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Mechanism of Peroxyacetyl Nitrate Formation

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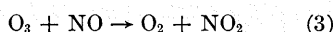
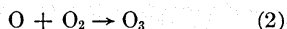
Environmental Protection Agency, Air Pollution Control Office

It is proposed that peroxyacetyl nitrate and its homologues are formed in polluted air by a reaction between acylate (or aroylate) radicals and nitrogen trioxide. The proposed reaction accounts for the delayed formation of peroxyacetyl nitrate upon the irradiation of low concentrations of hydrocarbons and nitrogen oxides in air. It also explains why peroxyacetyl nitrate is not formed in photooxidations at high reactant concentrations. It accounts for the formation of peroxyacetyl nitrate in the dark reaction of acetaldehyde, oxygen, and N_2O_5 ; and, finally, it explains the inhibiting effect that excess NO_2 has on that dark reaction. The proposed reaction could yield either the accepted peroxyacetyl nitrate molecular structure or a molecular structure called acetyl pernitrate that does not include an oxygen-oxygen bond. The chemical properties of the molecule can be reconciled with either formulation.

The mechanism of formation of peroxyacetyl nitrate (PAN) and its homologues in the polluted atmosphere is still somewhat uncertain. One of the basic questions of photochemical air pollution is why PAN formation occurs so late in the sequence of atmospheric chemical changes. It has been shown repeatedly that PAN does not appear in the photolysis of polluted air until after the NO has been reduced to a very low concentration, the NO_2 has reached its maximum, and the ozone has begun to build up in concentration. This is illustrated in Figure 1 by reactant loss and product formation curves similar to those recently presented for ambient polluted air by Kopczynski, Lonneman, Sutterfield, and Darley.¹ Similar data were presented in earlier studies of artificial pollutant mixtures by Schuck and Doyle and by Stephens.^{2,3} The delay in PAN formation was ascribed by Stephens to different rates at which NO and NO_2

react with peroxyacetyl radicals. This explanation still seems plausible, but an alternative explanation which may more satisfactorily account for the observations is set forth below.

The relative positions of the NO, NO_2 , and O_3 curves in Figure 1 can be accounted for without too much difficulty. The basic ozone generating reactions are the photolysis of NO_2 , followed by the reaction of atomic oxygen with molecular oxygen. The fast reaction between ozone and nitric oxide then regenerates NO_2 :



With excess NO in the system, the speed of the reaction between NO and O_3 will keep the steady-state O_3 concentration negligible. The hydrocarbon

disturbs the relative concentrations of the reactants by supplying peroxide radicals which oxidize NO to NO_2 without removing O_3 . As the NO_2 concentration increases, O_3 is generated at a proportionally faster rate; and its concentration increases while the NO concentration decreases, although it remains low until the NO is almost gone. Near the end of the NO conversion, the O_3 and NO concentrations exchange positions very quickly; detectable amounts of O_3 appear in the system, and the NO concentration becomes negligible. After the O_3 begins to accumulate, PAN formation follows.

In trying to determine why PAN formation takes so long, it is logical to suggest that the formation of PAN requires either O_3 as a direct reactant or some other reactant that does not appear in the system until after the O_3 has appeared.

The requirement of O_3 as a direct reactant appears to be ruled out by a key experiment reported in 1962 by Tuesday.⁴ He showed that PAN is readily synthesized in the dark thermal reaction between acetaldehyde, oxygen, and N_2O_5 . It is very unlikely that O_3 could be present in such a system.

The fact that acetaldehyde, oxygen, and N_2O_5 do yield PAN, however, suggests that NO_3 may be the key reactant in PAN formation. The NO_3 would exist in equilibrium with the N_2O_5 .

In atmospheric photolysis, NO_3 will begin to form after the O_3 builds up in the presence of NO_2 :



