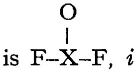
The Hydrolysis of Xenon Tetrafluoride at $-80°$

By J. S. OGDEN and J. J. TURNER
(*University Chemical Laboratory, Lensfield Road, Cambridge*)

WHEN xenon tetrafluoride reacts with water at room temperature, the final reaction products are xenon, hydrofluoric acid, oxygen, and an aqueous species of xenon from which the trioxide may be recovered on evaporation. Also observed during the course of the reaction is a transitory yellow species,[1] the possible nature of which is the subject of this Communication.

XeF_4 and H_2O vapour were sprayed from two separate vacuum systems on to a CsI window cooled to $-80°$ in a conventional all-metal Dewar vessel.[2] The solid deposit was bright yellow. Using a Perkin–Elmer 521 infrared spectrometer (range 4000—250 cm.$^{-1}$), three infrared absorption bands were observed at 747, 520, and 490 cm.$^{-1}$ ($\pm$ 5 cm.$^{-1}$, half width $\sim$12 cm.$^{-1}$) in addition to bands due to ice and HF. XeF_4 alone gave a broad (half width $\sim$25 cm.$^{-1}$) band centred at 530 cm.$^{-1}$, together with a sharper band at 282 $\pm$ 3 cm.$^{-1}$. Deposition of H_2O on top of this produced the same three bands, but reaction ceased quickly, presumably because H_2O cannot diffuse into XeF_4 at this temperature. The three bands grow in intensity together, and disappear together on warming up the CsI window, and due to reaction with the excess of water the final product, identified by its i.r. spectrum, is XeO_3. The three bands thus belong to the same species. On using D_2O, the higher-frequency bands due to hydrofluoric acid and ice shifted to lower frequency, but the three low-frequency bands remained unaffected. On using a mixture of $H_2{}^{18}O/H_2{}^{16}O$ ($^{18}O:{}^{16}O \sim 3:2$) bands were observed at 747, 710, 520, and 490 cm.$^{-1}$; this spectrum is shown in the Figure.

Williamson and Koch[1] observed no e.s.r. signal from the yellow solid trapped in an ice matrix. We have condensed XeF_4 and H_2O together in a quartz apparatus at $-80°$ and also observed no e.s.r. signal from the product. The e.s.r. and i.r. work *suggest* that the reaction product at $-80°$ contains no H (no D shift with D_2O), one atom of O (only *two* bands around 700 cm.$^{-1}$ using a 3:2 $^{18}O:{}^{16}O$ mixture) and hence, assuming the species contains xenon, and is uncharged, must contain an even number of fluorine atoms (no e.s.r. signal). The i.r. spectra of the known oxygen fluorides and of $XeOF_4$[3] do not correspond to the observed bands; $XeOF_6$ seems unlikely, and hence $XeOF_2$ is the most likely product. The only previous reports of $XeOF_6$ are by Streng *et al.*[4] who suggest $XeOF_2$ is a colourless transparent solid, and by Edwards *et al.*[5] who state "preliminary experiments suggest [the product] may be $XeOF_2$". It is of course possible that the yellow intermediate is not present in sufficient quantities to give an i.r. spectrum, and that we are looking at a different colourless compound produced at the same time.

If the product (yellow or colourless) is $XeOF_2$, the most likely structure is  $\overset{\overset{\displaystyle O}{|}}{F{-}X{-}F}$, *i.e.*, planar, with an O–Xe–F angle of about 90°. The O–Xe–F angle in $XeOF_4$ is 92° and is thus similar to the pentafluorides of Br and Cl where the $F{-}X{-}F_4$ angle is $\sim$90°. $XeOF_2$ might therefore be compared with ClF_3, where the $F{-}X{-}F_2$ angle is $\sim$89°. On this analogy, $XeOF_2$ has C_{2v} symmetry, and six fundamental normal modes of vibration: ν_1 (A_1), Xe–O str., ν_2 (A_1) Xe–F sym. str., ν_3 (A_1) OXeF sym. bend, ν_4 (B_2) Xe–F asym. str., $\nu_5(B_2)$ OXeF asym. bend, $\nu_6(B_1)$ out-of-plane bend. We assign 747 (710) as ν_1, 520 as ν_2, and 490 as ν_4. Begun *et al.*[3] in their normal-co-ordinate analysis of $XeOF_4$ report little mixing of vibrations. If this is so for $XeOF_2$, we can estimate the Xe–O stretching force constant, assuming a diatomic Xe–O group, and using the frequency 747 cm.$^{-1}$; a value of 4·7 mdynes/Å is obtained. A similar calculation for $XeOF_4$ gives 7·2 mdynes/Å compared with 7·08 mdynes/Å using the full force-field.[3] The difference between the two Xe–O force constants is not surprising since the force constant is expected to decrease with lowering of the oxidation state of xenon (*cf.*, the interhalogens XF_3 and XF_5).

FIGURE

I.r. spectrum of reaction products: $XeF_4 + H_2{}^{16}O/H_2{}^{18}O$ *at* −80°.

The bands at 520 and 490 are reasonably assigned to Xe–F stretching vibrations. The Xe–F stretching vibrations in $XeOF_4$ are not very different from the approximately corresponding vibrations in XeF_4, and the two Xe–F stretching frequencies in XeF_2 are at 557 (asym.) and 496 (sym.) cm.$^{-1}$. We have assigned 520 as the symmetric stretch, by analogy with ClF_3, where the corresponding symmetric stretch is higher in frequency than the asymmetric stretch.

Other possible species are FXeOF, FXeOH, and $(FXeO)^-$. The first is unlikely, apart from chemical reasoning, since there would be Xe–O–F "sym." and "asym." vibrations which would *both* be sensitive to oxygen-isotope substitution. The spectrum of the second would be deuterium-sensitive. We cannot entirely eliminate the third, which would presumably be linear, since the bands at 520 and 490 cm.$^{-1}$ could arise from a single Xe–F vibration split either by correlation field coupling or by Fermi resonance with $2\nu_2$, and this mode can be shown to be rather insensitive to ^{18}O substitution. Further work is in progress on this, and we hope to obtain the low-frequency bending vibrations. The formation of the intermediate $XeOF_2$

$$XeF_4 + H_2O \rightarrow XeOF_2 + 2HF$$

and its subsequent decomposition are consistent with the overall stoicheiometry of the room-temperature reaction.[1]

(*Received, August* 18*th*, 1966; *Com.* 611.)

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[1] S. M. Williamson and C. W. Koch, "Noble-Gas Compounds" ed. H. H. Hyman, University of Chicago Press.
[2] W. H. Duerig and I. L. Mador, *Rev. Sci. Instr.*, 1959, **23**, 421.
[3] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, 1965, **42**, 2236.
[4] A. G. Streng, A. D. Kirshenbaum, L. V. Streng, and A. V. Grosse, "Noble-Gas Compounds", ed. H. H. Hyman. University of Chicago Press.
[5] A. J. Edwards, J. H. Holloway, and R. D. Peacock, *Proc. Chem. Soc.*, 1963, 275.