The Reactions between $O_2(^1\Delta_g)$ and Tetramethylethylene and 2,5-Dimethylfuran in the Gas Phase

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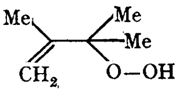
THERE is strong evidence[1] that $O_2(^1\Delta_g)$ reacts with olefins in solution but the corresponding gas-phase reactions have received little attention. Winer and Bayes[2] studied the kinetics of the decay of $O_2(^1\Delta_g)$, generated by use of a microwave discharge, in the presence of tetramethylethylene (TME) vapour. They identified the hydroperoxide (I) as a product but did not measure the yield. However, Corey and Taylor[3] found no reaction between $O_2(^1\Delta_g)$ and TME in the gas phrase. Murray and Kaplan[4] mixed $O_2(^1\Delta_g)$, generated from a triphenyl phosphite–ozone complex, with TME vapour but the results were inconclusive. We have therefore studied the reactions of $O_2(^1\Delta_g)$ with TME vapour and with 2,5-dimethylfuran (DMF) vapour which is believed to react rapidly with $O_2(^1\Delta_g)$ in solution.

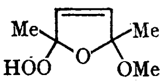
High-purity O_2 was passed through a microwave discharge at 1—10 torr pressure and then over a film of HgO to remove oxygen atoms. Vapour of TME or DMF was injected downstream from the film. The products were trapped with liquid nitrogen.

With TME, the trap contained unchanged TME plus a clear viscous liquid which had i.r. and n.m.r. spectra and g.l.c. retention volumes identical with those of a sample of (I).[5] Thus Winer and Bayes' results are confirmed. Quantitative g.l.c. analysis of the contents of the trap indicated that (I) is the only product and that about 50 mole-% of the TME was converted into (I). The gas stream was also monitored directly using a 10 m. path-length i.r. cell. The hydroperoxide (I) was readily detected by its intense bands at 3595 and 906 cm.$^{-1}$; it was not formed without the discharge.

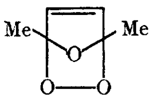
The reaction between $O_2(^1\Delta_g)$ and DMF in solution was studied[6] using methanol as solvent; the final product was (II), which was probably formed *via* the unstable ozonide (III). For the gas-phase reaction, we injected DMF into the O_2 stream with the discharge off and the i.r. spectrum of the gas stream was identical with that of DMF vapour. On switching on the microwave discharge, new bands appeared at 1334 and 1131 cm.$^{-1}$ which we tentatively assign to the ozonide (III). Methanol vapour was then injected into the gas stream as it entered the i.r. cell; the new bands were unaffected. The gas stream was passed through a trap cooled in liquid nitrogen, and a viscous, involatile liquid remained after removal of unreacted DMF and MeOH. The i.r. and n.m.r. spectra of the white crystalline material recovered from the liquid were the same as those of an authentic sample of (II).[6] The gas-phase bands assigned to (III) were not present in the spectrum of (II). About 50 mole-% of the DMF was converted to (II) which we estimate to have a purity of better than 80%. The i.r. spectrum of the viscous liquid indicated that other products were present in small amounts; these probably arose from cracking of the ozonide (III).



(I)



(II)



(III)

These results show conclusively that both TME and DMF react readily with $O_2(^1\Delta_g)$ in the gas phase to give relatively pure products.

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