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The Reaction between Triphenylmethyl Isoselenocyanate and Tervalent Phosphorus Compounds. A Kinetic Study

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Triphenylmethyl isoselenocyanate has been found to be deselenated rapidly and cleanly by various tervalent phosphorus compounds. Triphenylmethyl isonitrile and the corresponding selenophosphorus compounds are formed in close to quantitative yields.

A kinetic study has been performed with cyclohexane and acetonitrile as solvents and the reactions were found to follow second-order kinetics. The rates of deselenization are enhanced in the solvent of highest polarity, but the rate enhancement is very dependent upon the nature of the applied tervalent phosphorus compound.

From observed reactivity sequences in the two solvents, solvent influence on reaction rates, and activation parameters in cyclohexane, various possible reaction mechanisms are discussed.

Organic and inorganic selenium compounds appear to be considerably less studied than the corresponding sulfur compounds.[1–4] Apart from the obvious difference in biological importance of the two classes of compounds, studies of the chemistry of the selenium compounds appear to have been seriously hindered due to their generally lower stability, their toxicity and, in the case of most organic selenium compounds, their most unpleasant odour.[2]

When focusing on the reactivity of selenium compounds and the various allotropic forms of selenium, no accurate kinetic studies appear to have been performed apart from studies where the selenocyanate ion is involved. In many respects, the chemistry of the selenium compounds appears to be far more difficult to examine than the chemistry of the corresponding sulfur compounds. Due to the lower electronegativity and the greater polarizability of selenium compared with sulfur, selenium compounds are generally better electrophiles than the corresponding sulfur compounds. Furthermore, the greater polarizability of the selenium atom causes selenium compounds having a lone pair or a negative charge to be generally better nucleophiles than the corresponding sulfur compounds toward soft substrates.[5] The selenocyanate ion is thus able to react as a biphile towards certain substrates, in contrast to what has been found for the thiocyanate ion.[6] Due to the large difference in size between selenium and first-row elements like carbon and oxygen, the bonds between

these elements are considerably weaker than the corresponding S – O and S – C bonds.[7,8] When linear three-center systems, however, are possible, the selenium compounds are considerably more stable than the corresponding sulfur compounds.[9]

The combination of weaker bonds to most elements and the ability of the selenium atom in the various compounds to act as both acceptor and donor as required, causes the majority of the reactions where selenium is involved to be extremely rapid and not readily accessible to kinetic studies.[2]

With regard to the various modifications of elemental selenium, several reactions indicate the anticipated close similarity with the corresponding reactions of elemental sulfur.[10] Very polarizable nucleophiles like tervalent phosphorus compounds react most readily with both elements.[11,12] The reactions of sulfur and selenium with organic isonitriles are usually very slow reactions, but provide important routes to organic isothiocyanates and isoselenocyanates which are not readily obtainable by other means.[13–20] Interestingly, triethylamine is able to catalyze reactions of both elemental sulfur [21] and selenium,[22,23] probably by polarization of the S – S and the Se – Se bonds. This extreme dependence of reaction rates upon polarizing agents, present as for example impurities in solvents and reactants, combined with the limited solubility of these two elements in most solvents, make kinetic studies of this type of reaction most difficult.[11,24]

For kinetic studies toward selenium one thus has to find compounds which readily, but not too rapidly, expel the selenium atom, make stable selenated products, and most important, make deselenated products of very low selenium basicity to ensure complete reaction.

