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A Reexamination of the Ozone−Triphenyl Phosphite System. The Origin of Triphenyl Phosphate at Low Temperatures

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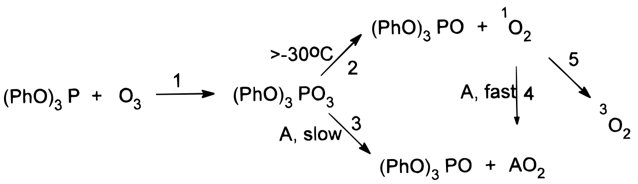
The reaction of ozone with triphenyl phosphite (P) at −78 °C affords a labile 1:1 complex (PO3) together with small amounts of triphenyl phosphate (PO) (Q. E. Thompson, *J. Am. Chem. Soc.* **1961**, *83,* 845). In this work we found that the amount of PO present initially after complete ozonation of P in toluene was 12 ± 2% at −78 °C and 11 ± 2% at −95 °C. Partial ozonation of solutions of P in toluene at −78 °C gave mixtures of P, PO, and PO3 whose composition changed with time as a result of the reaction of P with PO3 to give additional PO. Between −25 and −60 °C, the rate constant of the latter reaction is given by the expression $\log k\ (\mathrm{M^{-1}\ s^{-1}}) = (8.64 \pm 0.04) - (11.44 \pm 0.74)\ \mathrm{kcal}/RT$. This reaction at −78 °C is too slow to account for the PO formed during the ozonation, which is proposed to arise instead by competitive reactions of an intermediate. The solubility of PO in toluene at −78 °C was measured as 0.06 M, and that of PO3 about 6 times greater.

Introduction

In 1961 Thompson reported the observation of labile intermediates in the low-temperature ozonation of triphenyl phosphite, which had oxidizing powers and decomposed above −30 °C with evolution of oxygen and formation of triphenyl phosphate.[1] This system subsequently attracted attention as a source of singlet molecular oxygen[2−5] and because of an unusual "singlet oxygenoid" reaction involving bimolecular insertion of two oxygen atoms into organic molecules (Scheme 1).[6−8] The system is interesting from a synthetic standpoint because the slow, direct reaction with oxidizable substrates (A = sulfides, phosphines, phosphites, reactive olefins) via reaction 3 potentially can give a higher yield of oxidized product (AO_2) than the much faster reaction of singlet oxygen (reaction 4) because of losses by the competing fast decay of singlet to triplet molecular oxygen (reaction 5). Since the rate of the bimolecular reaction 3 increases with reactant concentrations, the limiting solubility of PO3 at low temperature was also of interest. Finally triphenyl phosphite itself is an oxidizable substrate and can reduce its ozonide, so the measurement of the rate constant of that reaction was desired, with the objective of optimizing the overall system for synthetic applications.

Scheme 1



Experimental Section

Triphenyl phosphite was vacuum distilled from Na and divided into screw-cap vials of 2-mL capacity, which were discarded after 1−2 openings to avoid accumulation of hydrolyzed products. The ozonide was prepared by passing oxygen from a cylinder through a commercial Welsbach ozonizer and bubbling the effluent into solutions of the phosphite at −78 °C (acetone/dry ice for all preparations unless otherwise stated) or −95 °C (toluene/liquid N_2). For solubility studies, the excess ozone was removed with a stream of nitrogen. The ozone−oxygen stream passed into one arm of a glass T-joint with the vertical opening attached to a steel needle inserted in a 5-mm NMR tube (hood) and the second arm to a short piece of plastic tubing that could be constricted with a screw-clamp to control the rate of gas flow into the NMR tube. The concentrations of P, PO, and PO3 were determined from the initial concentration of P, and the integrated ratios of the three products by NMR in a Varian 400 MHz instrument. A total sample (solvent and solute) weight of 0.60 ± 0.02 g was maintained for the kinetic experiments, except for that shown in Figure 3 (0.56 g). Density changes of a 0.1 M solution of P in toluene were measured by filling a 5-mm NMR tube with the solution and noting the change in length of the liquid column at a series of temperatures between 25 and −78 °C. Correction factors of 1.04, 1.06, and 1.08 were determined for −25, −40, and −60 °C, respectively, and applied to derive corrected low-temperature concentrations. Temperature calibration of the NMR cavity was carried out in the usual way with methanol, which showed a temperature of −42 °C at an instrument setting of −40 °C. An error of ±2 °C was assumed in our measurements. Satisfactory, narrow resonances were acquired without decoupling or lock. Shimming was achieved by optimizing the intensity of the FID. Integration of the ^{31}P NMR spectra of

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(1) Thompson, Q. E. *J. Am. Chem. Soc.* **1961**, *83*, 845−851.

