short-range interactions, as shown by direct "experiments" with the model calculation. Also, the $Li^+$–$Li^+$, $Li^+$–$Mn^{2+}$, and $Mn^{2+}$–$Mn^{2+}$ pair correlation functions, which presumably strongly reflect three-particle configurations involving two cations and an anion, show markedly non-Debye–Hückel ionic strength dependence. These results provide a tentative explanation for certain data for the rate constant of an electron-transfer reaction which otherwise would suggest complexes involving perchlorate ions in very dilute solutions. Perhaps equally important, this study provides specific examples that contradict the tempting assumption that the ionic strength dependence of a mixing coefficient can be represented by a power series in $I$.

*Acknowledgment.* The support of this research by the National Science Foundation is gratefully acknowledged, as is the computing facility made available by the computing center in Kuala Lumpur for a portion of this research. T.K.L. thanks Prof. Friedman for his warm hospitality during his sabbatical leave in Stony Brook.

### Appendix

Concerning the $h_1$ data reported by Cassel and Wood,[9] there is a sign discrepancy. According to theory,[10] $h_1$ and $g_1$ have opposite signs in the limiting law region, but according to Figure 1 the calculated $g_1$ and the experimental $h_1$ are both positive unless the latter function changes sign below the experimental $I$ range. This contradiction has not been resolved. Because the present study involves only the free energy coefficients, it is more important to know whether there is evidence of a corresponding sign discrepancy involving calculated and experimental $g_1$.

To investigate this question, we can use the exact equation[12]

$$b_1 = g_1 + g_2 + \tfrac{1}{2}Ig_1' + \tfrac{1}{2}g_0' \qquad \text{(A.1)}$$

which, combined with the limiting laws for $g_1$ and $g_0$ and the presumed negligibility of $g_2$ compared to $g_1$ in the small-$I$ region, leads to the conclusion that $b_1/g_1 \rightarrow 1$ as $I \rightarrow 0$.

In ref 12 the model results for $b_1(I)$ are compared with experimental data for[36] $CoCl_2$–HCl mixtures; qualitative agreement is found, not only for the sign of $b_1$ but also its $I$ dependence. Moreover, the same qualitative features are shown by $b_1$ measured[37] for $AlCl_3$–HCl mixtures, as one can see by using the relation found[12] between the coefficients reported by Khoo and co-workers and the coefficients employed here.

Finally, Lim[13] has applied a different data reduction method to the emf data for several HBr–$MBr_2$ mixtures and concluded that they give positive $g_1$ in the small-$I$ region.

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(36) K. H. Khoo, T. K. Lim, and C. Y. Chan, *J. Solution Chem.*, **10**, 683 (1978).

(37) K. H. Khoo, T. K. Lim, and C. Y. Chan, *Trans. Faraday Soc.*, **74**, 2037 (1981).

# CHEMICAL KINETICS

## Fourier Transform Infrared Spectroscopic Study of the Thermal Stability of Peroxyacetyl Nitrate

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*(Received: December 14, 1984; In Final Form: September 10, 1985)*

The unimolecular decomposition of peroxyacetyl nitrate (PAN) to form methyl nitrate and carbon dioxide has been studied over the temperature range 298–338 K by Fourier transform infrared spectroscopy (FTIR). Pure PAN samples (>98%; 2–30 torr) were found to decompose thermally, nearly quantitatively, to these products, with the only other observed product being nitromethane (<10%). Both PAN decomposition and methyl nitrate formation rates yielded the Arrhenius equation, $k = (2.1 \times 10^{12}) \exp(-24.800 \pm 1800\ \mathrm{cal/(K\ mol}/RT))\ \mathrm{s}^{-1}$. Perdeuterio-PAN was synthesized and observed to decompose to perdeuteriomethyl nitrate and carbon dioxide with no apparent isotope effect. Experiments adding nitric oxide to the PAN are described which confirm the existence of two unimolecular pathways for the decomposition of peroxyacyl nitrates. One pathway is a concerted reaction most likely proceeding via a cyclic intermediate, and the other the previously identified equilibrium between PAN and the peroxyacetyl radical and nitrogen dioxide. The rate of the PAN decomposition in a large excess of NO to form the peroxyacetyl radical and nitrogen dioxide was determined to be $2.2 \times 10^{-4}\ \mathrm{s}^{-1}$ at 298 K. This rate is somewhat slower than previously reported for this pathway. The results are discussed with respect to the atmospheric lifetime of PAN and the potential atmospheric production of methyl nitrate.