Nicpon and Meek[25] found that triaryl phosphines deselenated potassium selenocyanate rapidly in acetonitrile, a reaction which has proved to be a simple route to selenophosphorus compounds [25,26] (Eqn. 1).

$$R_3P + SeCN^- \xrightarrow{MeCN} R_3P{=}Se + CN^- \qquad (1)$$

This reaction, however, is not suitable for detailed kinetic studies as the rates of the reactions are highly dependent upon the cation, the solvent, and the purity of the solvent.[27] In a very pure aprotic solvent and by applying an onium cyanide, the reverse of the reaction in eqn. 1 takes place.[28]

Hofmann [29] noted more than a century ago that at elevated temperatures trialkyl phosphines desulfurized isothiocyanates while triphenylphosphine was inactive. We have found that several tervalent phosphorus compounds react readily with triphenyl isoselenocyanate at room temperature in the usual organic solvents in clean and non-malodorous reactions, forming the corresponding selenophosphorus compounds and triphenylmethyl isonitrile in close to quantitative yield, eqn. 2,

$$Ph_3CNCSe + P{<} \longrightarrow Ph_3CNC + Se{=}P{<} \qquad (2)$$

taking advantage of the low nucleophilicity of the isonitrile toward selenium as mentioned above.

As the rates of the reactions were in most cases found to be within an acceptable range for the determination of rate constants, a kinetic study of the reaction depicted in eqn. 2 using a variety of tervalent phosphorus compounds was performed. The reactions were most conveniently followed by UV spectroscopy at appropriate wavelength in the 250 – 270 nm range measuring the decrease in optical density.

Both in acetonitrile and in cyclohexane, the reactions followed second-order kinetics and it was in most cases possible to follow the reactions up to 4 or 5 half-lives. The only exception was the reaction of ethyl diphenylphosphinite in acetonitrile where no simple kinetic laws were found to be obeyed. As this reaction mixture rapidly started to yield malodorous by-products, it was not further examined.

Triphenylmethyl isoselenocyanate decomposes slowly in acetonitrile.[30] For this reason and as the reactions usually were too fast for accurate rate determinations, it was not possible to obtain thermodynamic parameters for the reactions in this solvent. The rate of reaction of tris(morpholino)phosphine was too rapid even in cyclohexane to allow the determination of sufficiently accurate rate constants for the calculation of thermodynamic parameters.

Due to extensive ring-opening in the reaction between the cyclic phosphite, 2-methoxy-1,3-dioxaphospholane, and the isoselenocyanate, the UV method was not applicable in this reaction. The rate of this reaction was therefore determined from the disappearance of the peak at 2100 cm^{-1} in IR. Due to the broadness of this peak, the rate constants for this reaction were considerably less accurate than the rates determined by the UV method. As the rate of the reaction in acetonitrile between the cyclic phosphite and the isoselenocyanate was rather low, the rate of reaction could not be determined due to the instability of triphenyl isoselenocyanate in this solvent at room temperature.

The reaction between ionic cyanide and triphenyl isoselenocyanate in acetonitrile appeared extremely rapid and the rate could thus not be determined. Solutions of triphenyl arsine and triphenylmethyl isoselenocyanate were found to be completely stable in cyclohexane and no reaction could be detected. The rate of decomposition of the isoselenocyanate in acetonitrile was found to be unaffected by the presence of triphenyl arsine. Triphenylmethyl isonitrile is probably a better selenium base in cyclohexane than is triphenyl arsine. The very unstable nature of triphenyl arsine selenide has been noted.[31]

The observed rate constants with calculated activation parameters are listed in Tables 1 and 2.

Tris(morpholino)phosphine was chosen as an example of a tris(dialkylamino)phosphine due to its facile synthesis and, as it is a crystalline compound with high melting point, its purification was rather simple. Furthermore, its stability and crystalline state facilitated the kinetic experiments.

Generally, tris(dialkylamino)phosphines exhibit a very small tendency to act as electrophiles forming pentacovalent phosphoranes. When reacting with biacetyl,[33] ketenes,[34] dialkyl peroxides,[35] and related compounds, with which phosphites and most phosphines readily form pentacovalent species, the aminophosphines react *via* an ionic mechanism. Only with α,α-diketones with strongly electronegative substituents are the aminophosphines capable of forming isolable phosphoranes.[33]

Table 1. Rate constants for the reaction in cyclohexane between triphenylmethyl isoselenocyanate (Ph_3CNCSe) and various tervalent phosphorus compounds (R_3P), together with calculated activation parameters.

