Inorg. Chem. 1984, 23, 2923-2929

Articles

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, L8S 4M1 Canada

Preparation of $O_2XeF_{2-x}(OTeF_5)_x$, $OXeF_{4-y}(OTeF_5)_y$, and $XeF_{4-y}(OTeF_5)_y$ ($x = 0-2$, $y = 0-4$) and Study by ^{129}Xe and ^{19}F NMR and Raman Spectroscopy: The Oxygen Primary Isotopic Effect in the ^{129}Xe NMR Spectra of XeO_2F_2 and $XeOF_4$

GERHARD A. SCHUMACHER and GARY J. SCHROBILGEN*

Received July 13, 1983

A series of mixed fluoro/pentafluroorthotellurate ($OTeF_5$) derivatives of the xenon(VI) oxyfluorides $XeOF_4$ and XeO_2F_2, as well as those of XeF_4, have been prepared and studied by ^{19}F and ^{129}Xe NMR spectroscopy. The compound $O_2Xe(OTeF_5)_2$ has been prepared and isolated for the first time and, along with the previously reported $Xe(OTeF_5)_4$ and $XeO(OTeF_5)_4$ derivatives, has been characterized by low-temperature Raman spectroscopy. An oxygen-17 NMR study of the $^{17}O/^{18}O$-enriched oxyfluorides XeO_2F_2 and $XeOF_4$ and their $^{18}O/^{16}O$ primary isotopic shifts in the ^{129}Xe NMR spectra are also reported.

Introduction

The effective group electronegativity of the $OTeF_5$ ligand has been shown to be only slightly less than that of F.[1,2] This group is capable of stabilizing nearly all of the same oxidation states as F including those of Xe(II),[3-5] Xe(IV),[6] and Xe(VI).[7] Since the preparations of the first xenon derivatives containing the $OTeF_5$ group by Sladky,[3-5] namely $FXeOTeF_5$, $Xe(OTeF_5)_2$, and $OXeTeF_5^+AsF_6^-$, the $OTeF_5$ group has been shown to stabilize the +4 and +6 and oxidation states of xenon as the $Xe(OTeF_5)_4$,[6] $OXe(OTeF_5)_4$, and $Xe(OTeF_5)_6$[7,8] compounds.

In the present work, we have undertaken to extend the range of known xenon(IV) and xenon(VI) derivatives containing the $OTeF_5$ group. Although the mixed series of xenon(VI) compounds $OXeF_{4-y}(OTeF_5)_y$ has been previously reported,[8] we have repeated the preparation of this series and have more accurately characterized these species by multinuclear magnetic resonance spectroscopy. These studies have been extended to the preparation of the new series of xenon(IV) derivatives $XeF_{4-y}(OTeF_5)_y$. Until the present work, the chemistry of XeO_2F_2 has been limited to the preparation of the thermally unstable XeO_2F^+ cation[9] and the $XeO_2F_3^-$[10] anion. Consequently, we have extended the chemistry of the dioxide difluoride by preparing the $OTeF_5$ derivatives $O_2Xe(OTeF_5)_3$ and $O_2XeF(OTeF_5)$ in solution and by isolating and characterizing $O_2Xe(OTeF_5)_2$ as a pure solid at low temperature.

Discussion

NMR Spectroscopy. Xenon-129 NMR spectroscopy is one of the most powerful techniques in assessing the structures of new xenon derivatives in solution.[11,12] The isotope is ideally suited to NMR observation, having a nuclear spin of $^1/_2$, natural abundance of 26.44%, and $D^c = 31.8$ (D^c = natural-abundance sensitivity relative to natural-abundance ^{13}C). As a precise absolute frequency for the accepted ^{129}Xe standard $XeOF_4$[10,13] is not available in the literature, we have determined a value of 27.810 184 MHz for pure liquid $XeOF_4$ at 24 °C (quoted relative to the protons in neat Me_4Si at 24 °C, which are taken to resonate at precisely 100.000 000 MHz).

$O_2Xe(OTeF_5)_2$ and $O_2XeF(OTeF_5)$. Dissolution of freshly prepared XeO_2F_2 in SO_2ClF followed by reaction with $B(OTeF_5)_3$ according to eq 1 yields pure $O_2Xe(OTeF_5)_2$ when

$$XeO_2F_2 + 2B(OTeF_5)_3 \rightarrow 3O_2Xe(OTeF_5)_2 + 2BF_3 \quad (1)$$

stoichiometric quantities of reactants are used. When an excess of XeO_2F_2 is allowed to react with $B(OTeF_5)_3$, a mixture of $O_2Xe(OTeF_5)_2$, $O_2XeF(OTeF_5)$, and XeO_2F_2 results.

The ^{129}Xe NMR spectra of $XeO_2(OTeF_5)_2$ and $O_2XeF(OTeF_5)$ are depicted in Figure 1a,b and their parameters are listed in Table I. The spectra of both compounds are consistent with a trigonal-bipyramidal arrangement about the xenon atom in which the formal double-bond oxygens occupy equatorial positions and the lone pair and the oxygen or fluorine ligand atoms occupy axial positions. The −74 °C ^{129}Xe spectrum of $O_2Xe(OTeF_5)_2$ in SO_2ClF consists of a multiplet (34-Hz line spacings) at 131.0 ppm from $XeOF_4$ with a set of satellites separated by 1684 Hz. The multiplet arises from coupling between ^{129}Xe and the equatorial fluorines on tellurium to give a partially resolved binomial nonet. The magnitude of this coupling is consistent with those previously observed for $OTeF_5$ groups bonded to xenon.[2,6-8] It was not possible to resolve the long-range coupling between the axial fluorine on tellurium and xenon. The satellites are the result of a two-bond coupling between natural-abundance ^{125}Te (6.99%) and ^{129}Xe. The spectra of solutions prepared by using an excess of XeO_2F_2 consisted of a superposition of $O_2Xe(OTeF_5)_2$ signals and a new set of signals arising from $O_2XeF(OTeF_5)$. There was no evidence for free XeO_2F_2, which was noted to be insoluble in SO_2ClF at the low temperatures at

---

(1) Sladky, F.; Kropshofer, H. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 195.

(2) Birchall, T.; Myers, R. D.; de Waard, H.; Schrobilgen, G. J. *Inorg. Chem.* **1982**, *21*, 1068.

(3) Sladky, F. *Monatsh. Chem.* **1970**, *101*, 1559.

(4) Sladky, F. *Monatsh. Chem.* **1970**, *101*, 1571.

(5) Sladky, F. *Monatsh. Chem.* **1970**, *101*, 1578.

(6) Lentz, D.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 356.

(7) Lentz, D.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 66.

(8) Jacob, E.; Lentz, D.; Seppelt, K.; Simon, A. *Z. Anorg. Allg. Chem.* **1981**, *472*, 7.

(9) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 2370.

(10) Schrobilgen, G. J.; Gillespie, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, 595.

(11) Schrobilgen, G. J.; Holloway, J. H.; Granger, P.; Brevard, C. *Inorg. Chem.* **1978**, *17*, 980.

(12) Schrobilgen, G. J. In "NMR and Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 14 and references therein.

(13) Brevard, C.; Granger, P. "Handbook of High Resolution Multinuclear NMR"; Wiley: Toronto, 1982; pp 176 and 177.