### Introduction

Peroxyacyl nitrates (PANs) are known to be produced during the photochemical oxidation of organic molecules in the troposphere, and the gas-phase chemistry of peroxyacetyl nitrate (PAN) has been investigated by a number of workers.[1-4] Measurements of PAN in the troposphere have found PAN to have a widespread occurrence in the clean troposphere as well as in polluted air and indicate that PAN can be an important reservoir for $NO_x$ and a measure of the photochemical age of an air parcel.[5,6] To better evaluate the impacts of this known phytotoxin on ecosystems and

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(1) C. T. Pate, R. Atkinson, and J. N. Pitts, Jr., *Environ. Sci. Health-Environ. Sci. Eng.*, **A11**, 19–31 (1976).

(2) R. A. Cox and M. J. Roffey, *Environ. Sci. Technol.*, **11**, 900–906 (1977).

(3) D. G. Hendry and R. A. Kenley, *J. Am. Chem. Soc.*, **99**, 3198–3199 (1977).

(4) U. Schurath and V. Wipprecht, "Proceeding of the First European Symposium on Physico-Chemical Behavior of Atmospheric Pollutants", Ispra, Italy, Oct 1979, B. Versino and H. Ott, Ed., EUR 6621, 1980, pp 157–166.

0022-3654/86/2090-0152$01.50/0

the atmosphere, a better fundamental understanding of its chemical and physical properties is needed. Recent work has examined the ultraviolet absorption cross section of PAN[7] and its reactivity with OH radical,[8] indicating that PAN is expected to be very stable with regard to these removal processes. As well, preliminary work in this laboratory[9] has found PAN to have a low aqueous solubility and to undergo slow hydrolysis in acidic aqueous solution in good agreement with the work of Holdren and Spicer.[6] All of this evidence has indicated that PAN thermal decomposition processes may be important in determining its atmospheric lifetime.

The thermal decomposition of PAN is known to produce two major products, methyl nitrate and carbon dioxide;[2,10-12] however, there has been some discrepancy as to the mechanism of this reaction. Stephens[10] has proposed a concerted unimolecular reaction which proceeds via a cyclic transition state to form the observed products. An alternative explanation has been proposed by Cox and Roffey[2] and more recently by Bruckmann and Willner[12] where the methyl nitrate is formed via reaction of methoxy radical with nitrogen dioxide to form methyl nitrate. Methoxy radicals are formed from the decomposition of the peroxyacetyl radicals, which is known to be in equilibrium with PAN, via the following reaction sequence:

$$\mathrm{PAN} \rightleftarrows \mathrm{CH_3COO_2 + NO_2} \qquad (1)$$

$$\mathrm{2CH_3COO_2 \rightarrow 2CH_3CO_2 + O_2} \qquad (2)$$

$$\mathrm{CH_3CO_2 \rightarrow CH_3 + CO_2} \qquad (3)$$

$$\mathrm{CH_3 + CH_3COO_2 \rightarrow CH_3O + CH_3CO_2} \qquad (4)$$

$$\mathrm{CH_3O + NO_2 \rightarrow CH_3ONO_2} \qquad (5)$$

A study using conventional infrared spectroscopy has indicated that PAN can have reasonably long thermal half-life on the order of hundreds of hours at room temperature.[12] This same work concluded that the cyclic unimolecular decomposition was not important and that the radical mechanism is responsible for the observed products.

If the observed methyl nitrate is produced by the reaction sequence above, (i.e., ultimately by the reaction of methoxy radicals with nitrogen dioxide, reaction 5), then one would also expect to observe approximately a 10% yield of formaldehyde and nitrous acid according to the following side reaction:[13]

$$\mathrm{CH_3O + NO_2 \rightarrow CH_3ONO_2} \quad (90\%) \qquad (5a)$$

$$\mathrm{\rightarrow HCHO + HONO} \quad (10\%) \qquad (5b)$$

With the advent of simple high-purity PAN synthesis,[10,14] the use of Fourier transform infrared (FTIR) spectroscopy and its computer-assisted digital spectral subtraction techniques made possible the reexamination of PAN thermal decomposition in the presence of and in the absence of nitric oxide to resolve the importance of these mechanistic pathways. Reported here are kinetic and products studies of PAN thermal decomposition at low pressure using FTIR over the temperature range 298–338 K, and in the presence of excess NO at 298 K, where the forward rate of the equilibrium reaction 1 was determined since the reverse reaction with $NO_2$ is negligible under these conditions. The implications of this work with regard to the atmospheric lifetime of PAN are discussed as well.

