

## $^{19}\text{F}$ Chemical Shift of Dioxygen Difluoride

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In the course of our studies of the spectroscopic properties of some oxygen fluorides, we have observed an unusually low value for the  $^{19}\text{F}$  chemical shift of dioxygen difluoride ( $\text{O}_2\text{F}_2$ ). We report the value here in view of the great current interest in these compounds.<sup>1</sup> A dilute solution of  $\text{O}_2\text{F}_2$  in  $\text{CF}_3\text{Cl}$  shows a single peak at  $865 \pm 10$  p.p.m. in the low-field side of the solvent peak. Since this value is so large, we have been anxious to make sure that it is a genuine chemical shift.

We have observed no change in the peak position, relative to  $\text{CF}_3\text{Cl}$ , over the temperature range  $-80^\circ$  to  $-130^\circ\text{C}$ , and only a small change with concentration:

$$\delta[\text{CF}_3\text{Cl} (90\%) - \text{O}_2\text{F}_2 (10\%)] = 865 \pm 10 \text{ p.p.m.}$$

$$\delta[\text{CF}_3\text{Cl} (50\%) - \text{O}_2\text{F}_2 (50\%)] = 880 \pm 10 \text{ p.p.m.}$$

Dioxygen difluoride, solid and liquid, is known to contain a paramagnetic species,<sup>2</sup> and using a

simple quartz apparatus<sup>3</sup> we were able to observe the e.s.r. and n.m.r. spectra of the same sample of  $\text{O}_2\text{F}_2$  in  $\text{CF}_3\text{Cl}$ . The e.s.r. spectrum is a doublet at  $g = 2.004 \pm 0.0005$  with hyperfine splitting  $12.5 \pm 1$  gauss, and may be due to  $\text{O}_2\text{F}$ , which is known to exist as a stable free-radical.<sup>4</sup> Exchange between  $\text{O}_2\text{F}$  and  $\text{O}_2\text{F}_2$  could affect the chemical shift and also the line-width of the  $\text{O}_2\text{F}_2$  signal. Addition of oxygen difluoride ( $\text{OF}_2$ ), which appears to contain the same free radical as  $\text{O}_2\text{F}_2$ , increased the intensity of the e.s.r. signal by an order of magnitude, but did not measurably change the chemical shift of  $\text{O}_2\text{F}_2$ . Furthermore, the line-width of the  $\text{O}_2\text{F}_2$  peak, measured under non-spin conditions, was the same as  $\text{CF}_3\text{Cl}$ —about 8c./sec. We therefore conclude that either no exchange is taking place, or that the concentration of free radicals is much too low to affect greatly the n.m.r. spectrum.

We think it highly probable that the value observed is the "true" chemical shift of  $\text{O}_2\text{F}_2$ ; it

might be compared with a value of  $-510$  p.p.m. for FNO<sup>5</sup> and approximately  $-800$  p.p.m. for the average <sup>19</sup>F shift in UF<sub>6</sub>,<sup>6</sup> both referred to CF<sub>3</sub>Cl. It is possible that low-lying excited

states of O<sub>2</sub>F<sub>2</sub><sup>7</sup> are chiefly responsible<sup>8</sup> for this value.

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<sup>1</sup> A. G. Streng, *Chem. Rev.*, 1963, **63**, 607.

<sup>2</sup> Private communication from F. I. Metz, to whom we are greatly indebted.

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