0020-1669/84/1323-2923$01.50/0

Table I. ^{129}Xe and ^{19}F NMR Parameters for $XeF_{4-y}(OTeF_5)_y$, $OXeF_{4-y}(OTeF_5)_y$, and $O_2XeF_{2-x}(OTeF_5)_x$ ($x = 0–2$, $y = 0–4$)

molecule	chem shift^a		coupling const, Hz		
	$\delta_{^{129}Xe}$	$\delta_{^{19}F}$^{b}	$^1J_{^{129}Xe-^{19}F}$	$^3J_{^{129}Xe-^{19}F_a}$	$^2J_{^{129}Xe-^{125}Te}$
$Xe(OTeF_5)_4$	−646.5			66	1008
$FXe(OTeF_5)_3$	−436.5	16.36	3506	66	1032 (E)^d 1292 (A)^d
trans-$F_2Xe(OTeF_5)_2$	−215.9	10.95	3503	69	1166
cis-$F_2Xe(OTeF_5)_2$	−242.6	−8.58	3714	69	1059
$F'F_2Xe(OTeF_5)$^{e}	−25.5	5.87 (F) −11.98 (F′)	3552 (F) 3733 (F′)	71	1192
XeF_4	202.9	−15.66	3817		
$OXe(OTeF_5)_4$	−204.1			52	1351
$OXeF(OTeF_5)_3$	−157.0	111.27	1206	52	
trans-$OXeF_2(OTeF_5)_2$	−106.4	108.24	984	53	1535
cis-$OXeF_2(OTeF_5)_2$	−117.8	112.59	1074	51	1536
$OXeF'F_2(OTeF_5)$^{f}	−66.3	106.78 (F′) 103.00 (F)	1148 (F′) 931 (F)	53	1364
$OXeF_4$	−29.9	101.59	1131		
$O_2Xe(OTeF_5)_2$	131.0			34	1684
$O_2XeF(OTeF_5)$	154.1		1046	37	1856
O_2XeF_2	171.0		1213		

[a] IUPAC conventions have been used in reporting chemical shift data: *Pure Appl. Chem.* **1972**, *29*, 627; **1976**, *45*, 217. I.e., a positive chemical shift denotes a positive frequency and vice versa. ^{129}Xe and ^{19}F spectra have been referenced relative to liquid $XeOF_4$ and $CFCl_3$ at 24 °C, respectively. [b] ^{19}F chemical shifts represent fluorines directly bonded to xenon. [c] Separate $^3J_{^{129}Xe-^{19}F_a}$ couplings between xenon and the axial fluorine on tellurium environments could not be resolved. [d] A and E in parentheses denote axial ($OTeF_5$ groups trans to each other) and equatorial ($OTeF_5$ group trans to F), respectively. [e] $J_{F-F'} = 355$ Hz. [f] $J_{F-F'} = 83$ Hz.

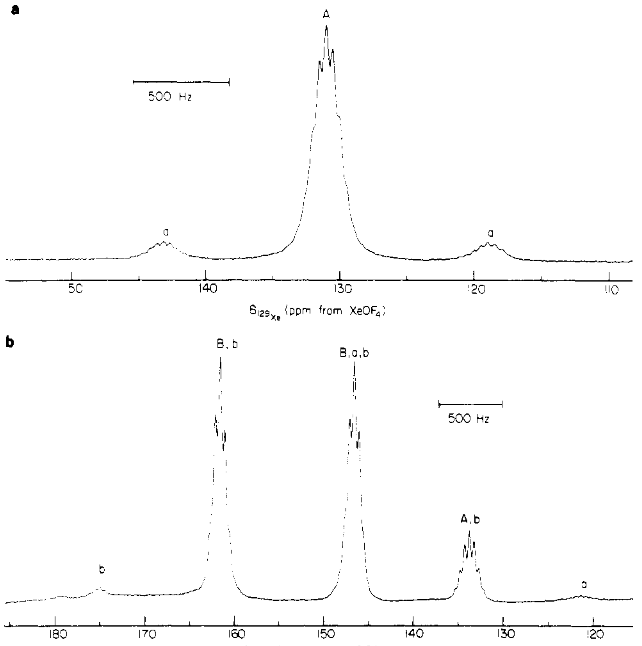


Figure 1. ^{129}Xe NMR spectra (69.561 MHz; SO_2ClF solvent; −74 °C): (a) $O_2Xe(OTeF_5)_2$ (A); (b) a mixture of $O_2XeF(OTeF_5)$ (B) and $O_2Xe(OTeF_5)_2$ (A). Lower case letters a and b denote ^{125}Te satellites belonging to $O_2Xe(OTeF_5)_2$ and $O_2XeF(OTeF_5)$, respectively.

which these spectra were obtained.

The ^{129}Xe NMR spectrum of $O_2XeF(OTeF_5)$ is a doublet of quintets with ^{125}Te satellites. The doublet results from the directly bonded spin–spin coupling between ^{129}Xe and ^{19}F (1047 Hz), and its value is similar to that previously observed for XeO_2F_2 in HF solvent (1217 Hz).[11] The magnitude of the quintet coupling (37 Hz) is again consistent with those previously observed for $OTeF_5$ groups bonded to xenon, and the ^{129}Xe–^{125}Te coupling (1856 Hz) in $O_2XeF(OTeF_5)$ represents the largest ^{129}Xe–^{125}Te coupling observed to date.

$XeF_{4-y}(OTeF_5)_y$ and $OXeF_{4-y}(OTeF_5)_y$. NMR spectra of the title systems were obtained by mixing the fluoro compound with the corresponding tetrakis(pentafluoroorthotellurate) compound in $CFCl_3$. Ligand redistribution of F and $OTeF_5$ groups was rapid at room temperature, resulting in all five species anticipated for each series. The apparent low resolution and/or signal to noise ratio in a previous ^{129}Xe NMR study[8] of the $OXeF_{4-y}(OTeF_5)_y$ system did not permit the observation of ^{129}Xe–^{125}Te couplings in the spectra of the mixed species nor the directly bonded ^{129}Xe–^{19}F′ coupling in $OXeF'F_2(OTeF_5)$. We have, however, been able to observe the latter in our study of this system. Furthermore, we note that the ^{129}Xe–^{19}F coupling reported for $OXeF(OTeF_5)_3$ (1082 Hz) is in error (corrected value 1206 Hz) and that the chemical shift assignments for *cis*- and *trans*-$OXeF_2(OTeF_5)_2$ are interchanged in the previous work.[8]

Xenon-129 spectra of the representative $XeF_{4-y}(OTeF_5)_y$ series are depicted in Figure 2a–d, and the ^{19}F NMR spectra of both series $XeF_{4-y}(OTeF_5)_y$ and $OXeF_{4-y}(OTeF_5)_y$ are depicted in Figure 3a,b. The less intense ^{129}Xe signals corresponding to the *cis*-difluorobis(pentafluoroorthotellurate) occur to low frequency of those belonging to the trans compound in both series of compounds. The ^{129}Xe NMR spectra of the $OTeF_5$ derivatives are also characterized by satellites arising from two-bond ^{129}Xe–^{125}Te couplings, directly bonded ^{129}Xe–^{19}F couplings in derivatives containing fluorine directly bonded to xenon, long-range coupling between the equatorial fluorines on tellurium and ^{129}Xe, and a monatonic increase in shielding with increasing number of $OTeF_5$ groups in the latter two series (Table I).