(2) Review: Mendenhall, G. D. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2, pp 203−231.

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solutions with known amounts of P and PO indicated an error of about ±2%.

We used the same device with a T-joint to produce a high concentration of ozone in about 0.6 mL of $CFCl_3$ in a tared 5-mm NMR tube that was immersed for brief periods in liquid nitrogen. The inlet tube was then removed, and the contents of the NMR tube frozen completely in liquid nitrogen. A small amount of $CFCl_3$ containing 8.0 μL (31 μmol) of triphenyl phosphite was added, and the tube was capped loosely and warmed in a dry ice/acetone bath. The contents were then mixed with the aid of a steel needle previously cooled briefly in liquid nitrogen. After mixing, an excess of ozone was indicated by a light blue color. Subsequent integration of the ^{31}P signals at −60 °C revealed a composition of 12.73% PO and 87.27% PO3. The contents of the tube were then weighed by difference (1.13 g), from which we estimated a total phosphorus concentration of 32 mM.

In a second experiment carried out similarly, triphenyl phosphite (8.0 μL) in 1.29 g of solution in $CFCl_3$ was ozonized at −78 °C in an NMR tube, and 2.0 min elapsed until the appearance of a blue color in the solution. Subsequent analysis by NMR at −60 °C showed the presence of 11.75% PO and 88.25% PO3.

Solubility of P and PO3 in Toluene at −78 °C. A solution of triphenyl phosphate (0.49 g) in 6.28 g of toluene in a serum-capped test tube was placed in a freezer at −78 °C. Portions of the supernatant were removed at intervals for GC analysis (HP Model 5890, J&W Scientific DB-WAX/0.25 μm poly(ethylene glycol) film, 0.32 mm × 30 m capillary column, injection 325 °C, oven 300 °C, FID detector 325 °C). The weight fractions of PO initially and after 19 and 23 days were 0.072, 0.022 ± 0.005, and 0.022 ± 0.005, respectively. A second trial with 0.67 g of PO and 1.98 g of toluene (wt. fraction PO 0.253) after 1 and 4 days at −78 °C similarly gave values of 0.045 ± 0.012 and 0.027 ± 0.004, respectively. Additional values could not be obtained because the liquid phase became indistinct.

Solid triphenyl phosphite ozonide was prepared by dilution of a solution in $CFCl_3$ with petroleum ether. The ozonide solution was prepared from 2.04 g of P and a total of 30 mL of $CFCl_3$ at −78 °C, by addition of a solution of P in $CFCl_3$ to magnetically stirred ozonized solvent at −78 °C in a 50 mL, three-necked flask equipped with an addition funnel, a glass gas-inlet tube, and a U-shaped drying tube. The ozonized solution, purged of excess ozone with N_2, was then added under positive N_2 pressure to 200 mL of low-boiling petroleum ether at −78 °C. After standing at −78 °C for 1 day (chest freezer), the supernatant was quickly poured off while playing a stream of N_2 into the flask. The flask was allowed to stand at −78 °C with a paper towel inserted into the flask to blot up residual solvent. Exposure to air in these operations was minimized, and containers were closed with serum caps except when transferring materials; serum caps at −78 °C were carefully warmed by hand until they could be removed.

A solution of PO3 was prepared as described above by inverse addition from P (2.63 g) and a total of 6.0 mL of toluene. The milky liquid was allowed to stand overnight at −78 °C. The towel was removed from the flask containing solid PO3, and the solution of PO3 in toluene was poured into the flask. The slurry was agitated, stoppered with a serum cap, and allowed to stand at −78 °C with intermittent agitation. After 10 days, an attempt to remove an aliquot of supernatant with a precooled pipet revealed a milky suspension.

