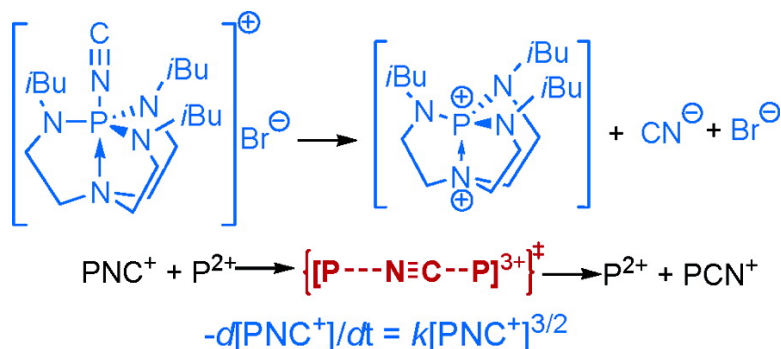## Communication

3/2-Order Chain Kinetics Involving a Postulated Dicationic Intermediate in the Isomerization of a P–Isocyano to a P–Cyano Azaphosphatrane Monocation

Jesudoss V. Kingston, John G. Verkade, and James H. Espenson

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3/2-Order Chain Kinetics Involving a Postulated Dicationic Intermediate in the Isomerization of a P−Isocyano to a P−Cyano Azaphosphatrane Monocation

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The isomerization of organic isocyanides to cyanides has sporadically piqued interest over the past 45 years.[1] In the gas phase, evidence has been put forth for a unimolecular sigmatropic pathway,[2] whereas in solution, sigmatropic, free radical, and cationic chain mechanisms can occur, depending on the conditions.[1a,3] Silyl cyanides have been shown to exist in equilibrium with the isocyanide form, exchanging intermolecularly in the liquid phase and intramolecularly in dilute solution.[4] Because of severe instability, the few compounds known in which isocyanide is bonded to a heteroatom[5] (O, S, N, P) have not been candidates for isomerization studies.
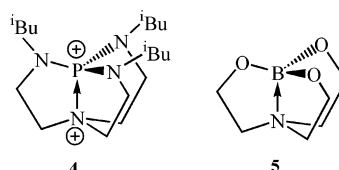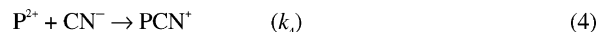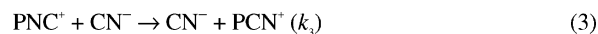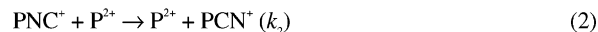
We recently reported the stable isomers **1** and **2**.[6] Here we report a detailed kinetic study of the isomerization of **1** in which we postulate an unusual dicationic intermediate in a chain mechanism.

$$\mathbf{1}, X = -NC$$
$$\mathbf{2}, X = -CN$$
$$\mathbf{3}, X = Br$$
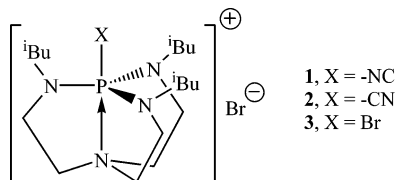
Isomerization of **1** to its more stable isomer **2** takes place slowly in acetonitrile (90% conversion in 96 h at 100 °C), but not in benzene (<2% conversion under the same conditions).[6] Failure of the reaction in benzene is consistent with the inability of this low dielectric constant solvent to support ionic intermediates. The bromo analogue **3**, when present, also plays an important role in the isomerization (see below).

The kinetics of the transformation of **1** to **2** was studied by ^{31}P NMR spectroscopy in CD$_3$CN. The reaction clearly does not follow first-order kinetics, in that plots of $\ln([\mathbf{1}]_t)$ against time are not linear; further, and even more telling, the approximate first-order rate constants increase with $[\mathbf{1}]_0$. These data rule out a mechanism in which **1** dissociates into its component ions which then recombine to form **2**. After reflection on the nature of the variation of $[\mathbf{1}]_t$ and other possible kinetic schemes, we decided to attempt to fit the kinetic data to the mathematical form for the reaction sequence presented in eqs 1−4, Scheme 1. Note that the reverse of eq 1 is not included because eq 4 takes precedence owing to the greater thermodynamic stability of **2**. Although this scheme appears to resemble that of a standard chain reaction, with eqs 1 and 4 being the respective initiation and termination steps and eqs 2 and 3 the propagation steps with the intermediates P^{2+} and CN$^-$, respectively, there is a major difference. One intermediate does not undergo a reaction to regenerate the other; rather, each regenerates itself (eq 2). Such a reaction step has been previously postulated for the isomerization of tritylisocyanide.[3b] The postulate of a bicyclic P^{2+} intermediate in Scheme 1 suggests structure **4**, which is isoelectronic/isostructural with boratrane **5** whose structure has been determined.[7]