We have previously determined the ^{129}Xe chemical shift difference [$\Delta\delta = \delta$(F derivative) − δ($OTeF_5$ derivative)] for XeF^+ and $XeOTeF_5^+$ (898 ppm/group), $Xe(OTeF_5)_2$ and XeF_2 (219 ppm/group), $Xe(OTeF_5)_4$ and XeF_4 (207 ppm/group), and $O{=}Xe(OTeF_5)_4$ and $XeOF_4$(53 ppm/group).[2] Within each of the title series and the series $O_2XeF_{2-x}(OTeF_5)_x$ and $XeF_{2-x}(OTeF_5)_x$, the ^{129}Xe chemical shifts are found to be additive (eq 2–5), yielding the chemical shift changes 207

$$\delta_{^{129}Xe}(XeX_2) = -207n - 1890 \quad R^2 = 0.964 \qquad (2)$$

$$\delta_{^{129}Xe}(XeX_4) = -211n + 195.0 \quad R^2 = 1.000 \qquad (3)$$

$$\delta_{^{129}Xe}(XeOX_4) = -43.9n - 26.1 \quad R^2 = 0.998 \qquad (4)$$

$$\delta_{^{129}Xe}(XeO_2X_2) = -20.0n - 172.0 \quad R^2 = 0.922 \qquad (5)$$

n = number of $OTeF_5$ groups

R^2 = correlation coefficient

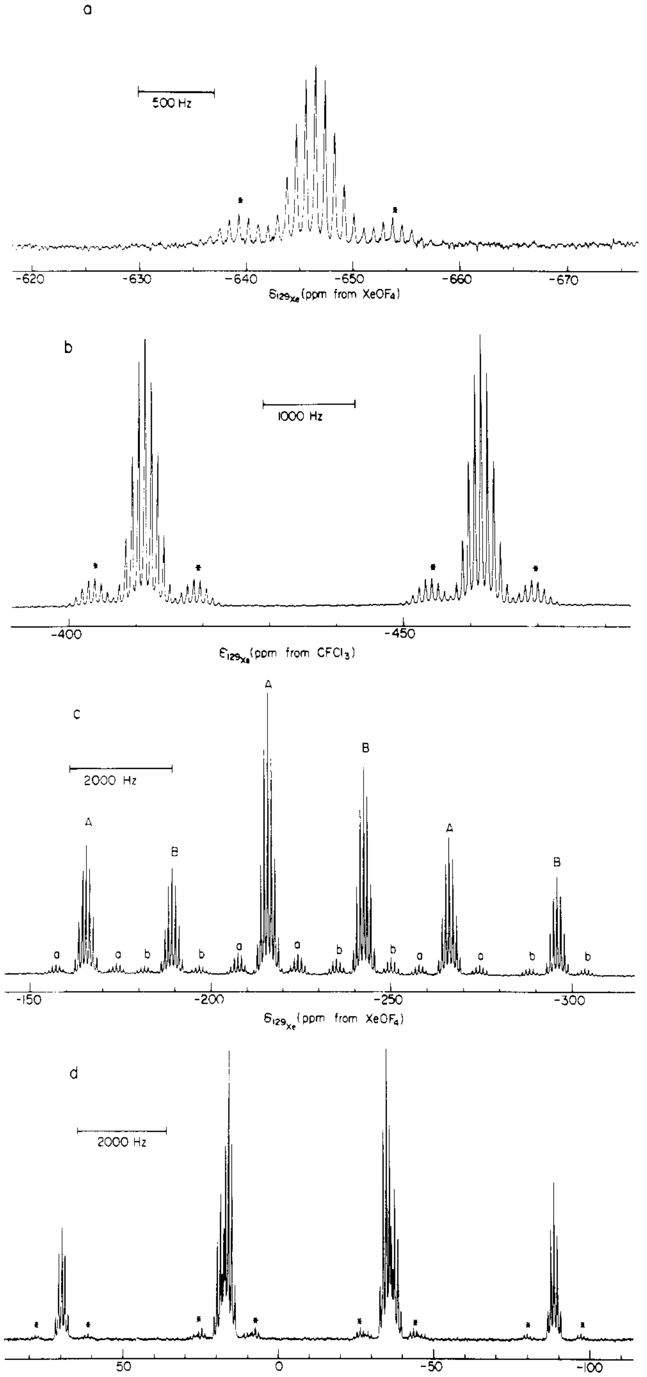


Figure 2. ^{129}Xe NMR spectra (69.561 MHz) of XeF$_{4-y}$(OTeF$_5$)$_y$ in CFCl$_3$ solvent (24 °C): (a) Xe(OTeF$_5$)$_4$; (b) XeF(OTeF$_5$)$_3$; (c) *cis*-XeF$_2$(OTeF$_5$)$_2$ (A), *trans*-XeF$_2$(OTeF$_5$)$_2$ (B) and accompanying ^{125}Te satellites a and b; (d) F'F$_2$XeOTeF$_5$. Asterisks denote ^{125}Te satellites.

ppm/group (XeX$_2$), 211 ppm/group (XeX$_4$), 44 ppm/group (XeOX$_4$), and 20 ppm/group (O$_2$XeX$_2$). These low-frequency changes with increasing number of OTeF$_5$ groups reflect the lower effective electronegativity of the OTeF$_5$ group compared to that of fluorine and support our earlier findings on the subject.[2]

We have also noted earlier the chemical shift change per group for XeX$_4$ and XeX$_2$ is nearly identical.[2] This appears to be in accord with a description of the XeX bonding, in a simplified MO description, for XeX$_2$ and XeX$_4$ in terms of one and two 3c–4e bonds (3-center 4-electron), respectively.[14]

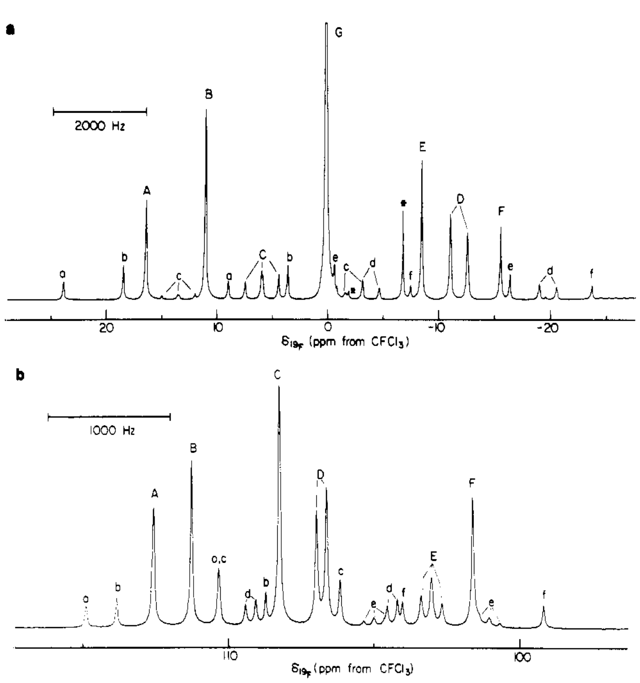


Figure 3. ^{19}F NMR spectra (235.362 MHz; CFCl$_3$ solvent; 24 °C): (a) XeF$_{4-y}$(OTeF$_5$)$_y$; (b) OXeF$_{4-y}$(OTeF$_5$)$_y$. Key for (a): XeF$_4$ (F); F'F$_2$XeOTeF$_5$ (C, D); *cis*-F$_2$Xe(OTeF$_5$)$_2$ (E); *trans*-F$_2$Xe(OTeF$_5$)$_2$ (B); FXe(OTeF$_5$)$_3$ (A); asterisk, impurity; (G) CFCl$_3$. Key for (b): OXeF$_4$ (F); OXeF'F$_2$(OTe$_5$) (D, E; *cis*-OXeF$_2$(OTeF$_5$)$_2$ (A); *trans*-OXeF$_2$(OTeF$_5$)$_2$ (C); OXeF(OTeF$_5$)$_3$ (B). Lower case letters denote ^{129}Xe satellites.

