# Krypton Bis[pentafluoro-oxotellurate(VI)], $Kr(OTeF_5)_2$, the First Example of a Kr–O Bond

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Krypton bis[pentafluoro-oxotellurate(VI)] provides the first example of a species containing a krypton–oxygen bond and has been prepared by the reaction of $KrF_2$ with natural abundance and $^{17}O$-enriched $B(OTeF_5)_3$ at −90 to −112 °C in $SO_2ClF$ solvent; characterization of the thermally unstable $Kr(OTeF_5)_2$ and its decomposition products has been achieved using $^{19}F$ and $^{17}O$ n.m.r. spectroscopy.

It is only recently that the chemistry of krypton has been extended beyond the Kr–F bonded species $KrF_2$,[1] $KrF^+$, and $Kr_2F_3^+$ [2] to include the Kr–N bonded cations $HC{\equiv}N{-}KrF^+$ [3] and $R_FC{\equiv}N{-}KrF^+$ ($R_F$ = $CF_3$, $C_2F_5$, n-$C_3F_7$)[4] which are thermally unstable above −50 °C. With the extension of the chemistry of $Kr^{II}$ to Kr–N bonds, it seemed likely that a suitable strongly electron withdrawing oxygen ligand might afford a Kr–O bond, albeit thermally unstable.

A previous published attempt to form Kr–O bonds reports the reaction of $KrF_2$ with $B(OTeF_5)_3$ in $ClO_3F$ at −100 °C for 16 h followed by a further 3 h at −78 °C.[5] However, instead of the anticipated products being formed according to equations (1) and (2), the $^{19}F$ n.m.r. spectrum of the sample only revealed resonances attributable to $F_5TeOOTeF_5$ and the solvent. Similar results have been obtained in this laboratory for the reaction of $KrF_2$ with $B(OTeF_5)_3$ in $SO_2ClF$ at −78 °C for several minutes.[6] In contrast, the reaction of $XeF_2$ with $B(OTeF_5)_3$ yields the thermally stable $Xe(OTeF_5)_2$.[7] It was proposed that the $F_5TeOOTeF_5$ resulted from the decomposition of the intermediates, $FKrOTeF_5$ or $Kr(OTeF_5)_2$, according to equations (3) and (4).[5]

$$3KrF_2 + 2B(OTeF_5)_3 \rightarrow 3Kr(OTeF_5)_2 + 2BF_3 \quad (1)$$

$$3KrF_2 + B(OTeF_5)_3 \rightarrow 3FKrOTeF_5 + BF_5 \quad (2)$$

$$Ng(OTeF_5)_2 \rightarrow Ng + F_5TeOOTeF_5 \text{ (Ng = Kr or Xe)} \quad (3)$$

$$2FNgOTeF_5 \rightarrow NgF_2 + F_5TeOOTeF_5 \quad (4)$$

The interaction of $KrF_2$ and $(IO_2F_3)_2$ in $SO_2ClF$ solvent has also been reported to lead to peroxide formation at −45 °C by the route proposed in equations (5) and (6).[8] The series of adducts $XeF_2{\cdot}nWOF_4$ ($n > 2$) undergo bond isomerization to give equilibrium mixtures of $FXeF{-}{-}{-}WOF_4(WOF_4)_{n-1}$ and $FXe{-}O{-}WF_5(WOF_4)_{n-1}$ in $SO_2ClF$ solvent while the $MoOF_4$ adducts and their $KrF_2$ analogues only exist as the $FNg{-}F{-}{-}{-}MoOF_4(MoOF_4)_{n-1}$ structures.[9] While it was thought that the reaction between $KrF_2$ and $WOF_4$ might lead to Kr–O bonded species, these mixtures, unlike their F bridged Mo analogues, are remarkably unstable, decomposing above −100 °C in $SO_2ClF$ to Kr, $O_2$, $WF_6$, and $WOF_4$.[9] Again, it was proposed that a Kr–O bonded structure may be an intermediate in the decomposition.

$$(IO_2F_3)_2 + KrF_2 \rightarrow Kr(OF_4I{=}O)_2 \quad (5)$$

$$Kr(OF_4I{=}O)_2 \rightarrow Kr + O{=}IF_4O{-}OF_4I{=}O \quad (6)$$

The thermolyses of $Xe(OTeF_5)_2$ and $FXeOTeF_5$ have been reinvestigated in glass at 160 °C in the present study and shown to yield almost quantitatively $F_5TeOOTeF_5$ and Xe, and $F_5TeOOTeF_5$ and $XeF_2$, according to equations (3) and (4), respectively. Contrary to previous reports in which the thermolyses of the two xenon compounds had been carried out in a Monel vessel at 130 °C,[10,11] only traces of $F_5TeOTeF_5$ (<2%) and other members of the series $TeF_n(OTeF_5)_{6-n}$ were observed for the thermolyses in glass tubes. These findings suggested that analogous decompositions of