R_3P	$k_2 \times 10^2$ M^{-1} sec^{-1} 25°C	$k_2 \times 10^2$ M^{-1} sec^{-1} 40.0°C	ΔH^*kcal M^{-1} ± 0.4	ΔS^* e.u. ± 4
$(Morph)_3P$	810			
$(n\text{-but})_3P$	190	430	9.5	−21
Ph_2POEth	113	263	9.4	−22
Ph_2POMe	99	230	9.7	−21
Ph_3P	19.3	30.8(35.0°C)[a]	8.6	−28
$(MeO)_3P$	2.4	6.0	10.7	−25
$PhP(OMe)_2$	1.6	3.9	10.6	−27
$\begin{matrix}CH_2-O\\CH_2-O\end{matrix}\!\!>P-OMe$	0.042	0.073(35°C)[b]	9.8 ± 0.8	-40 ± 8

[a] k_2 at 45°C = 0.51 $M^{-1}sec^{-1}$. [b] k_2 at 20°C = 3.2×10^{-4} $M^{-1}sec^{-1}$.

Table 2. Rate constants in acetonitrile, k_2 (MeCN) and cyclohexane, k_2 (chex), with calculated rate ratios at 25.0°C.

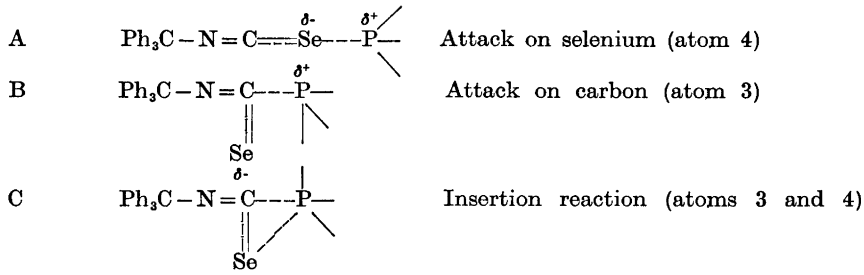
R_3P	$k_2(MeCN) \times 10^2 M^{-1}sec^{-1}$	$k_2(chex) \times 10^2 M^{-1}sec^{-1}$	$\frac{k_2(MeCN)}{k_2(chex)}$
Ph_3P	450	19.3	23
Ph_2POMe	410	99	4.1
$PhP(OMe)_2$	475	1.6	300
$(MeO)_3P$	45	2.4	19

Toward certain substrates, which are known to react *via* transition states with large charge separation, the aminophosphines are by far the most reactive tervalent phosphorus compounds,[36] probably as a result of their being able to act as α-nucleophiles.[37] The finding in this work that tris(morpholino)phosphine is the most reactive of the tervalent phosphorus compounds studied, clearly suggests that the tervalent phosphorus compounds act as nucleophiles in the present reaction. This conclusion is supported by the fact that triphenylphosphine, being a far better nucleophile than is trimethylphosphite, is more reactive than the latter compound and that the acyclic phosphite is considerably more reactive than is the cyclic homolog [38] (Table 1).

Fundamentally, compounds like triphenylmethyl isoselenocyanate and related compounds may react in a number of ways, and, neglecting the very improbable S_NAr reactions when tervalent phosphorus compounds are the nucleophiles, these compounds could possibly provide four different electrophilic centres and thus react in four different ways (1, 2, 3 and 4).

$$\underset{1}{Ph_3C}-\underset{2}{N}=\underset{3}{C}=\underset{4}{Se}$$

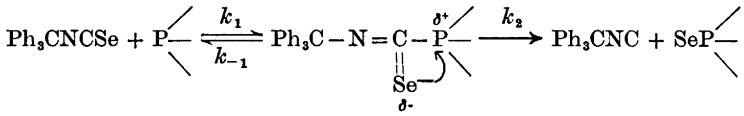
On chemical grounds, paths 1 and 2 can be readily dismissed although Leffler and co-workers [39] have shown that triphenyl phosphine attacks the α-nitrogen atom in triphenylmethyl azide. One is thus left with the following mechanisms where the transition states are depicted in the following scheme:



The simple deselenating mechanism depicted in A appears to be the most likely one as this transition state will have some charge separation and a rate increase from cyclohexane to acetonitrile is to be anticipated (Table 2). The rate increases observed, however, are considerably less than those observed for reactions between triaryl phosphines and elemental sulfur,[11] but this may be due to the greater polarizability of the selenium atom.