A glass-fritted funnel and receiver were cooled to −78 °C in the chest-freezer, and a portion of the slurry containing PO3 was added to the funnel. After standing overnight at −78 °C, about half of the slurry had passed through the filter. The clear filtrate was removed from the freezer, placed in a sample vial, and allowed to warm to room temperature. Analysis by GC revealed a weight fraction of PO = 0.15 ± 0.02.

A control experiment to determine the reactivity of triphenyl phosphate toward ozone was conducted by ozonizing 0.10 M PO in toluene at −78 °C for 40 min, followed by flushing with N_2 until colorless. The ^{31}P NMR spectrum at 25 °C showed neither broadening of the signal from PO nor any additional signals at high vertical expansion. Analysis of the solution by GC showed no change within error in the ratio of areas of PO and toluene.

Results

Reaction of P with PO3. The reduction of PO3 by P to give PO is assumed to proceed by the following steps:

$$\mathrm{P} + \mathrm{PO3} \rightarrow \mathrm{PO} + \mathrm{PO2} \qquad \text{rate constant } k_2$$

$$\mathrm{P} + \mathrm{PO2} \rightarrow 2\mathrm{PO} \qquad k_3 \gg k_2$$

The species PO2 may be similar to the initial reactive product of singlet molecular oxygen and phosphites, which reacts rapidly with phosphite to give phosphate as the isolated product.[9] A second, kinetically equivalent possibility is that the rate-limiting step is insertion of P into PO3 to give a labile five-membered heterocycle. Since we did not observe any new ^{31}P signals that could be ascribed to these intermediates, we assume that the intermediate in either case is reduced rapidly by a second molecule of P to PO even at low temperatures and is present only in low concentrations. Applying the steady-state assumption to PO2, we obtain the relations

$$\mathrm{dPO}/\mathrm{d}t = 3k_2[\mathrm{P}][\mathrm{PO3}] \qquad (1)$$

$$-\mathrm{dPO3}/\mathrm{d}t = k_2[\mathrm{P}][\mathrm{PO3}] \qquad (2)$$

$$-\mathrm{dP}/\mathrm{d}t = 2k_2[\mathrm{P}][\mathrm{PO3}] \qquad (3)$$

From modification of the usual second-order equation, we obtain also

$$\ln([\mathrm{PO3}]_o/[\mathrm{P}]_o) + \ln([\mathrm{P}]_t/[\mathrm{PO3}]_t) = ([\mathrm{P}]_o - 2[\mathrm{PO3}]_o)k_2 t \qquad (4)$$

At the lowest temperature studied, −60 °C, the reaction was too slow to follow to completion and initial rates of decay were measured (Figure 1; Table 1).

The slopes of the data in Figure 1 were analyzed according to the approximation

$$\Delta[\mathrm{PO3}]/\Delta t = -k_2[\mathrm{P}]_m[\mathrm{PO3}]_m \qquad (5)$$

where the subscript refers to the mean value during the experiment. Similar expressions of course defined the changes in P and in PO. The slopes of the plots for P, PO, and PO3 were experimentally in the ratio −2:3:−1, and the three derived values of k_2 were within a few percent of each other. The average of the three values generated one point for the Arrhenius calculation.

At −40 and −25 °C, the reaction of P with PO3 could be followed conveniently to completion, and the data were fitted to eq 4 over ranges of concentrations where the successive NMR integrations of the smallest component did not fluctuate wildly. Plots of data obtained at −25 °C are shown in Figure 2 (see Table 1). The reaction at −25 °C was fast, so that reactant concentrations decreased rapidly to levels whose NMR signals could not measured accurately. At the encouragement of a referee, we repeated the reaction at −25 °C with a more frequent rate of data acquisition and with manual instead of

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(9) (a) Bolduc, P. R.; Goe, G. L. *J. Org. Chem.* **1974**, *39*, 3178−3179. (b) Tsuji, S.; Kondo, M.; Ishiquro, K.; Sawak, Y. *J. Org. Chem.* **1993**, *58*, 5055−5059.