**Table 1.** $^{17}O$ and $^{19}F$ n.m.r. parameters for $Kr(OTeF_5)_2$ and related species.[a]

| | Chemical shifts[b] | | | | |
|---|---|---|---|---|---|
| | $\delta(^{17}O)$ | $\delta(^{19}F)$ | | | |
| Species | | A | $B_4$ | $^2J_{F_a-F_b}$ /Hz | $T$/°C |
| $F_5TeOOTeF_5$[c] | 314.5 | −50.8 | −52.3 | | −110 |
| | (314.6) | (−52.4) | (−53.1) | (200) | (30) |
| $F_5TeOTeF_5$ | 140.7 | −49.1 | −39.2 | 182 | −70 |
| $Xe(OTeF_5)_2$[d] | 152.1 | −42.6 | −45.3 | 183 | −16 |
| $FXeOTeF_5$[d] | 128.8 | −40.8 | −46.7 | 180 | −16 |
| $Kr(OTeF_5)_2$ | 95.2 | −42.1 | −47.2 | 181 | −90 |

[a] Recorded in $SO_2ClF$ solvent. [b] Chemical shifts were referenced with respect to $H_2O$ ($^{17}O$) and $CFCl_3$ ($^{19}F$). [c] Parentheses denote n.m.r. parameters obtained from a sample of the pure material in $SO_2ClF$. [d] N.m.r. parameters obtained from samples of the pure material in $SO_2ClF$.

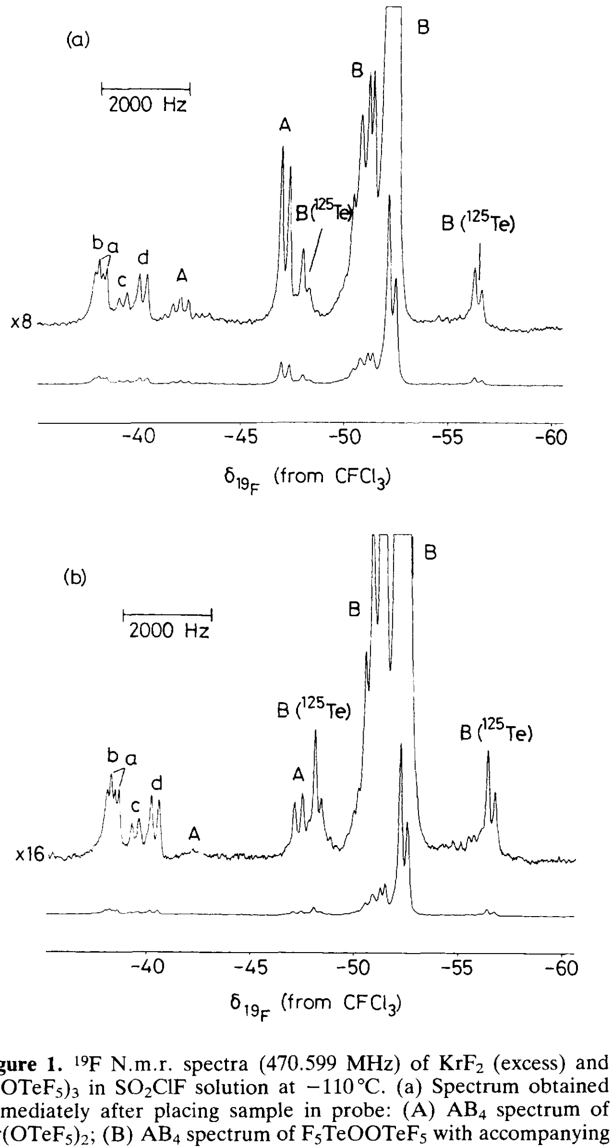

**Figure 1.** $^{19}F$ N.m.r. spectra (470.599 MHz) of $KrF_2$ (excess) and $B(OTeF_5)_3$ in $SO_2ClF$ solution at −110 °C. (a) Spectrum obtained immediately after placing sample in probe: (A) $AB_4$ spectrum of $Kr(OTeF_5)_2$; (B) $AB_4$ spectrum of $F_5TeOOTeF_5$ with accompanying $^{125}Te$ (6.99%, $I = \frac{1}{2}$) satellites; (a,b,c,d) $B_4$ parts of $AB_4$ spectra arising from species in the series $TeF_n(OTeF_5)_{6-n}$. (b) Spectrum obtained at −110 °C after warming sample to −78 °C for 3 min depicting the substantially diminished intensity of the $Kr(OTeF_5)_2$ resonances (A).

$FKrOTeF_5$ and/or $Kr(OTeF_5)_2$, but at much lower temperatures, may be responsible for the formation of $F_5TeOOTeF_5$ resulting from the reaction of $KrF_2$ and $B(OTeF_5)_3$. These findings prompted the reinvestigation of reactions (1) and (2) at lower temperatures with the view to providing definitive evidence for $FKrOTeF_5$ and/or $Kr(OTeF_5)_2$.

