strong O^{2-} and a weak OH^- ligand in the axial direction and that the strong O^{2-} ligand is preferable to the $S = 1$ spin state of the central metal ion.

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Supplementary Material Available: A table of anisotropic thermal parameters and a listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

Preparation and Thermal Decomposition of Pernitric Acid ($HOONO_2$) in Aqueous Media

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Abstract: Pernitric acid (PNA), $HOONO_2$, was prepared by reaction of HNO_3 or NO_2BF_4 with 90% H_2O_2 (either the neat liquid or in CH_3CN solution) at 273 K. Gaseous PNA was removed from the reaction mixtures with a stream of Ar and identified by its IR spectrum. Mass spectral data for PNA were obtained in a similar fashion. In aqueous buffer, PNA decomposes to give molecular oxygen and nitrite. This can be accounted for by the following reactions: $HOONO_2 \rightleftarrows H^+ + O_2NOO^-$ and $O_2NOO^- \rightarrow NO_2^- + O_2$. However, the possible intervention of radical reactions cannot be excluded. The observed first-order rate constant for oxygen evolution at 283.6 K and pH 4.7 is $(7.06 \pm 0.75) \times 10^{-3}\ s^{-1}$.

Pernitric acid (PNA), $HOONO_2$, can be viewed either as an inorganic peracid, ROOH (where R = NO_2), a mixed anhydride of two acids (HOOH and HNO_3), or as the parent member of the family of peroxynitrates, $ROONO_2$ (where R = H). As such, PNA can be expected to participate in either free radical or ionic reactions, and it therefore affords the opportunity for some interesting kinetic and mechanistic investigations.

In 1911 D'Ans and Friederich[1] reacted H_2O_2 with N_2O_5 and obtained a solution that liberated Br_2 from Br^-. They suggested that the solution contained $HOONO_2$ but did not offer definitive proof for the existence of PNA. Schwarz[2] reported similar observations in 1948.

In 1977 Niki et al.[3] studied the gas-phase reaction of photochemically generated chlorine atoms with a mixture of H_2, O_2, and NO_2 and obtained the infrared spectrum of a species to which they assigned the formula HO_2NO_2. Other authors[4,5] have reported analogous photochemical methods for generating $HOONO_2$ in the gas phase. Graham et al.[6] condensed H_2O_2 in a 253-K trap and passed a mixture of 1% NO_2 in N_2 through the trap. They then degassed the trap under N_2 flow to yield PNA vapor.

The foregoing methods for generating $HOONO_2$ give a product that is contaminated with impurities and side products. As batch-type methods the existing procedures are not suitable for continuous generation of PNA such as might be required for gas-phase kinetic studies in flow systems. Moreover, the methods necessarily yield gaseous PNA, thereby precluding the possibility of investigating some interesting solution-phase chemistry.

Table I. Mass Spectral Data for Pernitric Acid (PNA), NO_2, and HNO_3

compd[a]	inlet temp, K	rel intens at m/e[b,c] 16	17	18	28	30	32	34	46
PNA	300	0.56	0.31	0.53	*d*	0.95	2.0	*d*	1
PNA	600	1.73	2.0	5.3	*d*	3.4	3.0	*d*	1
HNO_3	300	*e*	*e*	*e*	0.24	1.16	0.17	*e*	1
HNO_3	600	*e*	*e*	*e*	0.20	1.20	0.10	*e*	1
NO_2	600	*e*	*e*	*e*	0.10	4.1	*e*	*e*	1

[a] PNA prepared by mehod 2; see experimental details. HNO_3 prepared by reaction of H_2SO_4 with $NaNO_3$. [b] Each mass spectrum is separately normalized to m/e 46. [c] Relative intensity ≤0.05 for m/e not listed. [d] Relative intensity ≤0.20. [e] Relative intensity ≤0.05.