We have also noted that while the Xe–X bonds of XeOX$_4$ may be described in terms of two 3c–4e bonds, the difference value derived for XeOF$_4$ is small compared to corresponding values for XeX$_2$ and XeX$_4$. This effect increases with two oxygens in the single 3c–4e system XeO$_2$X$_2$, yielding a value of only 20 ppm/group. The formal Xe=O bond serves to diminish the difference in deshielding effects between OTeF$_5$ and F. The less electronegative OTeF$_5$ groups place more electron density onto the central xenon. Oxygen substitution permits withdrawal of much of the additional electron density, resulting in a smaller shielding difference for F and OTeF$_5$ ligands. This is supported by the lower Xe=O stretching frequencies for O$_2$Xe(OTeF$_5$)$_2$ and OXe(OTeF$_5$)$_4$ reported in a subsequent section dealing with the Raman spectroscopy of these compounds.

Fluorine-19 NMR spectroscopy reveals that the fluorines directly bonded to xenon in the series XeF$_{4-y}$(OTeF$_5$)$_y$ and OXeF$_{4-y}$(OTeF$_5$)$_y$ become progressively less shielded with increasing OTeF$_5$ substitution. This is consistent with the opposite deshielding trend observed in the xenon spectra.

Both the increase in ^{129}Xe shielding and the overall decrease in the ^{129}Xe–^{125}Te coupling constant as x or y increases in O$_2$XeF$_{2-x}$(OTeF$_5$)$_x$, OXeF$_{4-y}$(OTeF$_5$)$_y$, and XeF$_{4-y}$(OTeF$_5$)$_y$ are consistent with the increased covalency of the Xe–OTeF$_5$ bond. Since F is more electronegative than OTeF$_5$ and a Xe–F bond is more ionic than a Xe–OTeF$_5$ bond, increasing the number of Xe–OTeF$_5$ bonds in a compound causes a decrease in the covalency of the Xe–OTeF$_5$ bonds, offsetting the relatively ionic nature of the Xe–F bonds. As covalency decreases, so do the magnitudes of the couplings to ^{129}Xe. The decrease in the directly bonded ^{129}Xe–^{19}F coupling with increasing x or y (Table I) results from the addition of relatively electropositive OTeF$_5$ groups, which increase the ionic character of the remaining Xe–F bonds, resulting in a decrease in $^1J_{^{129}Xe-^{19}F}$.

Both trifluoro compounds, F$_3$Xe(OTeF$_5$) and OXeF$_3$(OTeF$_5$), exhibit fluorine–fluorine spin–spin coupling between F' and F in their respective F'XeF$_2$ groups. These couplings

---

[14] Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.

Table II. ^{129}Xe and ^{17}O NMR Parameters for XeF_4 and XeO_2F_2[a]

molecule	chem shift[b]		coupling const, Hz	
	$\delta_{^{129}Xe}$[c]	$\delta_{^{17}O}$[d]	$^1J_{^{129}Xe-^{19}F}$[c]	$J_{^{129}Xe-^{17}O}$[d]
$XeOF_4$	23.7	316.3	1146	704
XeO_2F_2	171.0	302.5	1213	521

[a] NMR spectra were recorded in HF solvent. [b] ^{129}Xe and ^{17}O spectra have been referenced relative to liquid $XeOF_4$ and H_2O at 24 °C, respectively. [c] Recorded at −50 °C. [d] Recorded at 24 °C; $J_{^{129}Xe-^{17}O}$ could not be observed in the ^{129}Xe spectrum of XeO_2F_2 recorded at 24 °C owing to broadening arising from fluorine exchange with HF solvent.

are 355 and 83 Hz, respectively, and bear no clear relationship to the analogous couplings in XeF_3^+ (174 Hz) and $XeOF_3^+$ (103 Hz).[15]

^{17}O and ^{129}Xe NMR Spectra of ^{17,18}O-Enriched XeO_2F_2 and $XeOF_4$. In the course of our present studies of the derivatives of XeO_2F_2, we have noted the absence of ^{17}O data for this oxyfluoride. The ^{17}O NMR studies of $XeOF_4$[16] and XeO_6^{4-}[17] have been reported previously. In addition, there is a paucity of primary isotopic shift data for NMR-active heavy elements bonded to various ligand isotopes, and none had been observed previously for ^{129}Xe.

An HF solution containing XeF_6 and ^{17,18}O-enriched water in the mole ratio XeF_6:H_2O = 1:1.22 gave a mixture of $XeOF_4$ and XeO_2F_2 and their respective isotopic isomers. The ^{129}Xe and ^{17}O NMR parameters for both oxyfluorides are represented in Table II. The 24 °C ^{129}Xe NMR spectrum gave a well-resolved 1:4:6:4:1 $XeOF_4$ quintent while that of XeO_2F_2 consisted of a severely broadened 1:2:1 triplet ($\omega_{1/2} \approx 750$ Hz). Broadening in the latter case presumably arose from fluorine exchange with the solvent. Each of the quintet lines of $XeOF_4$ ($J_{^{129}Xe-^{19}F}$ = 1131 Hz) was further split into two lines of essentially equal intensity (Figure 4a). The high- and low-frequency branches (41-Hz spacing at 5.8719 T) were assigned to $Xe^{16}OF_4$ and $Xe^{18}OF_4$. The $Xe^{17}OF_4$ contribution was observed as a partially quadrupole-collapsed set of overlapping 1:1:1:1:1:1 sextets centered on each pair of ^{16}O/^{18}O quintet lines ($J_{^{129}Xe-^{17}O}$ = 704 Hz) (Figure 4b). Cooling of the solution to −50 °C led to quadrupole collapse of the $Xe^{17}OF_4$ multiplet into the spectral base line. However, the fluorine exchange responsible for broadening in the XeO_2F_2 portion of the spectrum was slowed sufficiently at this temperature to permit the observation of a well-resolved 1:2:1 triplet arising from ^{129}Xe–^{19}F coupling (1213 Hz) and additional splittings on each triplet branch attributed to primary isotopic shifts arising from ^{16}O- and ^{18}O-containing species. Contributions arising from isomers containing one or two ^{17}O atoms were not observed due to severe quadrupole relaxation, leading to broadening and collapse of the ^{129}Xe–^{17}O sextets into the base line. Consequently, only three equally spaced lines (37 Hz at 5.8719 T) were observed on each branch of the triplet; these are assigned in order of decreasing frequency to $Xe^{16}O_2F_2$, $Xe^{16}O^{18}OF_2$, and $Xe^{18}O_2F$ and have calculated relative intensities of 1.00:2.03:1.03, respectively, which are in accord with the observed relative intensities (Figure 4c). The magnitude of the ^{16}O/^{18}O isotopic shift is proportional to the number of ^{16}O atoms in the XeO_2F_2 molecule that have been substituted by ^{18}O. This trend has also been noted recently for the ^{99}Tc resonance in TcO_4^- (^{16}O/^{17}O/^{18}O substitution).[18] The ^{17}O NMR spectrum of this solution at 24 °C yielded values for the ^{129}Xe–^{17}O spin–spin couplings and ^{17}O chemical shifts of both $XeOF_4$ and XeO_2F_2 (Figure 4d; Table II).