The reaction of $B(OTeF_5)_3$ and 21% $^{17}O$ enriched $B(OTeF_5)_3$ with $KrF_2$ at −110 °C was monitored in $SO_2ClF$ by both high-field $^{19}F$ (470.599 MHz) and $^{17}O$ (67.801 MHz) n.m.r. spectroscopy. Owing to the increased dispersion afforded in the $^{19}F$ spectra at 11.744 T, it was possible to observe a new $AB_4$ pattern to high frequency of the $AB_4$ pattern of $F_5TeOOTeF_5$ (Figure 1) and this new pattern is assigned to $Kr(OTeF_5)_2$. The $AB_4$ pattern of this species resembles the corresponding $AB_4$ spectra of $Xe(OTeF_5)_2$ and $FXeOTeF_5$ in that the A part occurs to high frequency of the $B_4$ part and the A part is well separated from the $B_4$ part at an external field strength of 11.744 T (Table 1). Furthermore, the new $AB_4$ pattern cannot be attributed to any of the species in the $BF_n(OTeF_5)_{3-n}$ series, since the $^{19}F$ n.m.r. spectrum of a sample containing $BF_3$ and $B(OTeF_5)_3$ in a 1 : 1 mole ratio in $SO_2ClF$ reveals that, although the $AB_4$ spectra of the mixed species occur in the region −45 to −48 p.p.m., the A parts of the spectra are almost coincident with the $B_4$ parts. The absence of these species in the $KrF_2/B(OTeF_5)_3$ reaction mixture is corroborated by the fact that the F-on-B region of the $^{19}F$ spectrum shows only a single resonance attributable to $BF_3$ (−126.8 p.p.m.). The signals ascribed to $Kr(OTeF_5)_2$ slowly diminished at −90 °C and rapidly decreased upon warming to −78 °C for 3 min, yielding Kr and additional $F_5TeOOTeF_5$ (Figure 1). However, a new F-on-Kr signal was not observed in these spectra, ruling out the formation of $FKrOTeF_5$. The $^{19}F$ n.m.r. spectrum also showed four weak doublets in the region −38.2 to −40.3 p.p.m. These have been assigned to the $B_4$ parts of the $AB_4$ spectra arising from species in the series $TeF_n(OTeF_5)_{6-n}$ by comparison with $^{19}F$ n.m.r. data obtained at 470.599 MHz for solutions of $TeF_n(OTeF_5)_{6-n}$ in $SO_2ClF$ and with the literature data for these species.[12,13] The weaker A parts of the $AB_4$ patterns were not identified since they are obscurred by the $AB_4$ pattern of $F_5TeOOTeF_5$. The formation of small amounts of the $TeF_n(OTeF_5)_{6-n}$ species is analogous to the results obtained for the high-temperature decompositions of $FXeOTeF_5$ and $Xe(OTeF_5)_2$. The $^{17}O$ n.m.r. spectrum of the $KrF_2/B(OTeF_5)_3$ reaction mixture also yielded a new $^{17}O$ resonance to low frequency of the $F_5TeOOTeF_5$ resonance (Table 1). The new resonance displayed analogous behaviour to the new $^{19}F$ resonance when the sample was warmed and is assigned to

$Kr(OTeF_5)_2$. The new $^{19}F$ and $^{17}O$ chemical shifts are consistent with the $OTeF_5$ ligands possessing more ionic character than in their $FXeOTeF_5$ and $Xe(OTeF_5)_2$ analogues, whose $^{17}O$ chemical shifts are reported here for the first time (Table 1).[14] Thus, the $^{17}O$ resonance of $Kr(OTeF_5)_2$ appears at the lowest frequency in this series.

In contrast to the reaction of $XeF_2$ with one third the stoicheiometric amount of $B(OTeF_5)_3$, which yields an equilibrium mixture of $XeF_2$, $FXeOTeF_5$, and $Xe(OTeF_5)_2$ in $SO_2ClF$, the reaction of a three-fold excess of $KrF_2$ with $B(OTeF_5)_3$ has failed to produce any direct evidence for $FKrOTeF_5$ formation. Instead, $Kr(OTeF_5)_2$, Kr, and $F_5TeOOTeF_5$ with traces of $TeF_n(OTeF_5)_{6-n}$ were observed when the reaction was allowed to proceed at −90 to −110 °C in $SO_2ClF$. The high solubility of $B(OTeF_5)_3$ relative to $KrF_2$ in $SO_2ClF$ at the low temperatures required to stabilize $Kr(OTeF_5)_2$ presumably serves to maintain $B(OTeF_5)_3$ in excess, preventing the formation and observation of $FKrOTeF_5$.

The thermolysis of $Kr(OTeF_5)_2$ has been found to be analogous to that found for $Xe(OTeF_5)_2$, but occurs rapidly at considerably lower temperatures. It is therefore not surprising that the species was not observed under the previously reported reaction conditions and at the low dispersion field strengths used to observe the $^{19}F$ n.m.r. spectra.

In view of these findings further attempts to synthesize additional examples of Kr–O bonded species are presently underway in this laboratory.

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