It is well-known[7-10] that direct nitration of organic hydroperoxides yields peroxynitrates. The reaction can be generalized as in eq 1, where R = alkyl, acyl, and aroyl and X = OH, NO_3, or

$$ROOH + NO_2^+X^- \rightarrow ROONO_2 + HX \qquad (1)$$

BF_4, etc. The original method of D'Ans and Friederich can be considered as an example of this basic process if the reagents are written in an appropriate fashion, i.e. as in eq 2. Nitric acid can

$$HOOH + NO_2^+NO_3^- (=N_2O_5) \rightarrow HOONO_2 + HNO_3 \qquad (2)$$

also be written as $NO_2^+OH^-$ and nitryl fluoroborate as $NO_2^+BF_4^-$ by using this formalism.

In view of the foregoing we examined the potential utility of reaction 1 as a synthetic method for PNA. In this paper we describe the preparation of PNA in solution and the suitability of flow methods for generating relatively pure PNA vapor from the reaction mixtures. We also report on some decomposition reactions of $HOONO_2$.

Results and Discussion

Preparation and Identification of PNA. We used three general procedures (see Experimental Section) for preparation of PNA at 273 K: (1) reaction of neat 90% H_2O_2 with 70% HNO_3; (2) reaction of neat 90% H_2O_2 with NO_2BF_4; (3) reaction of NO_2BF_4 and 90% H_2O_2 in CH_3CN.

Successful preparation of PNA was confirmed for methods 1 and 2 by warming the reaction mixtures to ambient temperature and passing a stream of Ar into the solutions and through a 10-cm path length IR cell or into a long path cell. In both cases, the characteristic IR spectrum of PNA[3,6] was readily observed.

On the basis of the reported value of the $HOONO_2$ absorption coefficient at 803 cm^{-1},[11] we calculate that concentrations of

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(1) D'Ans, J.; Friederich, W. *Z. Anorg. Chem.* **1911**, *73*, 325.

(2) Schwarz, R. *Z. Anorg. Chem.* **1948**, *256*, 3.

(3) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Chem. Phys. Lett.* **1977**, *45*, 564.

(4) Hanst, P. L.; Gay, B. W. *Environ. Sci. Technol.* **1977**, *11*, 1105.

(5) Levine, S. Z.; Uselman, W. M.; Chan, W. H.; Calvert, J. G.; Shaw, J. H. *Chem. Phys. Lett.* **1977**, *48*, 528.

(6) Graham, R. A.; Winter, A. M.; Pitts, J. N. *Chem. Phys. Lett.* **1977**, *51*, 2–5.

(7) Hendry, D. G.; Kenley, R. A. In "Nitrogenous Air Pollutants, Chemical and Biological Implications"; Grosjean, D., Ed.; Ann Arbor Science: Ann Arbor, MI, 1979.

(8) Louw, R.; Sluis, G. J.; Vermeeren, H. P. W. *J. Am. Chem. Soc.* **1975**, *97*, 4396.

(9) Duynstee, E. F. J.; Housmans, J. G. H. M.; Vleugels, J.; Voskuil, W. *Tetrahedron Lett.* **1973**, *25*, 2275.

(10) Kenley, R. A.; Hendry, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 3198.

(11) Graham, R. A.; Winer, A. M.; Pitts, J. N. *Geophys. Res. Lett.* **1978**, *5*, 909.

0002-7863/81/1503-2203$01.25/0

$HOONO_2$ as high as 10^{-4} M were generated in the Ar stream by using either method 1 or method 2. For method 1, we also observed variable, but large amounts (often exceeding the amount of PNA) of HNO_3 and NO_2 in the Ar stream. Using method 2, however, we found that the HNO_3 and NO_2 levels were normally less than 10% of the PNA level for cases where the concentration of PNA was on the order of 10^{-6} M.