This NO_3 can remain free to react because at parts-per-hundred million

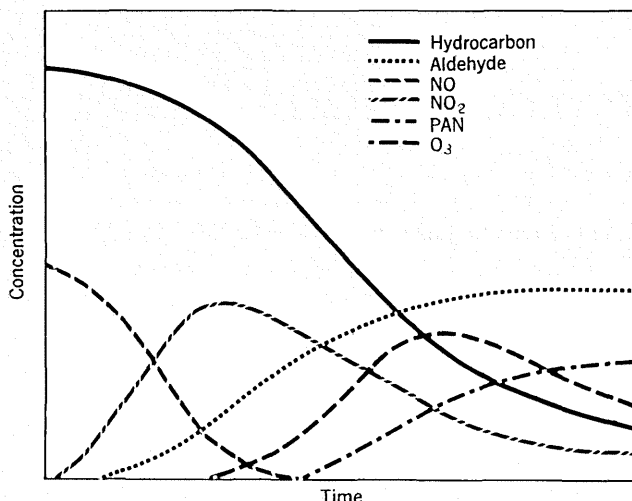
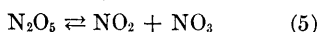


Figure 1. Reactant loss and product formation in photochemical oxidations.

(pphm) levels, N_2O_5 will be substantially dissociated.⁵



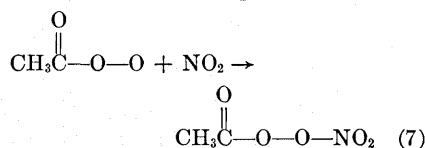
$$K = \frac{(NO_2)(NO_3)}{(N_2O_5)} = 1.33 \times 10^{-10} \text{ moles/liter} \quad (6)$$

If (N_2O_5) is 1 pphm, (NO_2) and (NO_3) will each be about 0.5 pphm.

If NO_3 is the reactant that forms PAN, several other previously unexplained phenomena can be explained. One of these is the observation by Stephens that although PAN formation takes place in the dark reaction involving N_2O_5 , acetaldehyde, and oxygen, this same reaction is inhibited by the presence of excess NO_2 .⁶ As Stephens states, the excess NO_2 will greatly reduce the NO_3 concentration in the system by N_2O_5 formation. From the equilibrium constant given above and Stephens' data, the concentrations of the gases he reacted with acetaldehyde have been calculated and compared with his observed PAN yields. The results of these calculations are given in Table I.

The table shows that the PAN yield does not correlate with the N_2O_5 , NO_2 , or O_3 concentrations, but that it does correlate very closely with the NO_3 concentration. In fact, the PAN yield appears to be directly proportional to the NO_3 concentration, as plotted in Figure 2.

A reaction previously suggested⁶ as the final step in atmospheric PAN formation is the following:



There is some difficulty, however, in reconciling this reaction with several of the experimental observations, as follows:

(a) Reaction (7) should occur quite early in the sequence of photochemical reactions. In fact, it should begin almost immediately, contrary to the observations.

(b) There is actually little evidence

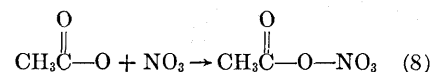
that peroxy radicals such as $CH_3C(=O)O-O$ have an appreciable lifetime in the atmosphere. On the contrary, there is experimental evidence that suggests that peroxyacyl radicals in polluted air will convert to acylate radicals,

$CH_3C(=O)O$, in preference to forming peroxy compounds. Stephens, Hanst, Doerr, and Scott, for example, report that photooxidation of aldehydes produces peroxy acids at Torr-level partial pressures but not at parts-per-million levels.⁷

(c) If reaction (7) is the correct PAN-forming reaction, it should take place in photooxidations conducted at Torr-level partial pressures, but it is a fact that PAN is never formed under those conditions.

(d) The data of Table I also argue against reaction (7) because the PAN yield does not correlate with the NO_2 concentration.

A PAN-forming reaction involving NO_3 , which will fit with many or all of the known facts, is the following:



This reaction fits observations in the following ways:

(a) The above NO_3 reaction could occur in the acetaldehyde-oxygen- N_2O_5 synthesis of PAN.

(b) The above NO_3 reaction could not occur in the atmosphere until after the NO was gone from the reaction system and O_3 had begun to appear.

(c) The above NO_3 reaction could never occur in photooxidations conducted at Torr-level partial pressures because at such partial pressures O_3 and, hence, NO_3 are never formed.

(d) The above NO_3 reaction predicts a direct proportion between the concentration of NO_3 and the rate of PAN formation, which is a relationship demonstrated experimentally, and shown in Figure 2.

