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SYNTHESIS OF t-BUTYL AND METHYL PEROXYNITRATE

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Acylperoxynitrates ($R-\overset{O}{\overset{\|}{C}}-OONO_2$) are known constituents of photochemical smog[1]. These compounds are supposed to be formed from acylperoxy radicals and NO_2. Although alkylperoxy radicals undoubtedly play an important role in photochemical smog formation[2] and gasphase reaction of these radicals with NO_2 seems likely[3], alkyl peroxynitrates (I) have thus far not been detected in photochemical smog. From the investigations of Lachowicz[4] and ourselves[5] we learned that β-nitroalkyl peroxynitrates are relatively stable compounds. Considering this it seemed worthwhile to try to synthesize some simple alkyl peroxynitrates by reaction of the alkylhydroperoxides with N_2O_5:

$$ROOH + N_2O_5 \longrightarrow \underset{(I)}{R-O-O-NO_2} + HNO_3 \qquad \begin{matrix}(a\ \ R = t\text{-}C_4H_9)\\(b\ \ R = CH_3)\end{matrix}$$

The feasibility of the method was first tested for the case $R = t\text{-}C_4H_9$. A solution of N_2O_5[6] (in $CHCl_3$) was slowly added to a cooled (-20^o) solution of t-BuOOH in CCl_4 in the presence of excess dry $NaHCO_3$*). After removal of the solids the resulting solution showed a strong IR band at 1692 cm^{-1} and a sharp NMR singlet at δ 1.36 indicating[4,5] the presence of Ia. Removal of the solvent and distillation yielded a liquid ($bp_{11} \sim 22^o$) which was shown by NMR to consist of 70 mole % of Ia and 30 mole % of $t\text{-}BuONO_2$[7] (δ 1.57). An IR spectrum obtained after sucking the vapour above

*) Without $NaHCO_3$ the alkylperoxynitrate is rapidly destroyed by the nitric acid which is formed in the reaction.

the liquid mixture (at 23°) into an evacuated cell (10 cm) showed a sharp band at 1712 cm^{-1} ($-OONO_2$) clearly indicating the presence of Ia in the vapour. Other bands indicated that t-$BuONO_2$ and traces of residual solvent were also present in the vapour. By following the decay of the band at 1712 cm^{-1} it was found that the half life of Ia in the gas phase (estimated pressure 5-10 mm Hg) was about 30 hours. In $CHCl_3/CCl_4$ solution at 23° the half life was about 11 days (NMR; the only decomposition product detected was t-$BuONO_2$).

Our method to prepare I was then applied to the more interesting case of R = CH_3 (Ib is more likely to be formed in photochemical smog than Ia). Starting from methyl hydroperoxide*) and using slightly modified reaction conditions ($CDCl_3$, -28°) a solution of Ib in $CDCl_3$ was obtained. The NMR spectrum at -30° only showed one sharp singlet at δ 4.17; the peaks of CH_3OOH were absent. The yield of Ib (conc. 0.4 M) was close to 100 % ($CHCl_3$ was used as the internal NMR standard). The IR spectrum of the solution at -20° showed a strong band at 1698 cm^{-1}. After standing of the filtered solution at 23° for 4 days the NMR singlet at δ 4.17 and the IR band at 1698 cm^{-1} had disappeared indicating complete decomposition of Ib. Methyl nitrate[10] was the major decomposition product (0.4 mole per mole of Ib) as indicated by NMR (broad peak at δ 4.11[11]), IR (band at 1635 cm^{-1}) and G.L.C. Other decomposition products identified were methanol, dimethoxymethane, paraformaldehyde, methyl formate and strong acid (probably HNO_3). Attempts to isolate Ib and to obtain a gas phase IR spectrum have thus far failed because volatilities of Ib and $CDCl_3$ appeared to be very similar.

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*) Prepared according to a known procedure[8]. Because CH_3OOH is a hazardous compound[9] only small portions ($\leq$ 5 g) of the crude product were distilled; purity of the samples obtained was 90 % as determined by NMR (δ_{CDCl_3} 3.89) and iodometric titration.