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Note

Kinetics of the Oxidation of Triphenylphosphine by Nitric Oxide

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In 1962, Drago and co-workers[1] described the reactions of nitric oxide (nitrogen monoxide) with various Lewis bases. Among the bases examined was triphenylphosphine, which was shown to undergo oxidation to triphenylphosphine oxide. The second product was shown to be nitrous oxide (eq 1), and the analogous reaction has been described for the NO oxidation of triethyl phosphite to triethyl phosphate.[2] The now well-established roles of NO in mammalian biology[3] have drawn renewed attention to the reactivity of this stable free radical with various substrates including metal centers and functional groups such as thiols and phosphines. However, there is a dearth of kinetics and mechanistic information regarding reactions of the latter. In this context, we describe an investigation of the NO oxidation of PPh_3 in toluene, chloroform, and dichloroethane in order to use this as a model system to gain insight into the mechanisms of such oxygen transfer reactions of NO.

$$PPh_3 + 2NO \rightarrow Ph_3PO + N_2O \qquad (1)$$

Results and Discussion

The stoichiometry of the reaction was established by preparing a deaerated closed vessel containing a solution of PPh_3 (5.73 mmol in 5 mL of toluene) plus gaseous NO (3.8 mmol) added by vacuum line techniques. After 9.5 h of reaction with stirring and periodic agitation to ensure complete mixing, the products were analyzed by GC and NMR techniques. GC−MS analysis showed nearly quantitative consumption of NO and production of N_2O (1.8 ± 0.1 mmol) and was consistent with the 2:1 NO:N_2O stoichiometry described by eq 1. The ^1H and ^{31}P NMR spectra of the product solution demonstrated that Ph_3P (3.6 ± 0.2 mmol) was still present. The only NMR active product identified was Ph_3PO, the amount formed (2.2 ± 0.2 mmol) equal (within experimental uncertainty) to the amount of Ph_3P consumed (2.1 ± 0.2 mmol). These values exceed slightly those predicted (1.9 mmol) by eq 1 based on the NO consumption in the reaction. Other than potential errors in the different analytical procedures, a higher Ph_3PO yield relative to that for N_2O would also be the likely result of NO_2 formation by the rapid NO reaction with adventitious O_2 (i.e., $2NO + O_2 \rightarrow 2NO_2$).[4] In accord with this possibility, NO_2 was found to oxidize PPh_3 to Ph_3PO (presumably, $NO_2 + PPh_3 \rightarrow Ph_3PO + NO$) at a rate much faster than the reaction with NO described below. In this context, a second experiment starting with 5.72 mmol of PPh_3 and 0.70 mmol of NO gave 0.39 ± 0.05 mmol of N_2O (GC/TCD) and 0.34 ± 0.02 mmol of PPh_3PO (^{31}P NMR) as well as 5.39 ± 0.02 mmol of unreacted PPh_3 matching better the predicted stoichiometry.[5]

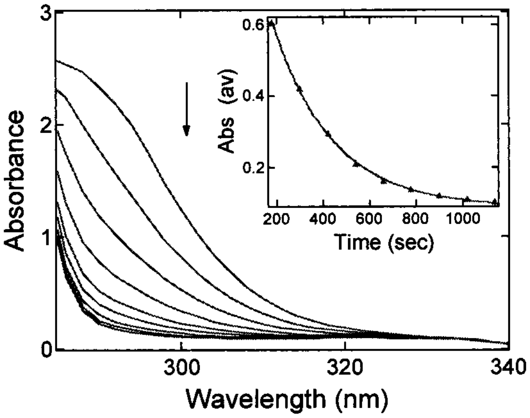

Figure 1. Optical absorption spectra recorded during the oxidation of PPh_3 (1 mM) by NO (6.24 mM) in 294 K toluene. Inset: plot of Abs(av) (average absorbance over the range 296−334 nm) vs time (triangles) and a best-fit exponential curve (dark line) giving a k_{obs} of 3.99×10^{-3} s^{-1}.

Kinetics studies were performed by following temporal changes in [PPh_3] by periodically recording the electronic spectrum (Figure 1) of a reaction solution prepared from PPh_3 and a large excess of NO. Thus, the rates were studied under pseudo-first-order conditions (constant [NO]) in each case (see Experimental Section). The inset in Figure 1 shows an

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(1) Longhi, R.; Ragsdale, R. O.; Drago, R. S. *Inorg. Chem.* **1962**, *1*, 768−770.

(2) Kuhn, L. P.; Doali, J. O.; Wellman, C. *J. Am. Chem. Soc.* **1960**, *82*, 4792−4794.

(3) *Nitric Oxide, Biology and Pathobiology*; Ignarro, L. J., Ed.; Academic Press: San Diego, 2000.

