New Krypton Difluoride Adducts

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Summary The adducts $KrF_2{\cdot}TaF_5$ and $KrF_2{\cdot}2MF_5$ (M = Ta, Nb) have been prepared and their Raman spectra obtained at low temperature; $2KrF_2{\cdot}MF_5$ adducts were not isolated but possible evidence for $Kr_2F_3^+$ in solution has been obtained.

ALTHOUGH the XeF_2 adducts $XeF_2{\cdot}MF_5$ and $XeF_2{\cdot}2MF_5$, where M = Sb,[1–7] Ta[1,8] and Nb[8] and $2XeF_2{\cdot}SbF_5$[2,6,7,9] are known only one KrF_2 adduct, $KrF_2{\cdot}2SbF_5$, has been reported.[10]

We have found that tantalum pentafluoride reacts with krypton difluoride to give both $KrF_2{\cdot}TaF_5$ and $KrF_2{\cdot}2TaF_5$ but niobium pentafluoride gives only the 1:2 adduct. These new compounds were prepared from bromine pentafluoride solutions at low temperature. Qualitative evidence for the existence of $KrF_2{\cdot}SbF_5$, from the direct combination of the component molecules, has also been obtained. The Raman spectra of the solid adducts at −196° show that, as in the case of their xenon difluoride analogues,[9] the bonding in the adducts has both ionic and fluorine bridged contributions. Recently we have shown that the main Raman shifts which can be assigned to $\nu(Xe\text{–}F^+)$ in both the $XeF_2{\cdot}MF_5$ and $XeF_2{\cdot}2MF_5$ (M = Sb, Ta, Nb) series of adducts decrease $SbF_5 > TaF_5 > NbF_5$. This means that the Xe–F bond-length in XeF^+ is progressively lengthened and an increasing contribution from the fluorine–bridged structure is indicated.[9] The krypton difluoride adducts also appear to exhibit a similar trend. The main Raman shift which can be attributed to a $Kr\text{–}F^+$ stretch in each complex lies at slightly lower frequency than that for the corresponding xenon difluoride analogue (see Figure). Our value for $\nu(Kr\text{–}F^+)$ in $KrF_2{\cdot}2SbF_5$ differs slightly from that recently reported by Bartlett *et al.*[11] and coincides with the value predicted by Liu and Schaefer.[12]

$KrF_2{\cdot}2SbF_5$ can be pumped on for several hours without serious decomposition.[10] The new compounds are thermally much less stable; $KrF_2{\cdot}2TaF_5$ can be retained in a dynamic vacuum at −50° but decomposes slowly at −20° while $KrF_2{\cdot}2NbF_5$ decomposes very slowly at −50° and rapidly at −20°. In both cases the decomposition gives

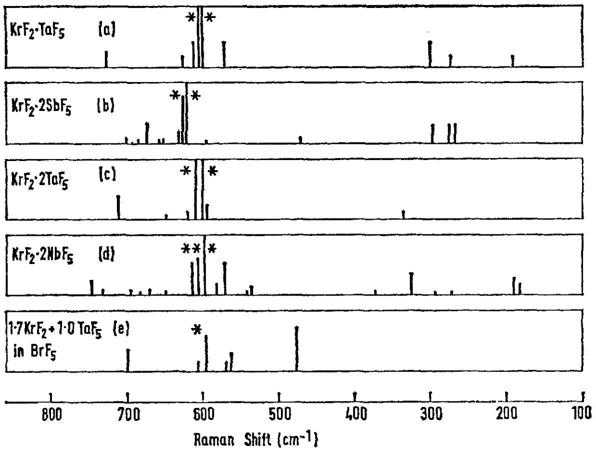

FIGURE. *Raman spectra of solid krypton difluoride adducts. Relative intensities are given in parentheses. Bands associated with* Kr–F$^+$ *stretching are marked* *. *They are split presumably due to the existence of two or more crystallographically non-equivalent sites in the solids. Unmarked bands are attributable to* MF_6^- *or to* $M_2F_{11}^-$ *related species.*