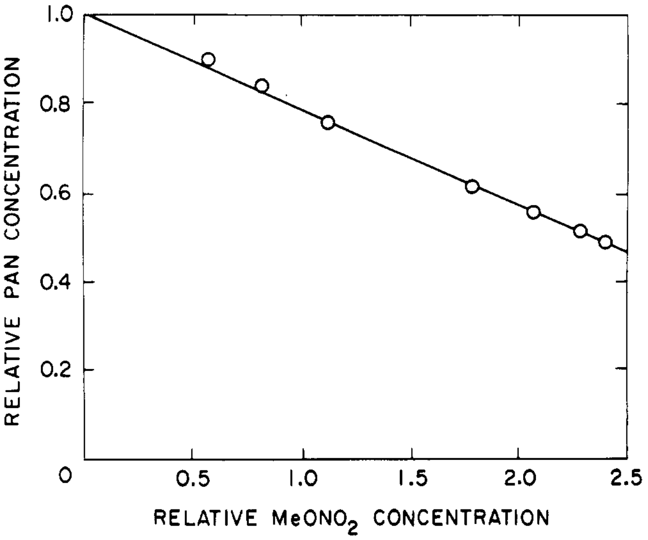

**Figure 1.** Typical plot for PAN decomposition and methyl nitrate formation at 298 K.

## Experimental Section

PAN was synthesized by a modified version of that reported by Nielsen et al.[11,14] Tridecane was substituted for the heptane solvent to facilitate the high-purity production of gaseous PAN (>98%). PAN/tridecane solutions were stored in a freezer at 253 K, and PAN gas-phase samples obtained by thawing the solutions and simple vacuum distillation of the PAN.[14] PAN samples stored in this manner have been found to be very stable over a period of several months. The major impurity in the gaseous PAN samples used in this study was peracetic acid (besides the negligible amount of tridecane vapor). No nitric oxide, nitrogen dioxide, or nitric acid was observed in these PAN samples.[14]

A Nicolet 7199 Fourier infrared spectrometer and associated software was used to obtain FTIR spectra at a resolution of one wavenumber. All of the gas-phase spectra were taken with a 10-cm pathlength gas cell equipped with a Teflon stopcock and Viton O-rings. Sodium chloride, potassium bromide, and sapphire windows were attached to either a pyrex or quartz glass gas cell body by using a low vapor pressure epoxy resin (Torr seal, Varian Assoc.). The composition of the gas cell did not effect the rate of PAN decomposition. Gas pressures were measured with a 0–10 torr and 0–1000-mbar capacitance manometer heads and associated electronics (MKS Baratron, Model PDR-A). Methyl nitrate was prepared by scaling down a previously reported synthetic procedure.[15] Nitromethane was purchased from Aldrich (gold label >99%) and used without further purification. All chemicals used were >98% purity as determined by FTIR, unless otherwise stated.

For the determination of the temperature dependence of PAN decomposition in the gas cell, a thermostated oven was used in which the cell was placed for a specified time period, and FTIR spectra were taken immediately before and after thermal exposure. Tabulated integrated band strengths and band positions for PAN determined previously[14] were used in this study. Kinetic data, i.e. PAN concentrations as a function of time, were obtained by computerized digital comparison of an initial reference PAN spectrum with spectra recorded during the thermal decomposition.

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(5) H. B. Singh and P. L. Hanst, *Geophys. Res. Lett.*, **8**, 941–44 (1981).

(6) C. W. Spicer, M. W. Holdren, and G. W. Keigley, *Atmos. Environ.*, **17**, 1055 (1983).

(7) G. I. Senum, Y.-N. Lee, and J. S. Gaffney, *J. Phys. Chem.*, **88**, 1269 (1984).

(8) T. J. Wallington, R. Atkinson, and A. M. Winer, *Geophys. Res. Lett.*, **9**, 861 (1984).

(9) Y.-N. Lee, G. I. Senum, and J. S. Gaffney, presented at CACGP Symposium on Tropospheric Chemistry, Oxford, U.K., Aug/Sept 1983, BNL 33071R.

(10) E. R. Stephens, *Adv. Environ. Sci. Technol.*, **1**, 119–146 (1969).

(11) T. Nielsen, A. Hansen, and E. Thomsen, *Atmos. Environ.*, **16**, 2447–2450 (1982).