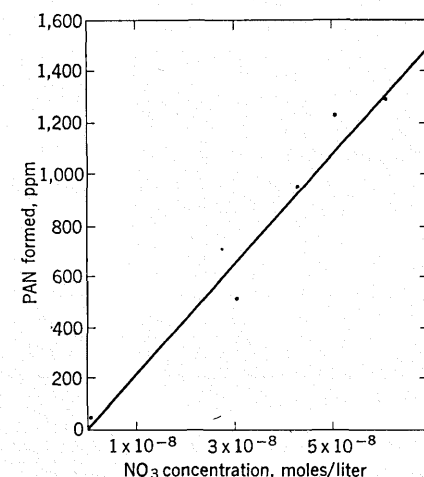


Figure 2. First order dependence of PAN formation of NO_3 concentration.

Table I. Reactants and products in the dark synthesis of PAN from NO₂, Ozone, Oxygen, and Acetaldehyde.

Reactant concentrations Moles/liter ^b			Gas concentrations in NO ₂ -O ₃ stream Moles/liter				Conc. of acetaldehyde mixed with NO ₂ -O ₃ stream Moles-liter	PAN Yield, ppm
NO ₂ /O ₃	NO ₂	O ₃	N ₂ O ₅	O ₃	NO ₂	NO ₃		
0.5	1.35×10^{-5}	2.7×10^{-5}	0.67×10^{-5}	2.03×10^{-5}	3.0×10^{-8}	3.0×10^{-8}	2.7×10^{-5}	510
1.0	2.7×10^{-5}	2.7×10^{-5}	1.35×10^{-5}	1.35×10^{-5}	4.2×10^{-8}	4.2×10^{-8}	2.7×10^{-5}	950
1.5	4.0×10^{-5}	2.7×10^{-5}	2.0×10^{-5}	0.68×10^{-5}	5.0×10^{-8}	5.0×10^{-8}	2.7×10^{-5}	1,240
2.0	5.4×10^{-5}	2.7×10^{-5}	2.7×10^{-5}	0	6.0×10^{-8}	6.0×10^{-8}	2.7×10^{-5}	1,300
2.5	6.6×10^{-5}	2.7×10^{-5}	2.7×10^{-5}	0	1.4×10^{-5}	1.4×10^{-10}	2.7×10^{-5}	2.7×10^{-5}

^a Table prepared from data presented by Stephens in reference 6.

^b All reactant concentrations are approximate to within 20%.

If reaction (8) is the correct PAN-forming reaction, the structure of PAN may or may not include an oxygen-oxygen bond, but if reaction (7) is correct, the structure of PAN must include an oxygen-oxygen bond. The generally

accepted PAN formation, $\text{CH}_3\text{C}(=\text{O})\text{O}-\text{NO}_2$, could result from reaction (8) as well as from reaction (7). An alternate formulation without an oxygen-oxygen bond that could result from reaction (8) but not from reaction (7) is acetyl pernitrate, APN, which may be

written as $\text{CH}_3\text{C}(=\text{O})\text{O}-\text{NO}_3$. PAN can be regarded as a mixed anhydride of peroxyacetic acid and nitric acid, whereas APN would be a mixed anhydride of acetic acid and pernitric acid.

The chemical properties of the substance may be as easily explained with one formula as with the other. The formation of nitrite ion and the evolution of oxygen on hydrolysis, as reported by Mudd⁸ and Stephens,⁹ for example, can be explained by the attack of OH⁻ ions on the carbonyl carbon with formation and decomposition of the NO₄⁻ ion. This ion may be called pernitrate on either formulation. Salts of pernitric acid have been prepared, and it is known that they decompose on solution, releasing oxygen.¹⁰ The esterification of PAN reported by Nicksic, Harkins, and Mueller can likewise be satisfactorily explained with either formula.¹¹

Although the discussion of this paper is intended to present support for the NO₃ mechanism of PAN formation, reaction (8), it is recognized that most of the experimental facts can also be reconciled with the NO₂ mechanism, reaction (7). What is indicated, therefore, is mainly that the mechanism of formation of PAN and its homologues, as well as the structure and properties of the molecules, are by no means closed subjects. Further experimental studies should be conducted on the conditions under which PAN and its homologues are formed and on the physical and chemical properties of the compounds. Direct observation of NO₃, perhaps by means of its infrared spectrum, should be attempted. Synthesis of PAN by mixing NO₃ gas with aldehyde vapor in oxygen should be undertaken. Further laboratory studies of the photooxidation of aldehydes may also yield new data. The great importance of PAN in understanding the effects of air pollution requires that such studies be continued.

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