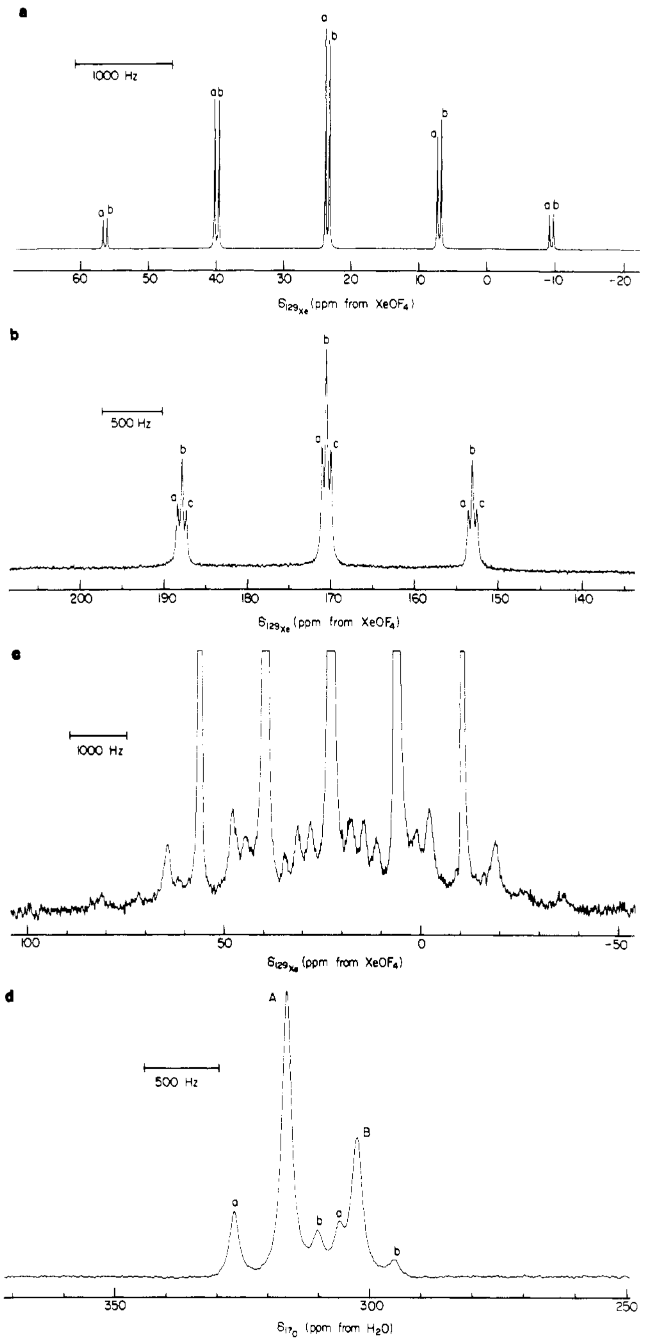


Figure 4. ^{129}Xe (69.561 MHz) and ^{17}O (33.909 MHz) spectra of ^{17}O- (26.5%) and ^{18}O- (37.0%) enriched preparations of $XeOF_4$ and XeO_2F_2 recorded in HF solvent: (a) ^{129}Xe NMR spectrum of $XeOF_4$ at −50 °C, where a and b denote $Xe^{16}OF_4$ and $Xe^{18}OF_4$, respectively; (b) ^{129}Xe NMR spectrum of XeO_2F_2 at −50 °C, where a–c denote $Xe^{16}O_2F_2$, $Xe^{16}O^{18}OF_2$, and $Xe^{18}O_2F_2$, respectively; (c) ^{129}Xe NMR spectrum of $XeOF_4$ at 24 °C depicting ^{17}O couplings; (d) ^{17}O NMR spectrum of an $XeOF_4$ (A)/XeO_2F_2 (B) mixture at 24 °C, where a and b denote ^{129}Xe satellites.

The isotopic shifts 0.29 and 0.26 ppm/amu, respectively, for $XeOF_4$ and XeO_2F_2 are comparable to those previously reported for TcO_4^- in the ^{99}Tc spectrum (0.22 ppm/amu),[18] and the direction of the oxygen isotopic shifts (low frequency with increasing oxygen mass) in these examples is consistent with the smaller mean vibrational amplitude expected for the heavier oxygen isotope, leading to a more shielded central xenon or technetium atom.[19]

---

(15) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 2370.
(16) Shamir, J.; Selig, H.; Samuel, D.; Reuben, J. *J. Am. Chem. Soc.* **1965**, *87*, 2359.
(17) Reuben, J.; Samuel, D.; Selig, H.; Shamir, J. *Proc. Chem. Soc., London* **1963**, 270.
(18) Franklin, K. J.; Lock, C. J. L.; Sayer, B. G.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 5303.
(19) Jameson, C. J. *Bull. Magn. Reson.* **1980**, *3*, 3.

Table III. Raman Frequencies and Tentative Assignments for $O_2Xe(OTeF_5)_2$, $OXe(OTeF_5)_4$, and $Xe(OTeF_5)_4$[a]