(4) (a) Ford, P. C.; Wink, D. A.; Stanbury, D. M. *FEBS Lett.* **1993**, *326*, 1−3. (b) Nottingham, W. C.; Sutter, J. R. *Int. J. Chem. Kinet.* **1986**, *18*, 1289−1302. (c) Lorkovic, I. M.; Ford, P. C. *Inorg. Chem.* **1999**, *38*, 1467−1468.

(5) The product N_2O was found to be unreactive with PPh_3 under the experimental conditions. A solution of PPh_3 (1.5 mM) in toluene under 400 Torr of N_2O showed no spectral changes over a period of 10^4 s at ambient temperature. Replacement of the N_2O with 300 Torr of NO led to spectral changes indicating oxidation to Ph_3PO within 30 s.

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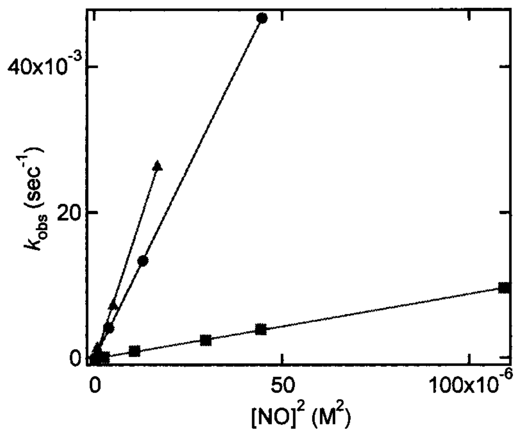


Figure 2. Plot of k_{obs} vs [NO]^2 for the reaction of NO with PPh_3 in chloroform (circles), dichloroethane (triangles), and toluene (squares) (all at 294 K). (NO solubilities for the chlorocarbon solvents were estimated according to footnote 6).

absorbance vs time plot for the PPh_3 reaction with NO (6.2 mM) in toluene. These data give a very good fit to an exponential decay function ($k_{obs} = 3.99 \times 10^{-3}$ s^{-1}); thus the reaction rate is first order in the limiting reagent PPh_3 (eq 2).

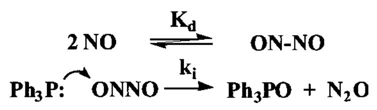
$$d[PPh_3]/dt = -k_{obs}[PPh_3] \qquad (2)$$

Values of k_{obs} were measured at different NO concentrations in toluene, and a plot of k_{obs} vs [NO]^2 proved to be linear (Figure 2). Thus, the reaction rate is second order in [NO] (eq 3), and the slope of this plot (91 ± 1 M^{-2} s^{-1} in 294 K toluene) is the third-order rate constant k_3. In the same manner, k_{obs} values determined in chloroform and in 1,2-dichloroethane gave linear plots vs [NO]^2 (Figure 2) with $k_3 = (1.05 \pm 0.01) \times 10^3$ and $(1.57 \pm 0.02) \times 10^3$ M^{-2} s^{-1}, respectively, at 294 K.[6]

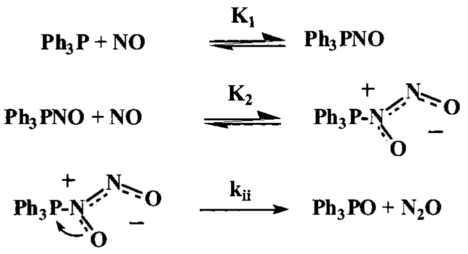
$$d[PPh_3]/dt = -k_3[PPh_3][NO]^2 \qquad (3)$$

Two prospective mechanisms for this reaction are illustrated in Schemes 1 and 2. In the first, the oxidation is proposed to occur by head to head dimerization of NO followed by oxygen atom transfer from the dimer to the PPh_3 substrate. Although the NO dimer is known, the equilibrium constant K_d for ONNO formation is small.[7] Therefore, the rate law for Scheme 1 would be $d[PPh_3]/dt = -K_dk_1[NO]^2[PPh_3]$, consistent with eq 3 for $k_3 = K_dk_i$. In the alternative pathway Scheme 2, the first steps lead to equilibrium formation of the adduct $Ph_3PN(O)NO$ followed by unimolecular oxygen transfer from nitrogen to phosphorus. If the equilibrium formation of the intermediate were small, the predicted rate law for Scheme 2 would also be consistent with eq 3 for $k_3 = K_1K_2k_{ii}$. A mechanism similar to Scheme 2 was proposed for the oxidation of $P(OEt)_3$; however, in that case formation of the first adduct was proposed to be rate limiting.[2]