(12) P. W. Bruckmann and H. Willner, *Environ. Sci. Technol.*, **17**, 352–357 (1983).

(13) R. F. Hampson, Chemical Kinetic and Photochemical Data Sheets for Atmospheric Reactions, FAA-EE-80-17, Washington, DC, 1980, and references therein.

(14) J. S. Gaffney, R. Fajer, and G. I. Senum, *Atmos. Environ.*, **18**, 215–218 (1984).

(15) "Organic Synthesis", Collected Vol. 2, A. H. Blatt, Ed., Wiley, New York, 1943, pp 412–414.

**TABLE I: Rate of Thermal Self-Decomposition of PAN and PAN-$d_3$**

| $t$, °C | compd | initial press., torr | $k$, min$^{-1}$ |
|---|---|---|---|
| 25 | PAN | 4.5 | $4.79 \times 10^{-5}$ |
| 25 | PAN | 2.4 | $7.9 \times 10^{-5}$ |
| 45 | PAN | 4.1 | 0.00138 |
| 47 | PAN | 3.5 | 0.00206 |
| 46.3 | PAN | 3.3 | 0.00212 |
| 42.5 | PAN | 27.5 | 0.00159 |
| 45.5 | PAN-$d_3$ | 10.6 | 0.00147 |
| 66 | PAN | 2.5 | 0.0105 |
| 66.1 | PAN | 20.8 | 0.0127 |
| 67.2 | PAN | 14.6 | 0.0108 |
| 66.5 | PAN-$d_3$ | 12.5 | 0.0124 |

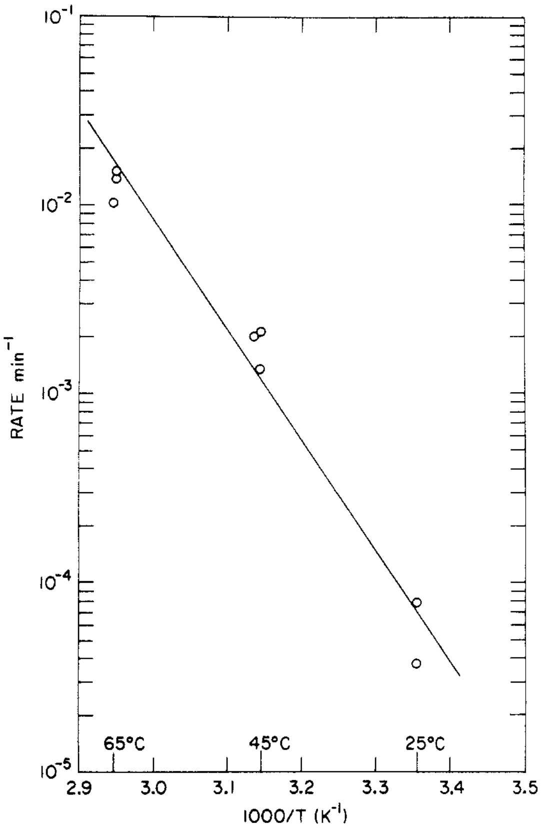

**Figure 2.** Arrhenius plot for PAN thermal self-decomposition.

Methyl nitrate formation rates were determined by computerized digital integration of its vibrational bands as a function of thermal exposure time.

## Results and Discussion

Samples of pure PAN were allowed to decompose thermally in infrared gas cells of Pyrex or quartz glass with either sodium chloride, potassium bromide, or sapphire windows. In all cases, the composition of the gas cell used did not have any effect on the observed rate of PAN decomposition at the pressures studied (<30 torr). These observations suggest that the observed PAN thermal decomposition are indicative of a homogeneous gas-phase process. The rates of PAN thermal decomposition were found to be equal to the rate of methyl nitrate formation in all cases. A typical plot of PAN decomposition and methyl nitrate formation for 298 K is given in Figure 1. The experimental rate determinations over the temperature range 298–338 K for pure PAN thermal decomposition to methyl nitrate and carbon dioxide are presented in Table I.

No formaldehyde or nitrous acid was observed to be formed in the thermal decomposition of pure PAN samples. The only other product observed besides the carbon dioxide and methyl nitrate was nitromethane. It is believed that this product is produced via the reaction of PAN or peroxyacetyl radicals with the gas cell surfaces to produce methyl radicals, the nitromethane being formed by the reaction of methyl with nitrogen dioxide. Nitromethane production was found to be variable, but always less than 10% of the decomposed PAN.