frequency, cm^{-1}			
$O_2Xe(OTeF_5)_2$[b]	$OXe(OTeF_5)_4$	$Xe(OTeF_5)_4$	approx description
889 (0.5)			$\nu_{asym}(XeO_2)$
880 (21)			
	887 (34)		$\nu(XeO)$
	873 (1)		
830 (3)			
824 (2)			$\nu_{sym}(XeO_2)$
822 (10)			
820 (100)			
770 (17)	778 (3)	785 (10)	
767 sh	754 (1)	747 (15)	$\nu_{asym}(TeF_4)$, sym to plane of sym
764 (10)	744 (16)	729 (2)	
743 (17)	741 sh	721 (8)	$\nu_{asym}(TeF_4)$, asym to plane of sym
731 sh	729 (22)		
726 (15)	725 (7)		
723 (14)			
717 (17)	718 (8)	717 (16)	
712 sh	714 (31)	710 sh	
710 (19)	707 (22)	707 (27)	$\nu(TeF')$
706 sh	704 sh	700 (13)	
699 (6)	701 (3)		
692 (2)			
687 (2)	668 (100)	691 sh	
673 (2)	662 (9)	689 (12)	$\nu_{sym}(TeF_4)$, breathing
664 (31)	658 (31)	661 (56)	
659 sh			
650 (11)	650 (6)	644 (23)	
633 (15)	632 (4)	638 (5)	$\nu_{sym}(TeF_4)$, out of phase
624 (3)	621 (1)	635 (6)	
620 sh			
604 (3)			
500 (1)	485 (28)	439 (29)	
465 (7)	481 (16)	432 (100)	$\nu_{sym}(XeOTe)$
456 (99)	452 (3)	417 (33)	$\nu_{asym}(XeOTe)$
450 sh	433 (58)		
440 (12)	419 sh		
435 (5)	415 (34)		
370 (2)	376 (4)		
354 (3)	357 (7)		$\delta(O-Xe=O)$
349 (6)	352 (3)		
344 (16)			
335 (4)	337 (3)	348 (1)	
328 (9)	329 (2)	341 (4)	$\delta(F'TeF_4)$, out of plane of sym
	325 (8)	332 (10)	
	320 (11)	320 (6)	
317 (10)	314 (4)	312 (2)	$\delta(F'TeF_4)$, in plane of sym
310 (10)	308 sh	306 (16)	$\delta_{sym}(TeF_4)$, out of plane
	306 (12)		
293 (2)	297 (2)	294 (3)	
	294 (2)		$\delta(TeF_4)$, in-plane scissors
	282 (3)		
	271 (5)		
260 (5)	262 (2)	246 (6)	
248 (37)	256 (1)	239 (65)	$\delta_{asym}(TeF_4)$, sym to plane of sym
236 (7)	238 (33)	233 (4)	$\delta_{asym}(TeF_4)$, asym to plane of sym
	232 (26)	230 (43)	
	226 (15)	220 (5)	
214 (3)	213 (2)	206 (4)	
	206 sh	200 (1)	$\delta(OTeF_4)$, out of plane
	202 (9)		
194 (1)	190 (1)		$\delta(OTeF_4)$, in plane
138 (12)	148 (16)	143 (45)	
131 (63)	135 (37)	129 (62)	$\delta(XeOTe)$
	129 (82)		
107 (4)	115 sh	112 (6)	
90 (4)	110 (9)	92 (12)	
82 (2)	104 (9)	79 (22)	
77 (1)	93 (6)	73 (11)	
67 sh	91 sh	62 (7)	lattice modes
60 (10)	84 (8)	55 (17)	
56 (6)	86 sh	51 (18)	
47 (17)	77 sh	46 (22)	
41 (6)	72 (9)		
	68 sh		
	54 (11)		
	45 (18)		
	42 sh		

[a] Raman spectra were recorded on FEP sample tubes at −196 °C with use of the 5145-Å exciting line. FEP lines have been deleted. Values in parentheses denote intensities; sh denotes a shoulder. [b] Modes arising from the XeO_2 group were assigned by comparison with the frequencies for XeO_2F, which were redetermined for the solid at −196 °C in the present work: ν_6 (b_1), 879 (33); ν_1 (a_1), 852 (100); ν_8 (b_2), 578 (0.2); ν_2 (a_1), 535 (29); ν_3 (a_1), 344 (3); ν_7 (b_1), 318 (4); ν_9 (b_2), 314 (6); ν_5 (a_2), 222 (1); ν_4 (a_1), 202 (2).

Raman Spectroscopy. $Xe(OTeF_5)_4$, $OXe(OTeF_5)_4$, and $O_2Xe(OTeF_5)_2$. Although the major features of the Raman spectra of $Xe(OTeF_5)_4$ and $OXe(OTeF_5)_4$ have been reported previously,[6-8] no detailed report of their assignments has been published. Moreover, the spectra reported in the present study were recorded at low temperature and are considerably better resolved than the previously reported spectra. The Raman spectra of the title compounds are complicated by strong vibrational coupling among $OTeF_5$ ligands and among stretches and bends associated with the XeOTe linkage.[20] Thus, it is not possible to provide unambiguous assignments of all the observed vibrationl bands. Rather, we have made tentative assignments based upon the previously assigned spectra of $Xe(OTeF_5)_2$,[20] $XeOF_4$,[21] XeO_2F_2[22] (see Table III, footnote b), and TeF_5Cl.[23] These assignments and their approximate descriptions are given in Table III.

The assignments of $OTeF_5$ group frequencies are based mainly on the assignments for the related C_{4v} molecule TeF_5Cl.[23] Although the vibrational spectrum of the $OTeF_5^-$ anion has been assigned,[24] the net negative charge leads to a substantial drop in the Te–F stretching force constants and a large increase in the Te–O stretching force constant. It is assumed that values of the $OTeF_5$ stretching and bending force constants in the title compounds will not be significantly different from those of TeF_5Cl. The assignments in Table III were consequently derived by correlating the relevant vibrational modes of TeF_5Cl under C_{4v} symmetry to those of the $OTeF_5$ group in the title compounds under reduced symmetry. This approach has been used successfully to assign the vibrational spectra of the $XeOTeF_5^+$ cation and $Xe(OTeF_5)_2$.[20]

The strongly coupled symmetric and asymmetric Te–O–Xe stretching frequencies of these derivatives occur in the range 415–500 cm^{-1} in accord with previous assignments for $XeOTeF_5^+$ (481 cm^{-1}),[20] $FXeOTeF_5$ (457 cm^{-1}),[4] and $Xe(OTeF_5)_2$ (434 cm^{-1})[20] (average values are given for vibrationally coupled

---

(20) Keller, N.; Schrobilgen, G. J. *Inorg. Chem.* **1981**, *20*, 2118.

(21) Classen, H. H.; Chernick, C. L.; Malm, J. G. In "Noble Gas Compounds"; Hyman, H. H., Ed.; University of Chicago Press: Chicago, IL, 1963; p 287.

(22) Classen, H. H.; Gasner, E. L.; Kim, H.; Houston, J. L. *J. Chem. Phys.* **1968**, *49*, 253.

(23) Brooks, W. V. F.; Eshaque, M.; Law, C.; Passmore, J. *Can. J. Chem.* **1976**, *54*, 817.

(24) Mayer, E.; Sladky, F. *Inorg. Chem.* **1975**, *14*, 589.

and/or factor group split lines). Very strong bands are observed at 129 and 148 cm^{-1}, which are assigned to strongly coupled Xe–O–Te bending modes. The corresponding modes occur at 132 cm^{-1} in $Xe(OTeF_5)_2$ and at 174 cm^{-1} in the $XeOTeF_5^+$ cation.

Both $OXe(OTeF_5)_4$ and $O_2Xe(OTeF_5)_2$ exhibit strong Xe=O stretching modes above 800 cm^{-1}. The Xe=O stretch of $OXe(OTeF_5)_4$ shows an additional weak splitting that may be attributed to a factor group effect. Like XeO_2F_2 (Table III, footnote b), $O_2Xe(OTeF_5)_2$ exhibits two intense Xe=O stretching frequencies that are assigned to the symmetric and asymmetric XeO_2 stretching frequencies. Without polarization measurements, it is not clear which one of the two Xe=O stretching bands belong to the totally symmetric species, but like XeO_2F_2, we have assigned the lower frequency band to the totally symmetric mode on the basis of the observed Raman intensities. Additional weak lines are observed in the region of each line, which are again assigned to factor group splittings. As we have already noted in the discussion pertaining to the NMR spectroscopy of these derivatives, the less electronegative $OTeF_5$ groups place more electron density onto the central xenon. In the vibrational spectra of $OXe(OTeF_5)_4$ and $O_2Xe(OTeF_5)_2$, this is manifested by an overall reduction of their Xe=O stretching frequencies relative to those of their parent fluorine derivatives: $XeOF_4$, 920 cm^{-1}; $OXe(OTeF_5)_4$, 880 cm^{-1}; XeO_2F_2, 852, 879 cm^{-1}; $O_2Xe(OTeF_5)_2$ 820, 875 cm^{-1}.