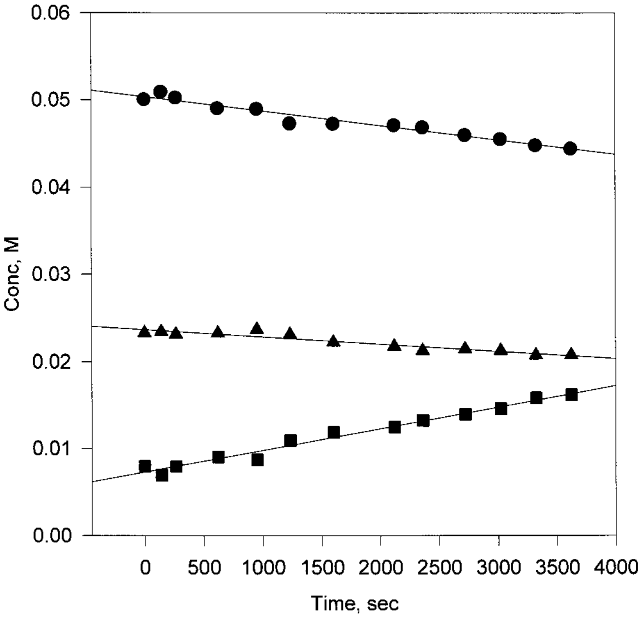

Figure 1. Initial changes of (top to bottom) PO3, P, and PO in toluene at −60 °C (Table 1, entry 7).

Table 1. Reaction of Triphenyl Phosphite with Triphenyl Phosphite Ozonide

	$[P]_o$, mM	$[PO_3]_o$, mM	T, °C	k_2, M^{-1} s^{-1}	r^2
1	49.2	7.27	−25	0.0400	0.919
2	14.2	50.5		0.0360	0.988
3	61.4	10.8		0.0329	0.914
4	38.5	19.2		0.0405	0.96
5	21.4	28.9	−40	0.0071	0.978
6	65.2	17.6		0.00879	0.904
7	50.1	23.3	−60	0.000796[a]	0.90−0.98
8	119	27.7		0.00086[a]	0.97−0.99

[a] Average value derived from initial decays of P, PO, and PO3.

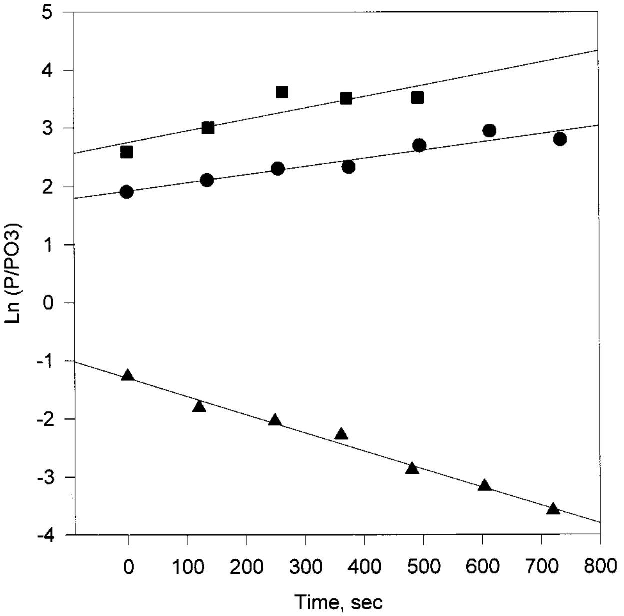

Figure 2. Second-order plots of the reaction of PO3 with P at −25 °C. The curves from top to bottom represent entries 1, 3, and 2, respectively, in Table 1.