For all three methods, PNA vapors could be continuously generated from a single reaction mixture for periods of up to 60 min. This suggested the possibility of developing a convenient flow method for generation and analysis of gaseous PNA. Accordingly, we constructed a glass inlet system for admitting PNA/Ar mixtures to a mass spectrometer. The inlet was divided into two sections, one at ambient temperature and one heated to 600 K (**Caution**! See experimental details). We prepared PNA via method 2 and admitted PNA vapors from the reaction mixture into the inlet system. We similarly obtained reference spectra for possible impurities (NO_2 and HNO_3), and the data are given in Table I.

The 300-K PNA mass spectrum does not exhibit a molecular ion at m/e 79. We attribute the peaks at m/e 46, 30, 18, and 17, respectively, to the fragmentation products $NO_2^{+}\cdot$, $NO^{+}\cdot$, $H_2O^{+}\cdot$, and $OH^{+}\cdot$. The m/e 32 peak may derive either from fragmentation of the PNA molecular ion or from O_2 generated by decomposition of PNA in the reaction mixture (vide infra). At 600 K, the PNA mass spectrum shows the same mass ions as at 300 K; the relative intensities of the peaks differ, however. The thermal decomposition of PNA at 600 K should proceed as in reactions 3 and 4.[7,11-17] H_2O_2 would also decompose at this

$$HOONO_2 \rightleftarrows HOO\cdot + NO_2 \quad (3)$$

$$2HOO\cdot \rightarrow H_2O_2 + O_2 \quad (4)$$

temperature via reactions 5 and 6. The expected products of the

$$HOOH \rightleftarrows 2HO\cdot \quad (5)$$

$$HO\cdot + HOO\cdot \rightarrow H_2O + O_2 \quad (6)$$

PNA decomposition are thus NO_2, O_2, and H_2O. The 600-K PNA spectrum shows enhanced peaks at m/e 32, 18, 17, and 16, consistent with O_2 and H_2O as decomposition products. Also for PNA the 30/46 mass ion ratio increases from 0.95 at 300 K to 3.4 at 600 K. By comparison, the mass spectrum of NO_2 at 600 K shows a 30/46 mass ion ratio of 4.1 while HNO_3 exhibits a mass ion ratio of 1.18 ± 0.02 at either 300 or 600 K. The value of 3.4 for PNA at 600 K is sufficiently close to the value of 4.1 for NO_2 to indicate the latter as a product of the decomposition. The presence of HNO_3 as an additional product (perhaps via wall reactions)[13] would account for the 30/46 ratio being somewhat lower for PNA than for pure NO_2. Thus, the change on heating of the 30/46 mass ion ratio serves to distinguish PNA from either NO_2 or HNO_3.

Decomposition of PNA in Solution. PNA reaction mixtures continually evolve oxygen (identified by mass spectroscopy) over a period of several hours. We examined the kinetics of oxygen evolution by measuring the increase in pressure of a closed system containing the reaction mixture from preparative method 2. Semilog plots of pressure vs. time were linear, and the corresponding observed first-order rate constant for oxygen evolution, k_{obsd}, was 2.6×10^{-5} s^{-1} at 273 K and 1.2×10^{-4} s^{-1} at 293 K.

Two possible mechanisms can account for the evolution of oxygen from PNA solutions. In either mechanism, PNA is assumed to participate in the acid-base equilibrium (reaction 7). PNA decomposition could then proceed via either free radical or

$$HOONO_2 \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} H^+ + O_2NOO^- \quad (7)$$

ionic reactions. In the latter case, pernitrate ion would undergo unimolecular elimination of O_2 and nitrite (reaction 8). In the

$$O_2NOO^- \xrightarrow{k_8} O_2 + NO_2^- \quad (8)$$

free radical mechanism, reversible homolytic O–N bond scission (reaction 9) is followed by hydroperoxyl radical disproportionation

$$HOONO_2 \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} HOO\cdot + NO_2 \quad (9)$$

(reaction 4). Oxygen and H_2O_2 are thus the expected free-radical-reaction products. Any NO_2 formed in reaction 9 would hydrolyze to a mixture of nitrite and nitrate.[18]