Scheme 1. Postulated Reaction Scheme for Isomerization of **1**

$$PNC^+ (\mathbf{1}) \rightarrow P^{2+} + CN^- \quad (k_1) \tag{1}$$

$$PNC^+ + P^{2+} \rightarrow P^{2+} + PCN^+ \quad (k_2) \tag{2}$$

$$PNC^+ + CN^- \rightarrow CN^- + PCN^+ \quad (k_3) \tag{3}$$

$$P^{2+} + CN^- \rightarrow PCN^+ \quad\quad (k_4) \tag{4}$$

With the steady-state approximation for the concentrations of the P^{2+} and CN$^-$ intermediates, these expressions result:

$$\frac{d[P^{2+}]}{dt} = \frac{d[CN^-]}{dt} = 0 = k_1[\mathbf{1}] - k_4[P^{2+}][CN^-] \tag{5}$$

$$\therefore [P^{2+}]_{ss} = [CN^-]_{ss} = \sqrt{\frac{k_1}{k_2}[\mathbf{1}]} \tag{6}$$

The expression for the reaction rate, with the further assumption that the kinetic chains are long (i.e., that the rate of propagation is much larger than initiation), is the following:

$$-\frac{d[\mathbf{1}]}{dt} = [\mathbf{1}] \times \{k_2[P^{2+}] + k_3[CN^-]\} =$$
$$\sqrt{\frac{k_1}{k_4}} \times (k_2 + k_3) \times [\mathbf{1}]^{3/2} \tag{7}$$

According to this analysis, the kinetic data should follow 3/2-order kinetics, with the apparent value of $^{3/2}k$ given by the composite constant that appears in eq 7. If this approach is valid, the variation of [**1**] can be expressed by this function:[8]

$$\sqrt{[\mathbf{1}]_t} = \frac{\sqrt{[\mathbf{1}]_0}}{1 + [\mathbf{1}]_0^{1/2}(^{3/2}kt/2)} \tag{8}$$

Analysis of the time-course data from a representative experiment is given in Figure 1. The average value of $^{3/2}k$ at 100 °C in CD$_3$CN is $(7.2 \pm 0.6) \times 10^{-5}$ L$^{1/2}$ mol$^{-1/2}$ s^{-1} over the range $0.04 < [\mathbf{1}]_0 < 0.29$ mol L^{-1}. When the spent reaction solution was used as the medium for the next measurement made after addition of a second portion of PNC$^+$, and in a separate experiment when PCN$^+$ was present at the outset, rate constants that agreed with the others were obtained.

A less precise approach to the kinetic data analysis was to study the initial rates. The values of $[\mathbf{1}]_t$ were fitted to a sixth-order
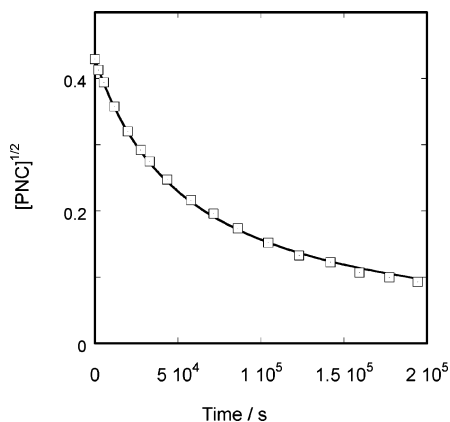
Figure 1. Analysis of the time-course data according to 3/2-order kinetics, eq 8, for $[\mathbf{1}]_0 = 0.184$ mol L^{-1} at 100 °C in CD$_3$CN.
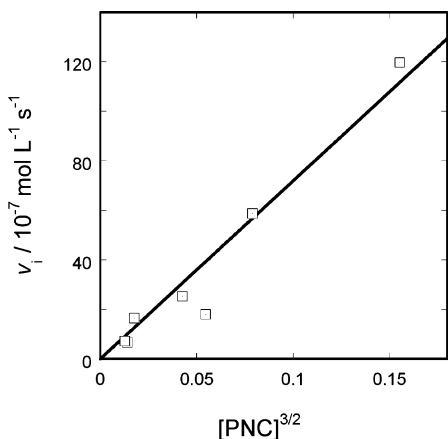

