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Promotion of the Oxidation of Nitric Oxide and Hydrocarbon by the Thermal Decomposition of Peroxyacetyl Nitrate (PAN) at Night

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The decomposition of PAN in the presence of nitric oxide and propene in the air was investigated at 30 ℃ under dark conditions. The number of nitric oxide molecules oxidized per each PAN molecule decomposed varied from 3.7 to above 5 with increase of the ratio of initial concentration of propene to that of nitric oxide.

It is well known that PAN and nitric acid are mainly photochemically generated from nitrogen oxides emitted into the atmosphere. In the daytime, PAN can accumulate up to a level of 40 ppb in the photochemically polluted atmosphere[1)] though it is thermally unstable. PAN easily decomposes into peroxyacetyl radical and nitrogen dioxide by reaction (1). In the daytime, the concentration of nitrogen dioxide is also high and then PAN is regenerated by the reverse reaction of (1). Therefore, PAN looks like a stable product in the presence of a higher concentration of nitrogen dioxide. When a large amount of nitric oxide is emitted into the atmosphere in the evening, the stability of PAN is lost by the sequential reactions (1)-(8).[2)]

$$CH_3C(O)O_2NO_2 \rightleftarrows CH_3C(O)O_2 + NO_2 \quad (1)$$
$$CH_3C(O)O_2 + NO \rightarrow CH_3C(O)O + NO_2 \quad (2)$$
$$CH_3C(O)O + O_2 \rightarrow CH_3O_2 + CO_2 \quad (3)$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (4)$$
$$CH_3O + O_2 \rightarrow HCHO + HO_2 \quad (5)$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad (6)$$
$$OH + NO \rightarrow HONO \quad (7)$$
$$OH + NO_2 \rightarrow HONO_2 \quad (8)$$

According to this scheme the thermal decomposition of each molecule of PAN can oxidize three molecules of nitric oxide to nitrogen dioxide and produce one molecule of hydroxyl radical. This hydroxyl radical can react with one more nitric oxide and/or other nitrogen dioxide, and so when one PAN molecule is decomposed, three or four nitric oxide molecules will usually be oxidized in the absence of active hydrocarbon. But in the presence of alkenes such as propene, hydroxyl radicals may react with them to promote the oxidation of nitric oxide to nitrogen dioxide and then the number of nitric oxide molecules that are involved in the oxidation by the decomposition of one PAN molecule may exceed four. If this is the case, PAN may promote the oxidation of nitric oxide and hydrocarbon in the atmosphere. Under these considerations, we investigated the reaction of PAN with nitric oxide in the presence of propene.

PAN was prepared in liquid phase according to the method reported by Nielsen et al.[3] As the first step, peroxyacetic acid was prepared by the reaction of acetic anhydride with 30% hydrogen peroxide aqueous solution. As the second step, peroxyacetic acid solution was reacted with nitric acid in the presence of tridecane as solvent and sulfuric acid as catalyst. Finally, purified PAN-tridecane solution was obtained after purification procedures and safely stored in a refrigirator at -30 ℃. The purity of PAN was confirmed by infrared spectroscopy and the concentration was determined by alkaline hydrolysis followed by wet chemical analysis (NEDA method).[4] Gaseous PAN was generated by passing purified air through a glass impinger containing PAN-tridecane solution and its concentration was determineded by GC-ECD. A FEP film bag of 300 l-volume was used as a reactor, which was controlled at 30±1 ℃. PAN and propene were analyzed by GC-ECD and GC-FID, respectively. Nitric oxide was monitored by a chemiluminescent nitrogen oxides analyzer.

In the presence of an excessive amount of nitric oxide the first order decay of PAN was observed in the first 30 min but thereafter a deviation appeared. The same profile was also observed when propene was coexisted and this deviation could be explained by the accumulation of nitrogen dioxide which disturbed the PAN decomposition by the reverse reaction of (1). The

Table 1. Initial Reaction Conditions for PAN-NO-C_3H_6-Air System

Exp.No.	$[PAN]_0$	$[C_3H_6]_0$	$[NO]_0$	$[C_3H_6]_0/[NO]_0$	$[NO]_0/[PAN]_0$
1	0.48	0	3.60	0	7.5
2	0.53	0.60	4.80	0.13	9.1
3	0.45	1.00	3.60	0.28	8.0
4	0.41	1.00	3.00	0.33	7.3
5	0.47	1.10	3.00	0.37	6.4
6	0.49	1.10	2.20	0.50	4.5
7	0.51	0.90	1.10	0.82	2.2

Concentration unit=ppm, $[H_2O]_0$=3000 ppm, reaction temperature=30 ℃

rate constant of decomposition of PAN was obtained as $k = (5.7 \pm 0.7) \times 10^{-2} \mathrm{min}^{-1}$ from the slope of first order decay line. This value agreed well with the value obtained by Cox et al.[2] and was not affected by the existence of propene. Table 1 lists the initial conditions of experiments for dark reaction of a PAN-NO-Propene-Air system. Initial concentrations of PAN and propene were nearly constant but that of nitric oxide was varied and then the ratio of initial concentration of propene to that of nitric oxide varied between 0.13 and 0.82. The reaction temperature was maintained at 30±1 ℃ and the concentration of water was ~3000 ppm. Both concentrations of PAN and propene did not substantially decrease until nitric oxide was injected, but just after injection of nitric oxide they started to decrease. In this study, the products analysis was not carried out.