Experimental Section

Apparatus and Materials. Manipulations were carried out under anhydrous conditions on vacuum lines constructed of 316 stainless steel, nickel, Teflon, and FEP. All preparative work was carried out in 9-mm o.d. lengths of FEP tubing heat sealed at one end and connected through 45° SAE flares to Kel-F valves.

Xenon tetrafluoride and xenon hexafluoride were prepared from xenon (Linde, CP grade) and fluorine (Air Products) according to the methods described by Malm and Chernick.[25,26] The ligand-transfer reagent $B(OTeF_5)_3$ was prepared as previously described by Sladky et al.[27] Sulfuryl chloride fluoride (Columbia Organic Chemicals) and trichlorofluoromethane (Du Pont) were purified as described previously. Enriched water, used in the preparation of $^{17}O/^{18}O$-enriched $XeOF_4$ and XeO_2F_2 contained 26.5% ^{17}O and 37.0% ^{18}O (ORIS, Saclay, France). Pure liquid $XeOF_4$ was made by the direct combination of water vapor with XeF_6 previously condensed in an evacuated 2-L nickel vessel (6-mm walls). In a typical preparation, 0.4573 g (24.25 mmol) of H_2O was condensed onto the vessel walls above XeF_6 (6.227 g, 25.38 mmol). The vessel was warmed to room temperature and allowed to stand for 4 h before being agitated (*caution*! danger of explosion). The vessel was allowed to remain at room temperature for another 8 h before the products, HF and $XeOF_4$, and excess XeF_6 were vacuum distilled into a Kel-F tube containing NaF (previously dried under vacuum at 300 °C for 24 h). Pure $XeOF_4$ was distilled from this storage vessel as required.

The preparation of gram quantities of XeO_2F_2, its derivatives, and their subsequent manipulation is *hazardous*. Xenon dioxide difluoride is best prepared in anhydrous HF solution by the interaction of XeF_6 with a stoichiometric amount of water. In a typical preparation, 1.3178 g (5.37 mmol) of XeF_6 was sublimed into a preweighed FEP reaction vessel outfitted with a Kel-F valve. Anhydrous HF (~7 mL) was distilled onto XeF_6, and the latter dissolved. The vessel was then introduced into a drybox and the solution frozen at −196 °C. The vessel was briefly opened, and with use of a calibrated microsyringe, 194 μL (10.8 mmol) of water was frozen on the reaction vessel walls 3–4 cm above the frozen HF solution. The vessel was closed and removed from the drybox while still cold. After reevacuation of the vessel at −196 °C, the frozen solution was rapidly warmed to room temperature by immersing this region of the vessel in water while allowing the water frozen on the walls to thaw slowly. When the HF solution was near room temperature, the tube was rapidly inverted by using a remote manipulator. Rapid mixing was continued until all white solid material, initially precipitated in the early stages of mixing, had dissolved. The tube and contents were immediately cooled to −80 °C, and the HF was removed under vacuum. Pumping was continued for an additional 3 h to ensure complete removal of HF. The vessel was briefly warmed to room temperature, pumped on to remove traces of $XeOF_4$ and HF still remaining, and reweighed for preparations requiring an exact stoichiometry.

$O_2Xe(OTeF_5)_2$. A vessel containing freshly prepared XeO_2F_2 was cooled to −196 °C and SO_2ClF solvent distilled onto it. The sample was briefly warmed to −80 °C in order to completely wet the XeO_2F_2. The frozen mixture was again taken into a drybox and maintained at −196 °C while a stoichiometric amount of $B(OTeF_5)_3$ was transferred into the vessel. The entire sample was resealed and evacuated at −196 °C. In a typical reaction, 1.0294 g (5.114 mmol) of XeO_2F_2 was combined with 2.4767 g (3.408 mmol) of $B(OTeF_5)_3$ in ~6 g of solvent. The vessel was warmed to −80 °C and pressurized to 1 atm with dry N_2 with the vessel open to the free volume of the vacuum manifold. Slow warming and agitation resulted in reaction with smooth evolution of BF_3. The reaction mixture was maintained below 0 °C to avoid the formation of $Xe(OTeF_5)_2$ from the decomposition

$$O_2Xe(OTeF_5)_2 \rightarrow Xe(OTeF_5)_2 + O_2 \qquad (6)$$

Pure $O_2Xe(OTeF_5)_2$ was isolated by pumping the SO_2ClF sample at −80 °C overnight. The solid sample was never warmed above this temperature.

$Xe(OTeF_5)_4$ and $OXe(OTeF_5)_4$. The preparative procedures for both derivatives were identical with that used to prepare $O_2Xe(OTeF_5)_2$ except that previously dried $CFCl_3$ was used as the solvent medium. Typical preparations involved the following quantities of reactants and solvents: XeF_4, 0.4598 g (2.218 mmol); $B(OTeF_5)_3$, 2.2462 g (2.246 mmol); $CFCl_3$, ~5 g; $XeOF_4$, 0.6727 g (3.013 mmol); $B(OTeF_5)_3$, 2.9186 g (4.017 mmol); $CFCl_3$, ~4 g.

Nuclear Magnetic Resonance Spectroscopy. All spectra were recorded unlocked (field drift <0.1 Hz/h) on a Bruker WM-250 superconducting spectrometer using a 10-mm probe (broad banded over the frequency range 23–103 MHz) tuned to 69.561 and 33.909 MHz to observe ^{129}Xe and ^{17}O, respectively. Fluorine-19 spectra were obtained on the same probe using the ^1H decoupler coils retuned to 235.361 MHz as the observe coils. Free induction decays were typically accumulated in a 32K memory. Spectral width settings of 50 and 100 kHz were employed, yielding data point resolutions of 3.0 and 6.1 Hz and acquisition times of 0.328 and 0.164 s, respectively. No relaxation delays were applied. The number of free induction decays accumulated varied with concentration and sensitivity of the nucleus under consideration, with 2000 scans being typical for ^{19}F, 10 000–30 000 scans being typical for ^{129}Xe, and 5000 scans being typical for ^{17}O (26.5% enrichment). Pulse widths corresponding to bulk magnetization tip angles, θ, of approximately 90° were 0.5 (^{19}F), 22 (^{129}Xe), and 80 μs (^{17}O). Line broadening parameters used in exponential multiplication of the free induction decays were 4–5 Hz.

The respective nuclei were referenced to neat samples of $CFCl_3$ (^{19}F), $XeOF_4$ (^{129}Xe), and H_2O (^{17}O) at 24 °C. In the chemical shift convention used, a positive sign signifies a chemical shift to high frequency of the reference compound and vice versa.

Variable-temperature studies were carried out with use of a Bruker temperature controller. Temperatures were measured with a copper–constantan thermocouple inserted directly into the sample region of the probe and were accurate to ±1 °C.

Laser Raman Spectroscopy. A Spectra-Physics Model 164 argon ion laser giving up to 900 mW at 5145 Å was used to excite the Raman spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with 1800 groves/mm holographic gratings. An RCA C31034 phototube detector in conjunction with a pulse-count system consisting of pulse amplifier, analyzer, and rate meter (Hamner NA-11, NC-11, and N-708A, respectively) and a Texas Instruments Model FSOZWBA stripchart recorder were used to record the spectra. The spectrometer was periodically calibrated by recording the discharge lines from an argon lamp over the spectral range of interest; the Raman shifts quoted are estimated to be accurate to ±1 cm^{-1}. Slit widths depended on the scattering efficiency of the sample, laser power, etc., with 100 μm being typical.