(a) The band assigned to the XeF^+ stretch occurs in $XeF_2\cdot TaF_5$ as a triplet at 600·9(87), 607·5(100), 614·2(54) cm^{-1}[9] *vs.* a KrF^+ stretching doublet at 599 (97), 603·5(100) cm^{-1}. (b) The band attributable to KrF^+ stretching occurs as a doublet at 620(100), 623(80) cm^{-1} whereas only a single line at 623·6(100) cm^{-1} is observed in the XeF_2 analogue of the adduct.[9] (c) The triplet attributable to XeF^+ stretching in the XeF_2 analogue occurs at 602(70), 609·4(100), 613·7(80) cm^{-1}[9] *vs.* a KrF^+ stretching doublet at 600(100), 609(100) cm^{-1}. (d) In the XeF_2 analogue a single line at 598·4(100) cm^{-1} related to XeF^+ stretching is observed[9] *vs.* a KrF^+ stretching triplet at 597(100), 605·4(63), 613·4(55) cm^{-1}. (e) Frozen solution in BrF_5 recorded at −196°. Bands attributable to the solvent are deleted. Intensities are given relative to the intense BrF_5 line at 527 cm^{-1}.

rise to the component molecules. The $KrF_2\cdot TaF_5$ complex decomposes slowly at −35° to give $KrF_2\cdot 2TaF_5$. Our lack of evidence for $KrF_2\cdot NbF_5$ probably means that the adduct has very low stability at −27°, the reaction temperature.

$2KrF_2\cdot MF_5$ adducts were not isolated under the conditions used but Raman spectra of frozen solutions containing excess of KrF_2 with TaF_5 in BrF_5 are different from those of the isolated adducts (see Figure). The Raman shift at 477(72) cm^{-1} is due to undissociated KrF_2 and those at 699(36) and 579·5(14) cm^{-1} to the ν_1 and ν_2 modes of TaF_6^-[13] or related species, while that at 603(17) cm^{-1} is almost certainly due to KrF^+. The expected related shift at *ca.* 599 cm^{-1} (*cf.* $KrF_2\cdot TaF_5$ and $KrF_2\cdot 2TaF_5$) was not observed but may be obscured by the intense band at 595(60) cm^{-1} which, together with the band at 571(30) cm^{-1}, could well be due to $Kr_2F_3^+$. This tentative assignment correlates well with the spectra of related xenon adducts and points to an equilibrium between KrF_2, KrF^+, and $Kr_2F_3^+$ in solution.

Preliminary investigations of the low-temperature fluorinating ability of KrF_2 have shown that it will oxidize iodine to IF_7 and xenon to XeF_6 at room temperature.

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[1] A. J. Edwards, J. H. Holloway, and R. D. Peacock, *J. Chem. Soc.*, 1963, 275.
[2] O. D. Maslov, V. A. Legasov, V. N. Prusakov, and B. B. Chaivanov, *Russ. J. Phys. Chem.*, 1967, **41**, 984.
[3] B. Cohen and R. D. Peacock, *J. Inorg. Nuclear Chem.*, 1966, **28**, 3056.
[4] F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc.*, 1969, 2179.
[5] V. M. McRae, R. D. Peacock, and D. R. Russell, *Chem. Comm.*, 1969, 62.
[6] G. S. Baranov, N. P. Egorov, A. N. Sopikov, and B. B. Chaivanov, *Russ. J. Phys., Chem.*, 1972, **46**, 10.
[7] B. B. Chaivanov, *Russ. J. Phys. Chem.*, 1972, **46**, 13.
[8] J. H. Holloway and J. G. Knowles, *J. Chem. Soc.* (*A*), 1969, 756.
[9] J. H. Holloway and B. Frlec, to be published.
[10] H. Selig and R. D. Peacock, *J. Amer. Chem. Soc.*, 1964, **86**, 3895.
[11] D. E. McKee, C. J. Adams, A. Zalkin, and N. Bartlett, *J.C.S. Chem. Comm.*, 1973, 26.
[12] B. Liu and H. F. Schaefer III, *J. Chem. Phys.*, 1971, **55**, 2369.
[13] O. L. Keller, jun., and A. Chetham-Strode, jun., *Inorg. Chem.*, 1966, **5**, 367.