In the next place, we tried to simulate this reaction system using an explicit reaction model developed by Sakamaki et al.[5] The original model contains 158 elementary reactions but in this work photochemical and ozone related reactions were omitted and the rate constant of PAN decomposition was replaced with our observed value. Computer calculations were performed by the Gear's method.[6] Fig.1 shows the comparison of time profiles obtained from No.6 experiment with its simulation. Circles, triangles and squares in the figure give experimental values while simulated values are given by line drawings. It is seen that the experimental results show good accord with the computer simulations.

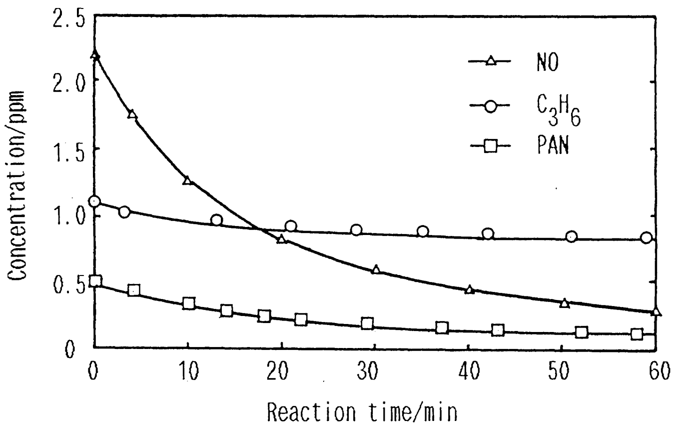

Fig.1. Comparison of time profiles obtained from experiment and simulation for PAN-NO-C_3H_6-Air System.

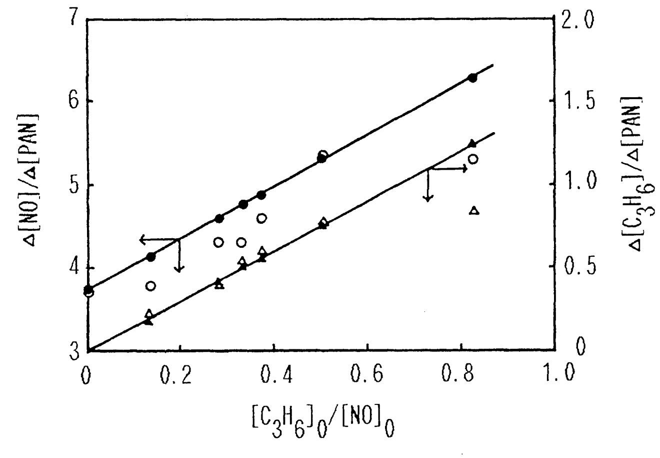

Fig.2. Dependence of Δ[NO]/Δ[PAN] and Δ[C_3H_6]/Δ[PAN] on $[C_3H_6]_0/[NO]_0$.

Based on these results, we plotted the molar ratios of the decreased amount of nitric oxide to that of PAN (Δ[NO]/Δ[PAN]) and the decreased amount of propene to that of PAN (Δ[C_3H_6]/Δ[PAN]) at 45 min of reaction time against the molar ratio of the initial concentration of propene to that of nitric oxide as shown in Fig.2. These values were almost independent of rection time. The filled-in symbols correspond to simulated values and open ones to the experimental values. It is seen that the number of nitric oxide oxidized to nitrogen dioxide for the decomposition of each PAN molecule increases linearly from 3.7 (in the absence of propene) to values larger than 6 with the increase of initial concentration ratio of propene to nitric oxide up to 0.8. The experimental results satisfy the calculated results. Furthermore, it is seen that the ratio of the decreased amount of propene to that of PAN ($\Delta[C_3H_6]/\Delta[PAN]$) is proportional to the initial concentration ratio of propene to nitric oxide. Again the experimental values satisfy the simulated ones except for $[C_3H_6]_0/[NO]_0=0.8$. It is concluded from the ratio of the gradients of two lines in Fig.2 that two more nitric oxide molecules can be oxidized to nitrogen dioxide when one propene molecule is attacked by hydroxyl radical. A rational explanation of the promotion of the oxidation of nitric oxide by PAN decomposition in the presence of propene is as follows. Propene reacts with hydroxyl radical to give two types of hydroxyl substituted propyl radicals which rapidly react with oxygen molecule to form hydroxyl peroxy radicals. These radicals easily oxidize nitric oxide to nitrogen dioxide and change themselves into hydroxyl propoxy radicals which also rapidly react with another oxygen molecule to give hydroperoxy radical, formaldehyde and acetaldehyde. Hydroperoxy radical can oxidize nitric oxide by the reaction (6) to regenerate hydroxyl radical. Aldehydes can also participate in the oxidation of nitric oxide. Propene competes with nitric oxide and nitrogen dioxide for hydroxyl radicals and so the increase of the concentration of propene directly proportionally affects to the decay rate of propene because hydroxyl radicals fairly maintain a similar concentration level until the complete consumption of PAN.

From these results, it is suggested that PAN promotes oxidation of nitric oxide and hydrocarbons such as propene at night if the latter two substances are emitted into the atmosphere and if the atmosphere is polluted by PAN.

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