Cylindrical sample tubes were mounted vertically. The angle between the incident laser beam and the sample tube was 45°, and

---

(25) Malm, J. G.; Chernick, C. L. *Inorg. Synth.* **1966**, *8*, 254.

(26) Chernick, C. L.; Malm, J. G. *Inorg. Synth.* **1966**, *8*, 258.

(27) Sladky, F.; Kropshofer, H.; Leitzke, O. *J. Chem. Soc., Chem. Commun.* **1973**, 134.

Raman-scattered radiation was observed at 45° to the laser beam or 90° to the sample tube. Low-temperature spectra were recorded by mounting the sample vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. $Xe(OTeF_5)_4$, 66255-64-9; $FXe(OTeF_5)_3$, 91002-50-5; *trans*-$F_2Xe(OTeF_5)_2$, 91002-51-6; *cis*-$F_2Xe(OTeF_5)_2$, 91108-44-0; $F_3Xe(OTe_5)$, 91002-52-7; XeF_4, 14989-42-5; $OXe(OTeF_5)_4$, 68854-32-0; $OXeF(OTeF_5)_3$, 68854-36-4; *trans*-$OXeF_2(OTeF_5)_2$, 68889-95-2; *cis*-$OXeF_2(OTeF)_2$, 68854-35-3; $OXeF_3(OTeF_5)$, 91108-43-9; $OXeF_4$, 13774-85-1; $O_2Xe(OTeF_5)_2$, 91002-53-8; $O_2XeF(OTeF_5)$, 91002-54-9; O_2XeF_2, 13875-06-4; ^{18}O, 14797-71-8; ^{17}O, 13968-48-4; ^{129}Xe, 13965-99-6.

Contribution from the Richard B. Wetherill Laboratory,
Purdue University, West Lafayette, Indiana 47907

Addition Compounds of Alkali-Metal Hydrides. 24. A General Method for Preparation of Potassium Trialkoxyborohydrides. A New Class of Reducing Agents

HERBERT C. BROWN,* JIN SOON CHA,[1] and BEHROOZ NAZER[1]

Received January 23, 1984

The generality of the synthesis of potassium triisopropoxyborohydride, stabilized toward disproportionation by storing over excess potassium hydride, was examined with seven additional organoborates of varying steric requirements. The reaction of trimethoxy- and triethoxyborane with potassium hydride proceeded readily at room temperature, but the products could not be stabilized by the presence of excess potassium hydride. Triphenoxyborane reacted readily, even at −10 °C, and stabilization was achieved. Tri-*sec*-butoxy- and tricyclopentoxyborane required refluxing in THF for 12–24 h, and the products were stabilized over potassium hydride. Finally, the reactions of tris(2-methylcyclohexoxy)- and tri-*tert*-butoxyborane were even slower, requiring a number of days for completion. Both products were stabilized toward disproportionation over potassium hydride. Indeed, potassium tri-*tert*-butoxyborohydride was quite stable toward disproportionation without excess potassium hydride. The stereoselectivities of these reagents in the reduction of representative cyclic ketones were examined. The stereoselectivities varied in an erratic manner with the steric requirements of the alkoxy group and did not approach the stereoselectivities previously achieved with lithium tri-*sec*-butylborohydride and lithium trisiamylborohydride.

Recently we reported an improved method for preparation of potassium triisopropoxyborohydride (K(IPBH)) from triisopropoxyborane and potassium hydride[2] (eq 1). Moreover,

$$(i\text{-PrO})_3B + KH \rightarrow K(i\text{-PrO})_3BH \qquad (1)$$

K(IPBH), thus prepared, is stable toward disproportionation at room temperature when maintained over a small excess of potassium hydride.

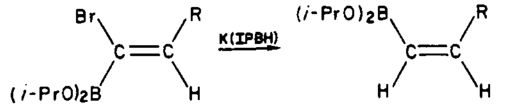
The reagent, K(IPBH), is a very mild reducing agent and, unlike sodium and potassium borohydrides, shows a high degree of stereoselectivity toward cyclic ketones.[3]

K(IPBH) readily transfers hydride to dialkylhaloboranes or trialkylboranes to produce the corresponding dialkylboranes and trialkylborohydrides, respectively[4,5] (eq 2 and 3).

$$R_2BX + K(i\text{-PrO})_3BH \rightarrow R_2BH + KX + (i\text{-PrO})_3B \qquad (2)$$

$$R_3B + K(i\text{-PrO})_3BH \rightarrow KR_3BH + (i\text{-PrO})_3B \qquad (3)$$

It also provides a valuable procedure for the synthesis of *cis*-vinylboronic esters[6] (eq 4).



(4)

Table I. ^{11}B NMR Spectra and Physical Properties of Trialkoxyboranes

trialkoxyborane	^{11}B NMR chem shift,[a] δ	bp, °C (*P*, torr)	n^{20}_D
trimethoxyborane	18.3	68.5–70 (748)	1.3555
triethoxyborane	17.8	43 (40)	1.3732
triisopropoxyborane	17.5	60 (42)	1.3741
tri-*sec*-butoxyborane	17.5	99–99.5 (29)	1.3941
tri-*tert*-butoxyborane	15.6	85 (42)	1.3871
tricyclopentoxyborane	17.8	132–133 (3.7)	1.4571
tris(2-methylcyclohexoxy)-borane[b]	18.6	162–164 (0.4)	
triphenoxyborane[c]	16.8[d]	232–234 (2.8)	

[a] All chemical shifts are reported relative to $BF_3 \cdot OEt_2$ with chemical shifts downfield from $BF_3 \cdot OEt_2$ assigned as positive. [b] Very viscous liquid. [c] Solid, mp 99–101 °C. [d] In THF.

These unique characteristics of K(IPBH) stimulated us to investigate other members of the potassium trialkoxyborohydride family. Accordingly, we undertook a study to develop a general procedure for the synthesis of potassium trialkoxyborohydrides in tetrahydrofuran (THF) with representative trialkoxyboranes of different steric requirements and to examine their stereoselectivities in the reduction of cyclic ketones.

Results and Discussion

Trialkoxyboranes were prepared from the corresponding alcohols and borane–methyl sulfide complex (BMS) according to the published procedure with a slight modification[7] (eq 5).

$$3ROH + BH_3 \cdot SMe_2 \xrightarrow{\Delta} (RO)_3B + 3H_2\uparrow + SMe_2 \qquad (5)$$

---

(1) Postdoctoral research associate on Grant ARO-DAAG-29-82-K-0047 supported by the U.S. Army Research Office.
(2) Brown, H. C.; Nazer, B.; Sikorski, J. A. *Organometallics* **1983**, *2*, 634.
(3) Brown, H. C.; Cha, J. S.; Nazer, B.; Kim, S. C.; Krishnamurthy, S.; Brown, C. A. *J. Org. Chem.* **1984**, *49*, 885.
(4) (a) Kulkarni, S. U.; Lee, H. D.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 4542. (b) Brown, H. C.; Sikorski, J. A.; Nazer, B.; Kulkarni, S. U.; Lee, H. D., manuscript in preparation.
(5) Brown, C. A.; Hubbard, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 3964.
(6) Research in progress with T. Imai.
(7) Brown, C. A.; Krishnamurthy, S. *J. Org. Chem.* **1978**, *43*, 2731.