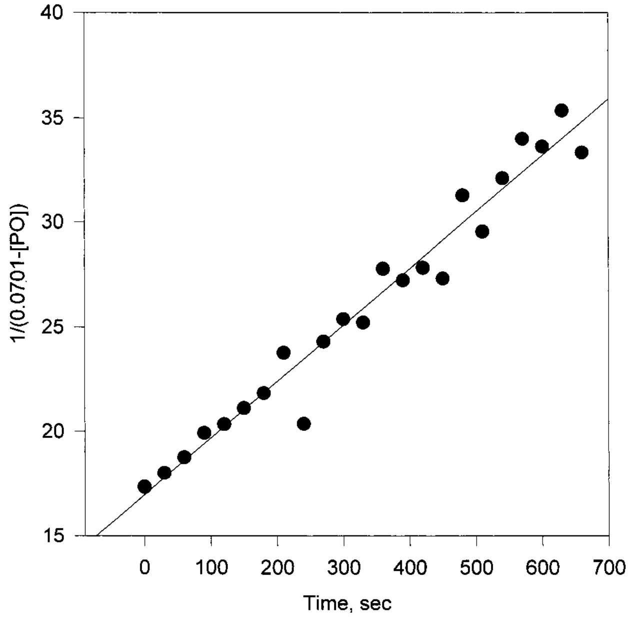

Figure 3. Second-order plot of the reaction of P with PO3 according to eq 7, corresponding to entry 4 in Table 1.

automatic phasing of the signals before integration. The first experiment led to a rate constant (0.034 M^{-1} s^{-1}) in agreement with the others, but the plot was badly scattered ($r^2 = 0.68$). A second experiment fortuitously showed initial concentrations of [P] = 2[PO3] within error, and eq 4 no longer applied. From this unique condition we derive a different set of equations:

$$1/[P] - 1/[P_o] = k_2 t \tag{6}$$

$$3/([P_{tot}] - [PO]) = 2k_2 t + \text{constant} \tag{7}$$

Application of eq 6 to the data led to $k_2 = 0.029$ M^{-1} s^{-1}, but the plot was scattered ($r^2 = 0.87$). The use of eq 7 was more satisfactory, since the term P_{tot}, the total concentration of P compounds, is constant, and the concentration of PO increased with time, so that the precision of its NMR integral did not deteriorate as the reaction proceeded. Unfortunately the data acquisition was accidentally stopped when the reaction was about 60% complete, but the plot (Figure 3) was satisfactory ($r^2 = 0.96$) and gave $k_2 = 0.0405$ M^{-1} s^{-1}.

Regression analysis of the Arrhenius plot of the reliable data for this reaction (Figure 4) led to activation parameters of $E_a = 11.44 \pm 0.74$ kcal/mol and log A (M^{-1} s^{-1}) = 8.64 ± 0.04. The value of the A factor lies within a generalized value of $10^{8.5\pm0.5}$ M^{-1} s^{-1} proposed for the somewhat analogous second-order reaction of radicals with molecules.[10]

Solubilities. Ozonation of concentrated solutions of triphenyl phosphite in a number of solvents gives opaque solutions due to the presence of solid material, which we suspected was PO. The solubility of PO in toluene was measured by sampling the supernatant above a mixture of the two, which revealed that equilibration at −78 °C required several days. When solid PO3 was slurried in a concentrated solution of P ozonized in toluene (containing PO3 and PO) at −78 °C, the liquid phase after filtration at that temperature and warming contained PO derived both from the initial synthesis of PO3 and from its thermal decomposition. The difference between the ob-

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[10] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, NY, 1976; p 156.

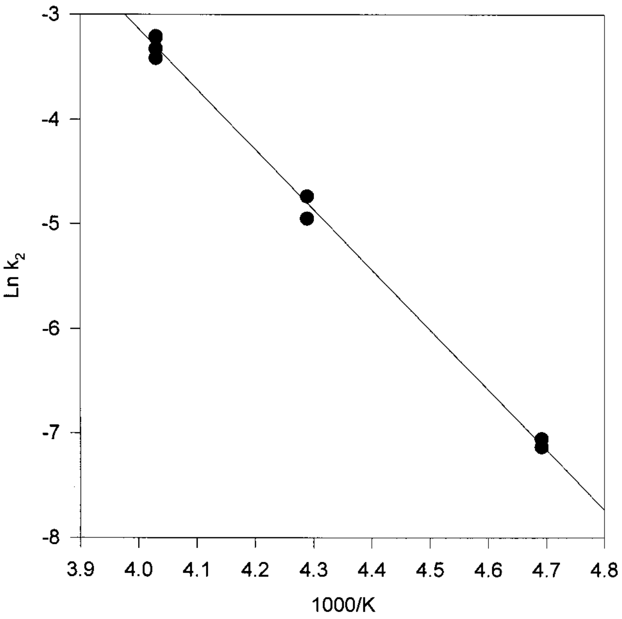
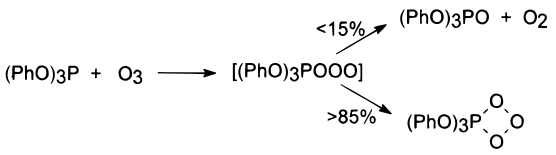


Figure 4. Arrhenius plot of data from Table 1.

served PO in that solution after warming and the solubility limit of PO was calculated as the solubility of PO3, which was 5.8-fold greater.