Figure 2. Plot of the initial rate against the 3/2-power of the initial concentration of **1** at 100 °C in CD$_3$CN.

polynomial function of time: $[\mathbf{1}]_t = [\mathbf{1}]_0 - m_1 t - m_2 t_2 - ... - m_6 t$,[6] in which m_1 is the initial rate, v_i. Figure 2 is a plot of v_i versus $[\mathbf{1}]_0^{3/2}$. Least-squares fitting gave $^{3/2}k = (7.2 \pm 0.5) \times 10^{-5}$ L$^{1/2}$ mol$^{-1/2}$ s^{-1}. Thus both methods of data analysis agree.

Further experiments were done, one pair of which consisted of the addition of [^{n}Bu$_4$N][CN] at the start. Addition of 1 equiv halted the reaction, whereas 0.1 equiv caused a considerable slowing. This effect is consistent with the chain-breaking effect of cyanide ions in eq 4, although it is inconsistent with CN$^-$ as a reagent that promotes isomerization, as implied by eq 3. We therefore eliminated reaction 3, which in any event seems less plausible as a propagation step than eq 2 owing to steric crowding in the transition state. Thus, $^{3/2}k$ can be identified as

$$k_2 \times \sqrt{k_1/k_4}$$

In additional experiments in which PBr$^+$, **3**, was added at the outset, isomerization went much more rapidly; reactions that otherwise took >80 h reached completion within 2 h. Moreover, the kinetic pattern was entirely different. The data from each experiment fit precisely to first-order kinetics, $v = {}^1k[\mathbf{1}]$, with the NMR data showing that the concentration of **3** remained constant at the added value. In a series of such experiments, values of ^1k were determined over the range $0.05 < [\mathbf{3}] < 0.25$ mol L^{-1}. A plot of log ^1k against log [**3**] was constructed to determine the order with respect to [**3**] (Figure 3). The least-squares line through the rather scattered points has a slope of 1.25 ± 0.26. (The scatter may be due to the relatively high temperature sensitivity of the reaction; from one experiment each at 35 and 40 °C, E_a is ca. 80 kJ mol^{-1}.)
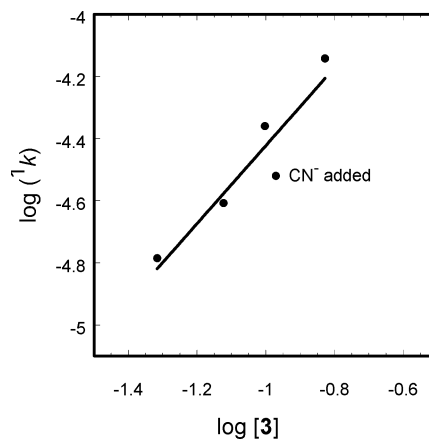

Figure 3. Kinetic data in experiments initiated by **3**, showing log ^1k versus log [**3**] at 25 °C in CD$_3$CN.

Therefore, the order was approximated with respect to [**3**] as unity, giving the rate law:

$$-\frac{d[\mathbf{1}]}{dt} = k_{Br}[\mathbf{3}][\mathbf{1}] \tag{9}$$

The fitting procedure described afforded the rate constant, $k_{Br} = (3.75 \pm 0.8) \times 10^{-4}$ L mol^{-1} s^{-1}.

Because Lewis acids, such as AlCl$_3$, also promote this isomerization,[6] **3** may be doing so via the cyclic transition state **6**. Efforts to isolate sterically stabilized analogues of **4** and theoretical studies aimed at a further understanding of energy changes involved in the isomerization of **1** in the presence and absence of **3** are underway.
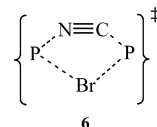
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