Scheme 1



Scheme 2



While Scheme 1 is attractive in its apparent simplicity, it is not clear how it should respond to changes in the solvent polarity. The N_2O_2 dimer has been characterized in low-temperature matrixes and in the gas phase[7] but shows only a small negative enthalpy for formation from monomeric NO ($\Delta H_d = -3.5$ kcal mol^{-1} in liquid argon).[8] Given that ΔS_d would also be negative, K_d is expected to be small at ambient temperature; indeed, a value $<3 \times 10^{-4}$ M^{-1} has been estimated for the gas phase at 306 K.[7b] We are unaware of any measurement of K_d or direct observation of ONNO in room temperature solutions. If one assumes that K_d in toluene has the same value as in the gas phase, this would imply a rather high rate constant k_i for the bimolecular oxygen atom transfer step of Scheme 1, i.e., $k_i = k_3/K_d \approx 3 \times 10^5$ M^{-1} s^{-1}. Given that orbital arguments indicate this to be symmetry forbidden,[9] such a fast rate would not be expected. On the other hand, the *cis* conformer of ONNO is the lowest energy form of this species, and one might argue that more polar solvents should increase K_d in a manner consistent with the larger values of k_3 in these media.

The expected solvent effect on the reaction rates according to Scheme 2 is less ambiguous. The more polar solvents would clearly favor the formation of the proposed phosphonium diazeniumdiolate intermediate $Ph_3PN(O)NO$, consistent with the reaction being faster in polar solvents. Furthermore, there is considerable precedence for the formation of such species formed by the reaction of NO with strong nucleophiles. For example, adducts of NO with very strong bases such as amide anions R_2N^- are well-known[1,10] although, a

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(6) (a) NO solubility for the chlorocarbon solvents was assumed to parallel O_2 solubility, which is known for each of the solvents used here. Therefore, the Ostwald coefficients for NO (L(NO), defined as the volume of NO at 1 atm absorbed by a volume of solvent)[6b] were estimated from the product of the known Ostwald coefficient for O_2 in that solvent, $L(O_2)$, times the average of the ratios of Ostwald coefficients, for two solvents in which both are known.[6c,d] These solvents were toluene ($L(NO)/L(O_2) = 1.094$) and carbon tetrachloride (1.043) giving the average value of 1.068 for the ratio. This led to L(NO) estimates of 0.296 and 0.189 for chloroform and 1,2-dichloroethane, respectively. (b) Battino, R. *Fluid Phase Equilib.* **1984**, *15*, 231. (c) Battino, R. Oxygen and Ozone. *IUPAC: Solubility Data Series*; Pergamon Press: New York, 1981; Vol. 7, p 452. (d) Shaw, A. W.; Vosper, A. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1239.

(7) (a) Kukolich, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 4715−4716. (b) Forte, E.; Van Den Bergh, H. *Chem. Phys.* **1978**, *30*, 325−331. (c) Dinerman, C. E.; Ewing, G. E. *J. Chem. Phys.* **1970**, *53*, 626. (d) Billingsley, J.; Callear, A. B. *Trans. Faraday Soc.* **1971**, *67*, 589.

(8) Sluyts, E. J.; Van der Veken, B. J. *J. Mol. Struct.* **1994**, *320*, 249−267.

(9) Pearson, R. G. *Symmetry Rules for Chemical Reactions*; John Wiley & Sons: New York, 1976; p 438.

much smaller formation constant would be expected for the weakly basic PPh_3 (pK_a 2.73).[11] Since formation of such intermediates should depend on phosphine basicity, the effect of para substituents on the kinetics of NO oxidation of several para-substituted triaryl phosphines $P(4\text{-X-Ph})_3$ was examined for a single set of experimental parameters ([NO] = 4.6 mM in 294 K toluene). The rates proved very sensitive to the electronic nature of the substituents and gave a 200-fold range in the k_{obs} values (1.3×10^{-4} s^{-1}, 2.5×10^{-3} s^{-1} , 6.1 $\times$ 10^{-3} s^{-1} and 3.4×10^{-2} s^{-1} for X = Cl, H, CH_3, and OCH_3, respectively). The linear plot of log(k_{obs}) vs phosphine pK_a [11] gave a slope of +0.64 (Hammett $\rho = -4.5$).