Discussion

The small amounts of PO formed during the initial ozonation can be explained most readily by stepwise formation of PO3 through a noncyclic adduct of P and ozone that partitions between pathways of scission and cyclization:



It is puzzling that the ratio of PO to PO3 is experimentally almost independent of temperature, because the cyclization of an open-chain intermediate should entail both ring strain energy and loss of O−O rotational modes in the transition state. Perhaps intersystem crossing of a singlet to a triplet biradical, $(PhO)_3POOO$, determines the extent of the minor pathway to PO. Alternatively, formation of PO from P and ozone may occur through an independent, “ballistic” transition state as suggested recently by Carpenter.[11]

Thompson reported the reduction of PO3 by P and noted that it proceeded rapidly only above about −40 °C.[1] Koch, however, reported that the same reaction took place at −90 °C and proposed that it gave PO2 that regenerated PO3 by disproportionation at higher temperatures.[7] In our hands, between −25 and −78 °C the ^{31}P NMR spectrum of samples of P incompletely ozonized at −78 °C revealed only narrow signals of P, PO, and PO3, and we have no evidence for these additional reactions or species. Although NMR is generally not the preferred method for kinetic measurements, the simplicity and intensity of the spectrum made it attractive for automated data collection and integration.

The kinetic data in Figure 4 give an extrapolated value of $k_2 = 7.1 \times 10^{-5}$ M^{-1} s^{-1} at −78 °C. In addition, two experiments were carried out in $CFCl_3$ in which the times required to react solutions of P with ozone to completion were recorded. The side reaction between P and PO3 in these experiments competed with the conversion of P to PO3 and was at a maximum when the two were present in equal concentrations. On this basis we can estimate conservatively that an upper limit of 2×10^{-7} and 8×10^{-6} M PO would have been formed during the approximate reaction times of 20 s and 2.0 min, respectively, in the experiments carried out by ozonizing P in $CFCl_3$ at low temperatures by inverse and normal ozonation. Since we observed concentrations of about 4×10^{-3} M phosphate in each case, the reaction between P and PO3 cannot account for more than 0.2% of the observed PO.

A reactive, open-chain adduct of P and ozone might undergo reduction by a second P in competition with cyclization to PO3. This explanation seems unlikely because observed fractions of PO were identical within error (0.12 ± 0.01) when ozone was added to P or P was added to a solution containing excess ozone.

The solubility experiments were carried out in containers exposed to the atmosphere. The explosive character of pure PO3 made it difficult to handle the compounds at low temperature with complete exclusion of moisture. We would argue that the low temperatures and low solubility of water in toluene and in $CFCl_3$ would tend to minimize the potential effects of residual water. We showed earlier that the rate of decomposition of PO3 in toluene did not change when the solution was deliberately exposed to moist air.[12]

Thompson inferred from the position of the ^{31}P NMR signal that the phosphorus atom in triphenyl phosphite ozonide was pentacovalent,[1] and Bartlett and Chu determined with freezing-point methods that the ozonide was monomeric.[13] The greater solubility of the pentacovalent PO3 over PO in a nonpolar solvent is consistent with the presence of the strong $P^{+}{-}O^{-}$ dipole in the phosphate.

The saturated limit of PO in toluene at −78 °C is 0.06 ± 0.01 M, so that ozonation of triphenyl phosphite in any concentration in excess of 0.4 M in that solvent will tend to precipitate PO. Our experimental solubility of PO3 corresponds to a saturated concentration of 0.37 ± 0.05 M at −78 °C. Higher concentrations might be achieved if the solid−solution equilibration in toluene is slow, as it is for PO.

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