

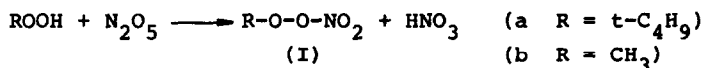
## SYNTHESIS OF t-BUTYL AND METHYL PEROXYNITRATE

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Acylperoxynitrates ( $R-\overset{\text{O}}{\parallel}{\text{C}}-\text{OONO}_2$ ) are known constituents of photochemical smog<sup>1)</sup>. These compounds are supposed to be formed from acylperoxy radicals and  $\text{NO}_2$ . Although alkylperoxy radicals undoubtedly play an important role in photochemical smog formation<sup>2)</sup> and gasphase reaction of these radicals with  $\text{NO}_2$  seems likely<sup>3)</sup>, alkyl peroxynitrates (I) have thus far not been detected in photochemical smog. From the investigations of Lachowicz<sup>4)</sup> and ourselves<sup>5)</sup> we learned that  $\beta$ -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  $\text{N}_2\text{O}_5$ :



The feasibility of the method was first tested for the case  $R = t\text{-C}_4\text{H}_9$ . A solution of  $\text{N}_2\text{O}_5$ <sup>6)</sup> (in  $\text{CHCl}_3$ ) was slowly added to a cooled ( $-20^\circ$ ) solution of  $t\text{-BuOOH}$  in  $\text{CCl}_4$  in the presence of excess dry  $\text{NaHCO}_3$ <sup>\*</sup>). After removal of the solids the resulting solution showed a strong IR band at  $1692 \text{ cm}^{-1}$  and a sharp NMR singlet at  $\delta 1.36$  indicating<sup>4,5)</sup> the presence of Ia. Removal of the solvent and distillation yielded a liquid ( $\text{bp}_{11} \sim 22^\circ$ ) which was shown by NMR to consist of 70 mole % of Ia and 30 mole % of  $t\text{-BuONO}_2$ <sup>7)</sup> ( $\delta 1.57$ ). An IR spectrum obtained after sucking the vapour above

\* Without  $\text{NaHCO}_3$  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<sup>-1</sup> (-OONO<sub>2</sub>) clearly indicating the presence of Ia in the vapour. Other bands indicated that t-BuONO<sub>2</sub> and traces of residual solvent were also present in the vapour. By following the decay of the band at 1712 cm<sup>-1</sup> 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<sub>3</sub>/CCl<sub>4</sub> solution at 23° the half life was about 11 days (NMR; the only decomposition product detected was t-BuONO<sub>2</sub>).

Our method to prepare I was then applied to the more interesting case of R = CH<sub>3</sub> (Ib is more likely to be formed in photochemical smog than Ia). Starting from methyl hydroperoxide<sup>\*</sup>) and using slightly modified reaction conditions (CDCl<sub>3</sub>, -28°) a solution of Ib in CDCl<sub>3</sub> was obtained. The NMR spectrum at -30° only showed one sharp singlet at δ 4.17; the peaks of CH<sub>3</sub>OOH were absent. The yield of Ib (conc. 0.4 M) was close to 100 % (CHCl<sub>3</sub> was used as the internal NMR standard). The IR spectrum of the solution at -20° showed a strong band at 1698 cm<sup>-1</sup>. 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<sup>-1</sup> had disappeared indicating complete decomposition of Ib. Methyl nitrate<sup>10)</sup> was the major decomposition product (0.4 mole per mole of Ib) as indicated by NMR (broad peak at δ 4.11<sup>11)</sup>), IR (band at 1635 cm<sup>-1</sup>) and G.L.C. Other decomposition products identified were methanol, dimethoxy-methane, paraformaldehyde, methyl formate and strong acid (probably HNO<sub>3</sub>). Attempts to isolate Ib and to obtain a gas phase IR spectrum have thus far failed because volatilities of Ib and CDCl<sub>3</sub> appeared to be very similar.

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\*<sup>8)</sup> Prepared according to a known procedure<sup>8)</sup>. Because CH<sub>3</sub>OOH is a hazardous compound<sup>9)</sup> only small portions (< 5 g) of the crude product were distilled; purity of the samples obtained was 90 % as determined by NMR (δ<sub>CDCl<sub>3</sub></sub> 3.89) and iodometric titration.