Thus, the reaction is strongly dependent on the phosphine basicity and solvent polarity, consistent with the pathway described in Scheme 2. In this context we favor Scheme 2 as the likely mechanism, although it is clear that the arguments against Scheme 1 are not unequivocal.[12]

The observation here of facile oxidation of PPh_3 by NO concurs with the earlier literature on this subject[1] but contrasts with a recent claim that, while the tetraphenylporphyrinatoiron(II) complex Fe(TPP)(NO) catalyzes NO oxidation of PPh_3, the uncatalyzed reaction does not proceed measurably over the course of hours in toluene.[13] When kinetics experiments analogous to those described above were carried out with added Fe(TPP)(NO), no enhancement of the oxidation rates was found. For example, the reaction of PPh_3 (1.0 mM) with NO (6.2 mM) in toluene gave a k_{obs} value of 3.99×10^{-3} s^{-1} while an experiment with the same PPh_3 and NO concentrations but with added Fe(TTP)(NO) (40 μM) gave a k_{obs} of 4.05×10^{-3} s^{-1}. Other studies performed with different iron porphyrin concentrations gave the same result. Thus, under such conditions there appears to be no significant catalysis of eq 1 by Fe(TPP)(NO).

In summary, the oxidation of Ph_3P by NO (eq 1) follows third-order kinetics, second order in nitric oxide (eq 3); however, catalysis by Fe(TPP)(NO) was not observed. The reaction is accelerated in more polar solvents and is strongly dependent on phosphine basicity. In these contexts, it is proposed that the mechanism proceeds via formation of a phosphonium diazeniumdiolate intermediate $Ph_3PN(O)NO$ followed by unimolecular decomposition to phosphine oxide plus N_2O.

Experimental Section

Materials. The nitric oxide (>99.0% purity; Matheson) used in these experiments was purified of higher nitrogen oxides by passage through a stainless steel column containing Ascarite II (NaOH on a silicate carrier; Thomas Scientific). All manipulations of NO gas and NO containing solutions were carried out in stainless steel or glass vessels and lines with greaseless fittings. Freshly distilled, dried solvents were used to prepare solutions in an argon-filled glovebox prior to each run. All other reagents were obtained from commercial sources and purified according to established procedures.

Instrumentation. Optical spectra in solution were recorded on a HP-8452a diode array spectrophotometer. NMR spectra were obtained on a Varian 400 MHz spectrometer. Gas chromatographic−mass spectrometric analysis of NO and N_2O was carried out using a HP-6890 GC system coupled to a HP 5973 mass selective detector.

Kinetics Procedures. Kinetics studies were performed by condensing a known amount of NO from a vacuum line into an airtight cuvette flask of known volume (110 mL) and then adding PPh_3 (1 mM) in the appropriate degassed, anhydrous solvent (5 mL) by syringe. Nitric oxide pressures within the cell ranged from 70 to 700 Torr, corresponding to NO concentrations of 1 to 10 mM in the toluene solutions.[6d] At the lowest P_{NO} (~70 Torr), [NO] was roughly equivalent to [PPh_3]; but the total NO in the flask (mostly in the headspace) was always in >25-fold stoichiometric excess of PPh_3. Since the reactions were slow ($t_{1/2}$ = 5−100 min), the cell was shaken to maintain pseudo-first-order conditions (constant [NO]). UV−vis spectra were recorded at regular intervals, and the reaction was followed quantitatively by temporal changes in absorbance due to PPh_3 (Figure 1). The observed rate constant was found by plotting the average change in absorbance (296−334 nm) versus time, the slope of the exponential fit being k_{obs} (3.99×10^{-3} s^{-1} with 6.24 mM NO). Rate constants determined by monitoring the first-order change of absorbance at single wavelengths, 290 nm (3.88×10^{-3} s^{-1}) and 308 nm (4.14×10^{-3} s^{-1}), were nearly the same.

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(10) (a) Saavedra, J. E.; Dunams, T. M.; Flippen-Anderson, J. L.; Keefer, L. K. *J. Org. Chem.* **1992**, *57*, 6134−6138. (b) Keefer, L. K.; Flippen-Anderson, J. L.; George, C.; Shanklin, A. P.; Dunams, T. M.; Christodoulou, D.; Saavedra, J. E.; Sagan, E. S.; Bohle, D. S. *Nitric Oxide* **2001**, *5*, 377−399. (c) Davies, K. M.; Wink, D. A.; Saavedra, J. E.; Keefer, L. K. *J. Am. Chem. Soc.* **2001**, *123*, 5473−5481.

(11) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650−658 and references therein.

(12) (a) The solvent effects might also be argued to support Scheme 1 in the following context. The faster rates in more polar solvents could be the result of a higher value of K_d if N_2O_2 were significantly more polar than is NO. However, theoretical calculations indicate that the relatively weak interaction between the NO monomers to form N_2O_2 is but a small perturbation of the electronic distribution. Hence, even though the more stable conformer of N_2O_2 is *cis*, the small net dipole[12b] is little more than twice that of NO, suggesting that solvent polarity would not perturb the equilibrium greatly. (b) Kishner, S.; Whitehead, M. A.; Gopinathan, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 1365−1371.

(13) Lin, R.; Farmer, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 1143−1150.