, 841 w, 749 m, 610 w cm^{-1}. The ^{19}F NMR spectrum, recorded as a liquid under autogeneous pressure at ambient temperature, consists of a broad singlet at ϕ −82.6 due to $CF_3{}^a$, a doublet of multiplets at ϕ −86.2 ($^4J_{FF}$ = 15 Hz) due to $CF_2{}^c$, a multiplet at ϕ −89.2 due to $CF_3{}^d$, and a triplet at ϕ −129.3 ($^4J_{FF}$ = 15 Hz) due to CF^b. The mass spectrum shows a molecular ion at *m/e* 265 (<1% of the base peak). Other fragments occur at *m/e* 235 ($C_4F_9O^+$), 130 ($C_2F_4NO^+$), 119 ($C_2F_5{}^+$), 111 ($C_2F_3NO^+$), 100 ($C_2F_4{}^+$), 97 ($C_2F_3O^+$), and 69 ($CF_3{}^+$). Molecular weight: found by *PVT* methods, 258; calcd, 265.

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Registry No. $CF_3CF(NO)(CF_2)_4CF_3$, 92844-16-1; NO, 10102-43-9; NF_3O, 13847-65-9; $CF_2{=}CF(CF_2)_4CF_3$, 355-63-5; $CF_3CF(NO)SF_5$, 92844-17-2; $CF_2{=}CFSF_5$, 1186-51-2; $CF_3CF(NO)OCF_2CF_3$, 92844-18-3; $CF_2{=}CFOCF_2CF_3$, 10493-43-3; FNO, 7789-25-5.

Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19716

The Effect of X^- = Cl^-, Br^-, I^- on the Kinetics of the Arbuzov Rearrangement Involving $[CpCo(dppe)X]^+$ and $P(OR)_3$ (R = Me, Et)

SHAYNE J. LANDON and THOMAS B. BRILL*

Received April 9, 1984

Rate constants and equilibrium and transition-state data for the reaction of $[CpCo(dppe)X]^+$ (X^- = Cl^-, Br^-, I^-) (**1**) with $P(OR)_3$ (R = Me, Et) to produce $\{CpCo(dppe)[P(O)(OR)_2]\}^+$ (**3**) and RX have been acquired by ^1H NMR spectroscopy. The rate of the overall reaction (X^- = I^- > Br^- > Cl^-) is traceable to the trend of X^- as a leaving group from the Co(III) center in the preequilibrium step that leads to the intermediate complex $[CpCo(dppe)P(OMe)_3]^{2+}$ (**2**). The rate of the dealkylation of **2** to form **3** is only moderately sensitive to X^-, suggesting that nucleophilicity of X^- plays a subordinate role. ΔH^* and ΔS^* for **2** → **3** are monotonically related and give an isokinetic temperature of −45 °C. ΔS^* is large and positive owing probably to the fact that ions having 2+ and 1− charge come together in the transition state. The entropy factor strongly influences the reaction rate above −45 °C. A comparison of the kinetic parameters for the Arbuzov reaction involving a transition-metal center vs. an alkyl center helps explain why the rearrangement is more facile in the former.

Introduction

The well-known Arbuzov (or Michaelis–Arbuzov) reaction[1] in which an alkyl phosphite and an alkyl halide react to form an alkyl phosphonate with alkyl transfer has precedence in transition-metal chemistry. In place of the alkyl halide, certain transition-metal–halide complexes undergo reaction 1 yielding,

$$L_nM{-}X + P(OR)_3 \rightarrow L_nMP(O)(OR)_2 + RX \qquad (1)$$

ultimately, a transition-metal–phosphonate complex as one of the final products.[2] An ionic mechanism has been put forth for this rearrangement in which $P(OR)_3$ first displaces the X^- and then is attacked by X^-, liberating RX and the phosphonate complex.[3-6] Dealkylation of phosphite ligands by a radical pathway also occurs and to date has arisen following metal–metal bond homolysis in the presence of $P(OR)_3$.[7-9]

In recent studies our attention has focused on fully characterizing the ionic mechanism.[2,5] A class of metal–halide cations having the general formula $[CpCo(L^\frown L)X]^+$ as $BF_4{}^-$ salts satisfactorily probe several features of this reaction.[10] $L^\frown L$ is a bidentate chelate ligand, and X^- is a halide ligand. The details of the reaction between $[CpCo(dppe)I]^+$ and $P(OMe)_3$ were established by ^1H and ^{31}P NMR spectroscopy in $CDCl_3$ solution.[5] The essential constituents and the mechanism are summarized in Figure 1. The final step, k_2, is rate determining, or **2** would not have been detected.

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(10) Abbreviations used: Cp = η^5-C_5H_5, dppe = 1,2-bis(diphenylphosphino)ethane, Ph = C_6H_5, Me = CH_3, Et = CH_3CH_2; b = broad, m = multiplet, s = singlet, t = triplet, q = quartet.

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