In an attempt to differentiate between the possible mechanisms, we investigated the pH dependence of the kinetics of oxygen evolution from decomposition of 10^{-3} M PNA in aqueous buffer. Table II lists values of k_{obsd} for PNA solutions at 283.6 K and various pH. From the table, it is evident that k_{obsd} increases with increasing pH over the range investigated. The good agreement for k_{obsd} values obtained in acetate buffer with use of both preparative methods 2 and 3 is taken as evidence that PNA was formed by the latter method. For PNA solutions prepared by method 3 and diluted in acetate buffer (pH 4.7), nitrite formation was detected spectrophotometrically ($\lambda_{max} = 365$ nm). For two runs at 293 K, the observed first-order rate constant for production of nitrite was $(22.5 \pm 1.8) \times 10^{-3}$ s^{-1}, which is in reasonable agreement with the rate constant for oxygen evolution at the same temperature but higher pH.

To the extent that only reactions 7 and 8 are operative, applying the steady-state approximation to O_2NOO^- gives equations 10

$$+d[O_2]/dt = [PNA]k_7k_8/([H^+]k_{-7} + k_8) = [PNA]k_{obsd} \quad (10)$$

and 11. With the assumption of the mechanism given by reactions

$$k_{obsd}^{-1} = k_7^{-1} + [H^+](k_{-7}/k_7k_8) \quad (11)$$

7 and 8, a plot of k_{obsd}^{-1} vs. $[H^+]$ will be linear. In actuality such a plot (Figure 1) shows pronounced downward curvature below pH 5. This indicates O_2 evolution by an additional mechanism and raises the possibility that PNA decomposition occurs at least in part by reactions 9 and 4.

It is interesting to compare the aqueous chemistry of PNA with that of other peroxynitrates. We have shown that formation of PNA via reaction 1 is entirely analogous to formation of alkyl, acyl, and aroyl peroxynitrates. There are also some interesting parallels in terms of decomposition mechanism. Alkaline hydrolysis of peroxyacetyl nitrate (PAN), $CH_3C(O)OONO_2$, yields stoichiometric amounts of acetate, nitrite, and (singlet) molecular oxygen.[20,21] Mudd[22] observed first-order kinetics for production of nitrite from hydrolysis of PAN ($k_{obsd} = 2 \times 10^{-3}$ s^{-1} at pH 7.6 and 300 K). On the basis of these results, Stephens[23] postulated a mechanism for alkaline hydrolysis of PAN involving the intermediacy of pernitrate anion, i.e., reaction 12, followed by

$$CH_3C(O)OONO_2 + OH^- \rightarrow CH_3C(O)OH + O_2NOO^- \quad (12)$$

reaction 8. Our results are consistent with this mechanism although a comparison of our kinetics with those of Mudd suggests that reaction 8, if it is involved in PAN hydrolysis, is not rate-limiting.

Conclusions

Nitration of concentrated H_2O_2 with NO_2BF_4 at 273 K yields PNA. PNA solutions thus prepared provide a convenient source of relatively pure PNA vapor. The analysis of PNA by infrared

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(12) Graham, R. A.; Winer, A. M.; Pitts, J. N. *J. Chem. Phys.* **1978**, *68*, 4505.

(13) Uselman, W. M.; Levine, S. Z.; Chon, W. H.; Calvert, J. G.; Shaw, J. H. In "Nitrogenous Air Pollutants, Chemical and Biological Implications"; Grosjean, D., Ed.; Ann Arbor Science: Ann Arbor, MI, 1979.

(14) Cox, R. A.; Derwent, R. G.; Hutton, A. J. L. *Nature (London)* **1977**, *270*, 328.

(15) Baldwin, A. C.; Golden, D. M. *J. Phys. Chem.* **1978**, *82*, 644.

(16) Graham, R. A.; Winer, A. M.; Atkinson, R.; Pitts, J. N. *J. Phys. Chem.* **1979**, *83*, 1563.

