

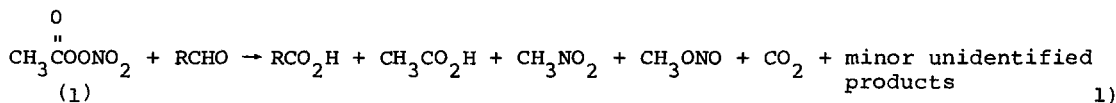
THE REACTION OF PEROXYACETYL NITRATE WITH ALDEHYDES


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Peroxyacetyl nitrate (PAN) is the most common member of the family of peroxyacyl nitrates which are formed in photochemically polluted atmospheres.<sup>1</sup> PAN (1) has been identified as a phytotoxant<sup>2</sup> and an eye irritant,<sup>3,4</sup> and it is lethal to mice if administered in sufficiently high concentrations.<sup>5</sup> Because of these biological effects, the biochemistry of PAN has been studied,<sup>6</sup> but its chemistry is not well defined.<sup>7-9</sup> As a result of these biochemical reactions and its potentially interesting chemistry, we have begun a comprehensive study of the reactions of PAN with a variety of organic compounds.

As part of this survey of PAN reactions, we have investigated the reaction of PAN with aldehydes. It was found that the addition of an aldehyde to solutions of PAN (0.2-0.3 M in CDCl<sub>3</sub>, CCl<sub>4</sub>, benzene-d<sub>6</sub>, and acetone-d<sub>6</sub>) resulted in the oxidation of the aldehyde to the corresponding acid (Reaction 1) in approximately 85% yield (by NMR in excess PAN). The identity of the product was in each case



R = Me, Et, iPr, t-Bu, 

proved by comparison of its NMR and IR spectra with those of an authentic sample (Aldrich, Eastman).

The principle products derived from PAN were established in a similar manner. Nitromethane was identified by its NMR and IR spectra (4.31 $\delta$ , CCl<sub>4</sub>; 1563 cm<sup>-1</sup>, CHCl<sub>3</sub>). Acetic acid was identified by its NMR spectrum (2.07 $\delta$ , CCl<sub>4</sub>) and its glpc retention time. Methyl nitrite was observed in the NMR (3.97 $\delta$ , CCl<sub>4</sub>), and the UV spectrum of the reaction mixture contained the characteristic structure of methyl nitrite ( $\lambda_{\text{max}}$  = 343, 356, 369, 387 nm, CHCl<sub>3</sub>).<sup>10</sup> The 2340 cm<sup>-1</sup> band of carbon dioxide was observed when the reaction was monitored by IR.<sup>11</sup>

Since PAN yields acetic acid as well as the nitrite and nitro compounds, there must be some  $\text{NO}_2$  produced which does not result in one of the nitrogenous products. Attempts to see free  $\text{NO}_2$  in the IR were unsuccessful because of interference from other product bands.

While the overall reaction products remained the same in the different solvents used, the reaction pathway varied with solvent. When the reaction was carried out in  $\text{CCl}_4$ , an intermediate was observed. This intermediate was shown to be the acid chloride corresponding to the product acid by comparison of its NMR with that of an authentic sample. Methyl chloride was demonstrated to be a minor product from PAN under these conditions. Reaction 2 illustrates this scheme. In addition, the relative amounts of the observed PAN products differed markedly in going from  $\text{CCl}_4$  to benzene (see Table 1).

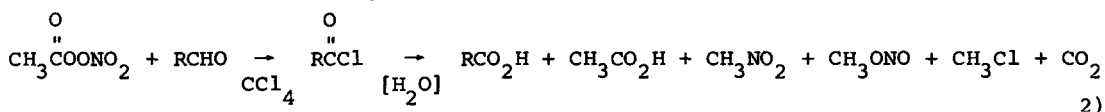
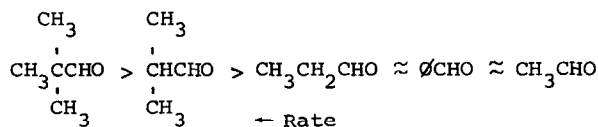


TABLE I  
PAN Products, % of Total, from Reaction of Isobutyraldehyde

SOLVENT	$\text{CH}_3\text{CO}_2\text{H}$	$\text{CH}_3\text{ONO}$	$\text{CH}_3\text{NO}_2$	$\text{CH}_3\text{Cl}$	Others
$\text{CCl}_4$	73	7	12	8	0
Benzene	39	12	35	0	14

The relative rates of reaction of the aldehydes studied were determined in benzene and  $\text{CCl}_4$ . These results are shown in Table II and were not affected by solvent change. It is clear from these data that the bulk of the substituent

TABLE II



does not inhibit the oxidation; however, the results do show a general trend of increasing rate with increasing electron donating ability.<sup>12</sup> The absolute rate data on this system is not yet available; however, studies in ten fold excess propanal have shown that the reaction is first order in PAN, with a pseudo first order rate constant of  $1.1 \pm 0.4 \times 10^{-4} \text{ sec}^{-1}$ .

The stoichiometry of the reaction is not simple. In the presence of excess aldehyde there are 1-3 moles of aldehyde consumed for each mole of PAN reacted. In the presence of excess PAN, the result is much the same with ~1.5 moles of aldehyde reacting for each mole of PAN.

The data obtained thus far do not permit the assignment of a mechanism for this reaction. The data do, however, point to a free radical mechanism as the most probable. The variable stoichiometry is consistent with a free radical process which is initiated by reaction with PAN. The two nitrogenous products might well arise from the coupling of a methyl radical and  $\text{NO}_2$ . The observation of methyl chloride when the reaction is run in  $\text{CCl}_4$  supports this hypothesis, and the observation of acid chlorides in  $\text{CCl}_4$  strongly suggests the presence of an acyl radical.

In its reaction with aldehydes, PAN has once again proven to be a unique reagent.<sup>7,9</sup> This oxidation of aldehydes to acids by peroxy compounds has analogy only in the Baeyer-Villiger reaction with peracids.<sup>13</sup> However, this reaction proceeds via an ionic mechanism with an acid catalyst and is observed with ketones as well as aldehydes. The reaction of PAN with aldehydes is, for the reasons cited above, almost certainly free radical in mechanism, proceeds without acid and is specific to aldehydes, ketones (e.g. acetone- $\text{d}_6$ ) being inert. It is clear that this reaction proceeds through a mechanism different from those common to most peroxy compounds.<sup>14</sup>

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