**TABLE II: Decomposition of PAN in the Presence of NO**[a]

| $\Delta t$, min | rel PAN concn | rel NO concn |
|---|---|---|
| 0 | 0.9802 | 1 |
| 9.133 | 0.8783 | 0.990 |
| 15.60 | 0.8150 | 1.000 |
| 26.50 | 0.7017 | 1.000 |
| 40.03 | 0.5864 | 0.995 |
| 51.833 | 0.5049 | 1.000 |
| 65.367 | 0.4177 | 1.000 |
| 80.900 | 0.3422 | 1.000 |
| 96.700 | 0.2789 | 0.995 |
| 109.95 | 0.2365 | 0.995 |
| 139.50 | 0.1710 | 0.995 |

$$d \ln [\mathrm{PAN}]/dt = 2.18 \times 10^{-4}\ \mathrm{s}^{-1}$$

$$r = -0.999919$$

[a] 2.11 torr PAN + 10.3 torr of NO at 25 °C.

**TABLE III: Results of PAN Decomposition in the Presence of NO**

| [PAN], torr | [NO], torr | $t_{1/2}$, min | comment |
|---|---|---|---|
| 2.15 | 2.0 | 53.7 | NO constant |
| 2.11 | 10.3 | 53.0 | NO constant |
| 1.86 | 0.2 | 51.4 | slight NO consumption |

$$k = (2.20 \pm 0.05) \times 10^{-4}\ \mathrm{s}^{-1}$$

An Arrhenius plot of the PAN decomposition to methyl nitrate and carbon dioxide over the temperature range studied is shown in Figure 2. Least-squares analysis of this rate data yields the rate equation

$$k = (2.1 \times 10^{12}) \exp[-24800 \pm 1800\ \mathrm{cal}/(\mathrm{K\ mol}/RT)]\ \mathrm{s}^{-1}$$

where $\log A = 12.3 \pm 1.2$. The observed frequency factor is consistent with a reasonably sterically hindered transition state.[16]

Synthesized perdeuterio-PAN samples were also observed to decompose thermally to the corresponding perdeuteriomethyl nitrate and carbon dioxide at a rate similar to PAN as is given in Table I, such that no kinetic isotope effect was observed.

PAN samples were also allowed to thermally decompose in the presence of a large excess of nitric oxide, as has been studied previously,[1–4] but in the absence of oxygen. This was done to determine if the decomposition of PAN to the peroxyacetyl radical and subsequent radicals would also lead to methyl nitrate production as proposed previously.[2,12] The low-pressure (<30 torr) forward rate of the equilibrium reaction 1 was determined under conditions of excess NO since

$$\mathrm{CH_3CO_3 + NO \rightarrow CH_3 + NO_2 + CO_2} \qquad (6)$$

with $k_6$ being $1.4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$,[17] thus allowing the forward reaction 1 to be rate limiting. In the absence of oxygen at reduced pressures, this decomposition mode of PAN was observed to be catalytic with respect to NO (see Table II), i.e., no acceleration of the PAN decomposition rate and no net NO consumption. This can be explained by the subsequent reaction

$$\mathrm{CH_3 + NO_2 \rightarrow CH_3O + NO} \qquad (7)$$

with $k_7 = 3.3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, followed by reaction 5a and 5b with $k_{5a} = 3.3 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_{5a}/k_{5b} = 9$ (see ref 16).

In the presence of oxygen, reaction 7 is replaced by the reaction of methyl radicals with $O_2$ to form the methylperoxy radical which subsequently reacts with NO to form nitrogen dioxide and the methoxy radical. Thus under these conditions, two molecules of

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(16) S. W. Benson and H. E. O'Neal, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. **21** (1970).

(17) D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, *J. Phys. Chem. Ref. Data*, **11**, 327–496 (1982).

**TABLE IV: Previous Rate Determination of PAN Decomposition in the Presence of NO at Atmospheric Pressure**

| [PAN] | [NO] | diluent | rate, $s^{-1}$ | ref |
|---|---|---|---|---|
| 4.1–17.6 ppm | 50–200 ppm | air | $2.7 \times 10^{-4}$ | 1 |
| | | $N_2$ | $3.3 \times 10^{-4}$ | 1 |
| 1–5 ppm | 3.5 ppm | air | $4.8 \times 10^{-4}$ | 2 |
| 1800–4000 ppm | *a* | NA | $4.0 \times 10^{-4}$ | 3 |
| 2200–8000 ppm | 1800–12000 ppm | NA | $3.7 \times 10^{-4}$ | 2 |
| 200 ppb | >[PAN] | $N_2$ | $5.0 \times 10^{-4}$ | 4 |

[a] Rate determined by an isotope $^{15}NO_2$ exchange experiment. NA = Not available.