(17) Cox, R. A.; Patrick, K. *Int. J. Chem. Kinet.* **1979**, *11*, 635.

(18) Kaufman, F. *Proc. R. Soc. London, Ser. A* **1958**, *247*, 123.

(19) "Handbook of Chemistry and Physics", 51st ed., Weast, R. C., Ed.; CRC: Cleveland, OH, 1971; p D-104.

(20) Nicksic, S. W.; Harkins, J.; Mueller, P. K. *Atmos. Environ.* **1967**, *1*, 11.

(21) Stephens, E. R. *Atmos. Environ.* **1967**, *1*, 19.

(22) Mudd, J. B. *J. Biol. Chem.* **1966**, *241*, 4077.

(23) Stephens, E. R. *Adv. Environ. Sci.* **1969**, *1*, 119.

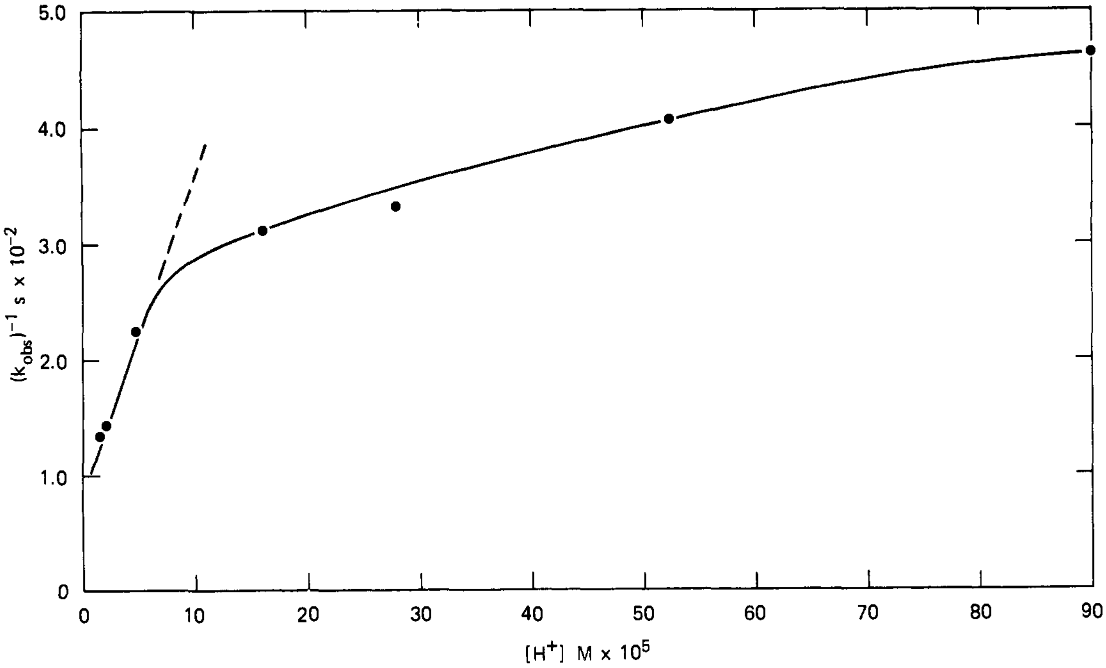

Figure 1. Reciprocal observed first-order rate constant, k_{obsd}^{-1}, vs. hydrogen ion concentration for decomposition of pernitric acid in aqueous buffer at 283.6 K (from data of Table II).

Table II. Observed First-Order Rate Constants for Oxygen Evolution (k_{obsd}) from 10^{-3} M Pernitric Acid in Aqueous Buffer at 283.6 K[a]

run	prep method[b]	buffer[c]	pH	10^3k_{obsd},[d] s^{-1}
1[e]	2	acetate	4.90	39.2 ± 2.9[f]
2	3	acetate	4.87	7.40
3	2	acetate	4.70	7.06 ± 0.75[g]
4	3	acetate	4.32	4.46
5	3	KHphth[h]	3.80	3.21
6	3	KHphth	3.55	3.05
7	3	KHphth	3.28	2.47
8	3	KHphth	3.04	2.17
9	3	HCl	1.36	1.57

[a] Temperature control to ±0.5 K. [b] See Experimental details. [c] Buffer = 5×10^{-2} M, prepared according to standard formulations[19] and made to ionic strength 0.5 with $NaClO_4$. [d] $k_{obsd} = 0.693/t_{1/2}$ from semi-log plot of pressure vs. time. [e] Temperature = 293 K. [f] Average of three runs. [g] Average of four runs. [h] phth, phthalate.

spectrophotometry or by mass spectroscopy in flow systems permits the study of reactions of PNA with radicals or other reactive species. These investigations are in progress and will be reported separately.

Aqueous PNA decomposes to molecular oxygen and nitrite. Unimolecular decomposition of the pernitrate anion to O_2 and NO_2^- seems a likely mechanism, though a free radical mechanism for decomposition of PNA may also be important.

Similarities in the hydrolytic chemistry of PNA and peroxyacetyl nitrate suggest that the pernitrate anion is an intermediate in both cases. PNA and peroxyacetyl nitrate both play important roles in the free radical chemistry of photochemical smog. One question that now obtains is whether the ionic chemistry of these pernitrates in heterogeneous phases (aerosols, surfaces, etc.) is also of environmental concern.

Experimental Section

Materials. NO_2BF_4 (Alfa Ventron), 90% H_2O_2 (FMC), and 70% HNO_3 (Baker) were used as received.

Safety Hazards. The procedures used for preparation and analysis of PNA are potentially dangerous and certain safety precautions should routinely be observed.

We encountered one explosion in the course of our work. While PNA vapor was passed through the heated glass inlet system of the mass spectrometer, we raised the temperature of the inlet to 700 K. There was a sudden pressure increase in the mass spectrometer chamber followed by a violent explosion that shattered the inlet system. Fortunately the inlet was behind a safety shield, and there were no injuries. In all subsequent work the inlet temperature was never raised above 600 K and there were no further incidents of this type (Note: Schwarz[2] also reported a violent explosion apparently involving concentrated PNA vapor).

For PNA reaction mixtures made by method 1 (see below) and allowed to stand at room temperature, gas evolution and the temperature of the reaction mixture increased over the period of a few hours. Eventually, gas evolution became so vigorous that the liquid bumped out of the reaction flask (again see ref 2). This behavior was not observed for PNA prepared by methods 2 and 3. The possibility of detonations due to large exotherms recommends that the synthetic reactions not be run on a scale exceeding ca. 5 g. PNA reaction mixtures prepared by methods 1 and 2 are highly acidic and are powerful oxidizing agents. Skin contact results in painful burns. The reaction mixtures exhibit a sharp odor characteristic of many peroxides. One of us (R.K.) has complained of respiratory problems apparently associated with repeated exposure to PNA and other peroxynitrate vapors. These materials should be handled in a hood or other well-ventilated area.

Preparation of HO_2NO_2 from 90% H_2O_2 and 70% HNO_3 (Method 1). A 2-g (2.2×10^{-2} mol) sample of 70% HNO_3 was added to a 1-dram specimen vial (A. H. Thomas) equipped with a 10-mm magnetic stirring bar. The acid was chilled in a small ice bath and 0.9 g (2.4×10^{-2} mol) of 90% H_2O_2 was added dropwise via a capillary pipet with vigorous agitation over a 10-min period.

Preparation of HO_2NO_2 from 90% H_2O_2 and NO_2BF_4 (Method 2). A 2-g (5.3×10^{-2} mol) sample of 90% H_2O_2 was chilled and stirred as described above. Solid NO_2BF_4 (0.4 g, 3×10^{-3} mol) was added in approximately 5–10-mg portions with use of a spatula. Effervescence and evolution of brown fumes accompany addition of NO_2BF_4.