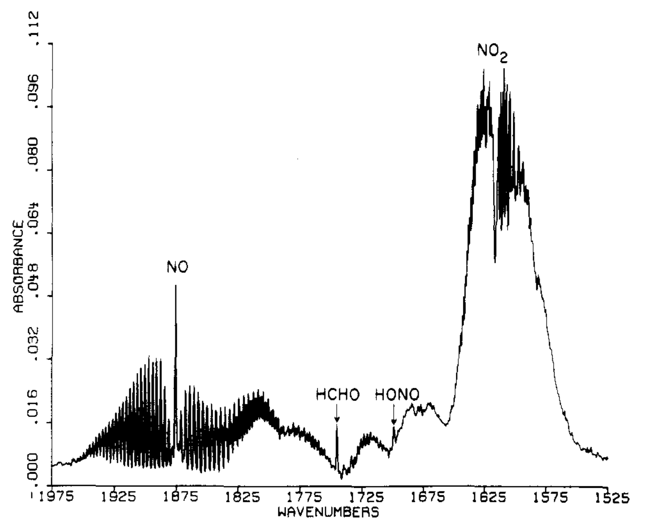


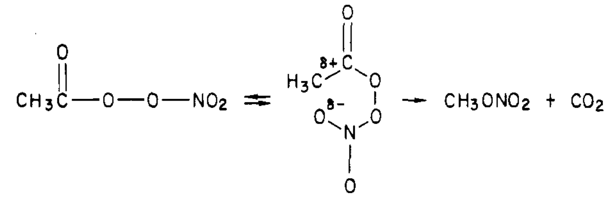
**Figure 3.** FTIR subtracted showing evidence for $H_2CO$ and HONO formation in PAN decomposition in the presence of NO.

nitric oxide are consumed per molecule of PAN as observed by previous workers.[1-4]

The low-pressure rate determinations for PAN thermal decomposition to the peroxyacetyl radical and nitrogen dioxide are given in Table III. The mean of three determinations at 298 K for the forward rate of equilibrium reaction 1 is $(2.20 \pm 0.05) \times 10^{-4}$ $s^{-1}$. This result is compared to the previous determinations of this value measured at atmospheric pressure in Table IV. The low-pressure decomposition rate determined for the forward rate of reaction 1 is in good agreement with the atmospheric decomposition rate of Pate et al.[1] However, a discrepancy between the other determinations of this rate and our value (see Table IV) is likely due to these studies being carried out under conditions where the NO to $NO_2$ ratios were such that the back reaction (i.e. the reverse reaction of equilibrium 1) to form PAN had to be considered and a correction made to the measured rates. Addison et al.[19] measured the reverse rate of reaction 1 at 715 and 28 torr to be $(6.0 \pm 2.0) \times 10^{-12}$ and $(2.1 \pm 0.1) \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, respectively. With NO in great excess, as in this study, and with the high-purity PAN used, the reverse reaction would only cause a <10% correction to the observed rate.

When PAN thermally decomposed in the presence of NO, besides the major products methyl nitrate and carbon dioxide, formaldehyde, methane, and nitrous acid were all measured along with an increased production of nitromethane (see Figure 3). Formaldehyde and nitrous acid yields were consistent with the formation of the major product methyl nitrate via reaction 5a.

These data indicate that PAN undergoes unimolecular thermal decomposition along two concurrent pathways. One is along the previously established equilibrium between PAN and the peroxyacetyl radical and nitrogen dioxide (see reaction 1). The apparent loss of PAN along this pathway will depend upon the ratio of NO and $NO_2$ with the apparent lifetime approaching infinity as NO goes to zero.[2] The second pathway is a concerted reaction of PAN leading directly to methyl nitrate and carbon dioxide, most likely via a cyclic transition state as proposed previously by Stephens.[10] The lack of an experimentally measureable deuterium isotope effect on the reaction rate for the thermal decomposition of pure perdeuterio-PAN indicates that the cyclic transition state is not a hydrogen-bonded structure which would be expected to have an isotope effect ($k_H/k_D$) of a minimum of 2, and an average of 7 for a free-radical mechanism. A comparison of the FTIR spectrum of PAN and it perdeuterio counterpart also supports this conclusion.[14] The measured frequency factor for the decomposition of pure PAN and the observed products suggest that PAN exists to some extent in a cyclic structure which is probably dipolar in nature.


(8)

This proposed cyclic structure of PAN would be expected to be less polar than an acylic PAN, and would be consistent with the fact that PAN has a low aqueous solubility[6,9,20] and is very soluble in nonpolar solvents.[11,14] The nonpolar nature of PAN has also been applied to its analytical chemistry, i.e. PAN is readily separated from other gaseous components in the atmosphere by use of short nonpolar columns in gas chromatography.[10] This six-membered ring structure may also explain the increased stabilities of PANs when compared to their peroxyalkyl nitrate counterparts.[21]

With regard to PAN atmospheric lifetimes, both pathways will have strong temperature dependences, with PAN lifetimes increasing with decreasing temperature.[20] With respect to the equilibrium reaction 1, PAN's apparent lifetime will depend on the reactions which will sink the peroxyacetyl radical,[2,20,21] with the known reactions being reaction with NO (see reaction 6), and the reaction with hydroperoxyl radical to form peroxyacetic acid.[20,22,23]

$$CH_3CO_3 + HO_2 \rightarrow CH_3CO_3H + O_2 \qquad (9)$$

The apparent lifetime of PAN will be determined by the $NO/NO_2$ ratio in the atmosphere for this loss mechanism as pointed out by Cox and Roffey,[2] since the forward reaction in this case is rate limiting. PAN will have an atmospheric lifetime of ~80 min at an $NO/NO_2$ ratio of one, with the lifetime approaching infinity as [NO] goes to zero.

Similarly the rate of reaction 9 is dependent on the $[HO_2]$ since this reaction is not the rate-limiting step.[16,17,22] For the case of a standard U.S. atmosphere, Hahn and Crutzen[20] have estimated PAN to have an atmospheric lifetime of ~3 days at 288 K. This can be compared with our data for the thermal decomposition via the concerted pathway (reaction 8) yielding a lifetime of approximately 25 days at 288 K. At colder temperature these lifetimes will begin to approach years.[20]

These lifetime estimates can be compared to tropospheric lifetime estimates for PAN loss due to photolysis (negligible, see ref 7 and 10) and for reaction with OH (~125 days, ref 8). Due to the expected very slow washout of PAN in the atmosphere, it is apparent from these comparisons that the thermal decomposition pathways for PAN can both be important under remote atmospheric conditions (i.e. low [NO]).

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(18) D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, *J. Phys. Chem. Ref. Data*, **9**, 295–471 (1980).

(19) M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, *Chem. Phys. Lett* **73**, 283 (1980).

(20) J. Hahn and P. J. Crutzen, *Phil. Trans. R. Soc. London, B, Sect.* **296**, 521 (1982).

(21) E. O. Edney, J. W. Spence, and P. L. Hanst, *J. Air Pollut. Control Assoc.*, **29**, 741 (1979).

(22) P. L. Hanst and B. W. Gay, Jr., *Atmos. Environ.*, **17**, 2259 (1983).

(23) J. S. Gaffney and G. I. Senum, presented at the Conference on Gas-Liquid Chemistry of Natural Waters, Brookhaven National Laboratory, April 1984, Paper No. 5, BNL 51757, Vol. 1, 1984.

For such situations, the formation of methyl nitrate via reaction 8 could be an important pathway for formation of an even more stable organic $NO_x$ species. The fate of methyl nitrate is not well understood. It does not appear that it will photolyze under tropospheric conditions and our studies have shown it to be thermally stable in the gas phase to 338 K, indicating that it will not thermally decompose in the atmosphere. Preliminary data indicate that its reaction rate with OH radical is slower than PAN, with lifetimes with respect to OH of greater than a year expected.[24] It has a comparable aqueous solubility to PAN ($\sim$5 M atm$^{-1}$; see ref 9) and has not been observed to undergo hydrolysis. Clearly measurements of the levels of methyl nitrate in the clean troposphere are needed to evaluate its contribution to the $NO_x$ cycles and stratospheric source terms and for its role as a potential trace gas in global greenhouse effects.