Preparation of HO_2NO_2 in CH_3CN (Method 3). The 90% H_2O_2 (0.1 g, 3×10^{-3} mol) was dissolved in 1 g of CH_3CN and cooled to 0 °C with stirring. NO_2BF_4 (0.2 g, 1.5×10^{-3} mol) was added as described in method 2.

Characterization of HO_2NO_2. Infrared spectra of PNA vapor in Ar carrier were obtained with use of a Perkin-Elmer model 457 spectrophotometer and either a Wilks 20-m variable path length cell or a 2.5-cm i.d. × 10-cm path length Pyrex flow-through cell. Observed absorption maxima at 1745, 1715, 1390, 1300, 940, and 800 cm^{-1} compared favorably with literature values for $HOONO_2$.[3,6] Impurities in the sample included NO_2 (1620 cm^{-1}) and HNO_3 (840 cm^{-1}).

Procedures. Vapor-phase samples of PNA for IR analysis were generated from liquid reaction mixtures as follows. A capillary pipet was used to transfer about 3 mL of reaction mixture from the specimen vial used as a reaction flash (and maintained at 273 K) to a 10-mL bulb equipped with an O-ring joint and a vacuum stopcock leading to an ebullation tube. The bulb was connected via the O-ring joint to the IR cell and allowed to warm to ambient temperature. Argon was admitted to the bulb via the stopcock at a rate of approximately 30 cm^3 s^{-1}, bubbled through the reaction mixture, and used to carry PNA vapor through the cell.

Vapor samples for mass spectral analysis were handled similarly, except that the argon flow was eliminated. Evolution of oxygen from decomposition of PNA in the reaction mixture was sufficient to sweep PNA vapors into the system. The mass spectrometer and inlet system have been described elsewhere.[24]

The evolution of oxygen from aqueous PNA solutions was monitored with a calibrated pressure transducer (Validyne model DP-7) connected via a three-way stopcock to a jacketed, 250-mL bulb equipped with magnetic sitrrer. To perform the experiments, we added 100.0 mL of buffer to the bulb and allowed the mixture to come to reaction temperature while O_2 was vigorously bubbled through the solution. Next, the O_2 flow was stopped, 25–100 μL of a PNA reaction mixture were added via syringe, the stopcock closed, and transducer output monitored with a strip chart recorder. For a 50-μL aliquot of preparative method 2, assuming 100% yield of PNA, the initial PNA concentration in 100 mL of buffer is calculated to be 7.5×10^{-4} M. For a 150-cm^3 gas volume, the final pressure of the system is calculated to be 9 torr, assuming complete decomposition to O_2. Consistent with these calculations, observed final pressures were typically 5–10 torr. Control experiments indicated significant oxygen evolution from excess H_2O_2 for PNA decompositions when preparative method 2 was used and pH ≤4. To circumvent this problem, we adopted preparative method 3, which does not require a large excess of H_2O_2.

Oxygen was identified as the reaction product by allowing a sample of PNA to decompose in a sealed, degassed tube and then analyzing the gas over the frozen solution by mass spectroscopy.

Nitrite evolution was followed by monitoring the absorption at 365 nm with a Perkin-Elmer model 554 spectrophotometer. The buffer solution was first equilibrated to the desired temperature and 50–100 μL of PNA solution was then injected into the buffer and mixed well. The absorbance at 365 nm was monitored until completion of the reaction.

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[24] Chang, J. S.; Barker, J. R.; Davenport, J. E.; Golden, D. M. *Chem. Phys. Lett.* 1979, *60*, 385.