It is apparent from this work and previous studies that PAN is much stabler than previously supposed; therefore, its role in the understanding of $NO_x$ long-range transport must not be neglected. It is also clear that the peroxyacetyl radical chemistry may be important in the formation of oxidants other than ozone and PAN. Its ability to react with $HO_2$ in the clean troposphere is expected to lead to peracetic acid and methyl hydroperoxide.[20,23] Preliminary investigations have shown peracetic acid to be a potentially very active plant and microorganism toxin[25] and, like PAN, should not be ignored when plant and other ecosystem damage effects due to air pollutants are being investigated.

*Acknowledgment.* This research was performed under the auspices of the United States Department of Energy under Contract No. DE-AC02-76CH00016.

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(24) J. S. Gaffney, G. I. Senum, and J. H. Lee, unpublished results.

(25) J. S. Gaffney, L. Schairer, and J. Vaughn, unpublished results.

# In Situ Study of the Hydrogenation of Diphenyl Ether in the Presence of Pyrrhotite and $H_2S$

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*(Received: April 16, 1985; In Final Form: June 24, 1985)*

In the present study we report the results of measurements of the conversion of diphenyl ether to benzene and phenols in the presence of a pyrrohotite catalyst. In situ Mössbauer measurements were performed during the catalytic conversion of diphenyl ether. The presence of $Fe_3O_4$ is detected in the residues after reaction; $Fe_{1-x}S$ is also observed. Under high $H_2S$ partial pressures in the reactor, the conversion increases, and for a 10% $H_2S$ partial pressure, the Mössbauer spectrum shows the presence of $FeS_2$. The amount of $Fe_3O_4$ is practically reduced to zero in this case with $Fe_{1-x}S$ dominating the spectrum. All the Mössbauer spectra show the presence of a singlet line after reaction. This spectrum results from the interaction of the iron in the pyrrhotites with the compounds present in the reactor at high temperatures. The conversion of diphenyl ether is negligible in the absence of pyrrhotite. The higher activity observed for conversion in the presence of $H_2S$ is related to the effect this compound has in controlling the stoichiometry of the pyrrhotites. The activity observed in the iron sulfides toward hydrogenation of diphenyl ether is suggestive of a catalytic role for such sulfides in the cleavage of oxygen bonds in direct coal liquefaction.

The direct liquefaction of coal is a process that involves the interaction between coal hydrogen, solvent, and catalyst. Many researchers have reported that the addition of mineral matter enhances the conversion of coal to liquid products.[1] A study by Hodek on four German coals showed that the pyrite present in the coal enhances the hydrogenation of the coals.[2] Recycling the mineral matter and liquefaction residues tends to increase the reaction rate and enhance the conversion of pyridine solubles to benzene solubles.[3] The addition or presence of pyrite in coal enhances the production of liquid products of lower viscosity. Because of these facts, many researchers are inclined to consider pyrite ($FeS_2$) as a catalyst for the hydrogenation of coal.[1] However, one has to remember that, under coal liquefaction conditions, pyrite rapidly transforms to a nonstoichiometric iron sulfide,[4,5] $Fe_{1-x}S$ ($0 \leq x \leq 0.125$). It is noted that the sulfur formed as a result of the decomposition of pyrite is able to extract hydrogen from poor donor solvents. The stoichiometry of the pyrrhotite formed from $FeS_2$ depends strongly on the partial pressure of $H_2S$ present in the reactor.[4,6] The activation energy of the process of pyrite decomposition is strongly particle size dependent.[5] This is in very good agreement with the suggested mechanism of sulfur diffusion as the rate-controlling process for such decomposition; a smaller particle size facilitates such diffusion.[7] Since pyrite decomposes during coal liquefaction, it cannot be considered a catalyst. The pyrrhotite generated thus appears to play a catalytic role in the conversion of coal into liquid

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(1) R. M. Davidson, Report ICTIS/TR22, IEA Coal Research, London, 1983.

(2) W. Hodek, "Chemical and Physical Valorization of Coal Meeting, Liege EUR-5954-d/e/f/i, Luxembourg, 1978", pp 87-103.

(3) B. Granoff, M. G. Thomas, P. M. Baca, and G. T. Noles, *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.*, **23** (1978).

(4) P. A. Montano, A. S. Bommannavar, and V. Shah, *Fuel*, **60**, 703 (1981).

(5) P. A. Montano, P. P. Vaishnava, J. A. King, and E. N. Eisentrout, *Fuel*, **60**, 713 (1981).

(6) A. S. Bommannavar and P. A. Montano, *Fuel*, **61**, 523, 1289 (1982).

(7) A. Attar, *Fuel*, **57**, 201 (1978).

0022-3654/86/2090-0156$01.50/0