Insertion of Carbon Monoxide into Metal–Nitrogen Bonds. Synthesis, Chemistry, Structures, and Structural Dynamics of Bis(pentamethylcyclopentadienyl) Organoactinide Dialkylamides and η^2-Carbamoyls

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Abstract: This paper reports the synthesis and characterization of chlorobis(pentamethylcyclopentadienyl)thorium and -uranium dialkylamides, $M[\eta\text{-}(CH_3)_5C_5]_2(NR_2)Cl$ (M = Th, U; R = CH_3, C_2H_5), and bis(dialkylamides), $M[\eta\text{-}(CH_3)_5C_5]_2(NR_2)_2$ (M = Th, U, R = CH_3; M = U, R = C_2H_5). NMR studies indicate restricted rotation about the M–NR_2 bonds. The amide compounds undergo facile migratory insertion of carbon monoxide to produce the corresponding η^2-carbamoyl complexes $M[\eta\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CONR_2]Cl$, $M[\eta\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CONR_2]NR_2$, and $M[\eta\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CONR_2]_2$ which were characterized by a variety of chemical and physicochemical methods. The infrared spectra of these compounds exhibit unusually low C–O stretching frequencies (1490–1560 cm^{-1}) for carbamoyl complexes, indicative of strong metal–oxygen bonding. The molecular structures of $Th[\eta\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CON(C_2H_5)_2]Cl$ and $U[\eta\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}CON(CH_3)_2]_2$ have been determined by single-crystal X-ray diffraction techniques. The former complex crystallizes in the monoclinic space group $P2_1/n$ (an alternate setting of $P2_1/c—C_{2h}^5$) with four molecules in a cell of dimensions: $a = 9.097$ (2) Å, $b = 21.291$ (4) Å, $c = 14.031$ (2) Å, and $\beta = 95.78$ (2)°; the latter complex crystallizes in the monoclinic space group $P2_1/c—C_{2h}^5$ with four molecules in a unit cell of dimensions: $a = 9.277$ (4) Å, $b = 16.143$ (5) Å, $c = 18.977$ (6) Å, and $\beta = 130.55$ (3)°. For the chloro complex, least-squares refinement led to a value for the conventional R index (on F) of 0.080 for 3156 independent reflections having $2\theta_{MoK\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$, while for the bis(carbamoyl), least-squares refinement led to a conventional R (on F) of 0.036 for 3689 independent reflections having $2\theta_{MoK\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$. The $M[(CH_3)_5C_5]_2$ fragments of both molecules are of the "bent sandwich" $M(C_5H_5)_2X_2$ configuration, with the carbamoyl ligands bound in a η^2 fashion. The chloro complex is disordered, with two isomers (one with the C–O vector pointing toward the Cl atom, one with it pointing away) having cocrystallized in nearly equal proportions. The Th–O distances are 2.383 (31) and 2.460 (16) Å; the average Th–C distance is 2.418 (20) Å; the Th–C–O angles accompanying the above distances are 70.1 (15) and 74.5 (1)°, respectively. In solution, the two isomers of the analogous uranium complex are in equilibrium ($\Delta H = 1.2 \pm 0.1$ kcal/mol; $\Delta S = 8 \pm 1$ eu) with interconversion rapid on the ^1H NMR time scale at room temperature (at –80 °C, $\Delta G^{\ddagger} = 8.9 \pm 0.5$ kcal/mol). In the bis(carbamoyl), the U–O distances are 2.370 (5) and 2.342 (7) Å, the corresponding U–C distances 2.405 (8) and 2.402 (9) Å, and the corresponding U–C–O angles 73.0 (4) and 71.8 (5)°. The structural and spectral data evidence dative nitrogen lone-pair donation to the "carbenoid" carbamoyl carbon atom. The complex $Th[\eta\text{-}(CH_3)_5C_5]_2[N(CH_3)_2]CH_3$ was also prepared; carbonylation occurs preferentially at the metal–carbon bond to yield $Th[\eta\text{-}(CH_3)_5C_5]_2[N(CH_3)_2](\eta^2\text{-}COCH_3)$.

The classic migratory insertion reaction of carbon monoxide into a two-center, two-electron metal–carbon bond (eq 1, X = a hydrocarbyl functionality) is an extremely important transformation in stoichiometric and catalytic organometallic chemistry.[2]

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