When neglecting the rate of reaction of the cyclic phosphite, the rate differences between the various tervalent phosphorus compounds is very small. This is further evidence for mechanism A as it is well known that increasing polarizability of the electrophilic center levels the reactivity of tervalent phosphorus compounds.[40]

The mechanism as depicted by B, being rather similar to the one for the Perkow reaction, is in principle far more complicated than suggested. A better picture of this mechanism may be the following one; eqn. 3:[41,42]



(3)

Thus, all rate constants, k_1, k_{-1}, and k_2 have in fact to be considered and it is impossible to predict the effect upon reaction rates of solvent and the groups linked to the phosphorus atom. From Borowitz' extensive studies on the Perkow reaction [41,42] and from similar studies,[43] the effect of solvent is very small, suggesting a very small charge separation in the transition state. The mere fact that the aminophosphine is by far the more reactive one does not accord with this mechanism. Although nitrogen bases are known to attack exclusively the carbon atom in organic isoselenocyanates forming selenoureas and selenocarbamates,[23] it is hard to imagine how very polarizable nucleophiles such as tervalent phosphorus compounds can bypass a very soft electrophilic atom like the selenium atom and attack a hard sterically hindered carbon atom alpha to it. The mechanism as depicted by B thus appears to be rather unlikely.

However, a simple mechanism as depicted by A does not provide a satisfactory explanation for the exceptional reactivity of the alkyl diphenyl-

phosphinites in cyclohexane and the very small observed rate dependence upon solvent (Tables 1 and 2). Numerous reactions between tervalent phosphorus compounds and various substrates are known where no solvent dependence is observed. The most notable examples are the reaction of episulfides,[44] β-peroxylactones,[45] peroxydicarbonates,[46] benzils,[47] various aromatic nitro compounds,[48] *etc.* with tervalent phosphorus compounds. As there appears to be limited evidence for radical mechanisms in these reactions, the only possible explanation seems to be the formation of non-charged pentacovalent species in the rate determining step. This may indicate that phosphinites in a non-polar solvent as cyclohexane react by mechanism C. There is considerable evidence for the more facile formation of phosphoranes from tervalent phosphorus compounds containing one and only one substituent of exceptional apicophilicity as for the case of phosphinites.[34,37]

In a more polar solvent like acetonitrile, the pentacovalent phosphorane mechanism, mechanism C, is probably unable to compete with the ionic mechanism, mechanism A.[49]

The thermodynamic parameters listed in Table 1 appear to be of little use in discussing the various possible mechanism. Only very accurate kinetic data, beyond the scope of the present study, may provide additional information. The rather similar values for ΔH^* and ΔS^* for the various reactions in cyclohexane accord with the small dependence of reaction rates upon substituents bonded to the reacting phosphorus atom. The fact that the cyclic phosphite reacts with an activation enthalpy which is not significantly larger than that of the acyclic phosphite is in accord with results obtained on alkylation reactions of acyclic and cyclic phosphites.[37] Hudson and co-workers [38] have recently discussed the various factors for the significantly more negative entropies of activation for reactions of cyclic phosphites than of acyclic phosphites.

The results obtained in this study do not shed much light upon the electrophilic nature of the selenium atom in selenium compounds. The very polarizable nature of this atom makes transition states of high charge separation less necessary than for the corresponding sulfur compounds and thus levels the reactivity of the tervalent phosphorus compounds.

The exceptional reactivity of the phosphinites in cyclohexane suggests that a special mechanism is available for these compounds in this solvent. Provided the pentacovalent species are sufficiently stable to undergo pseudo rotation [50] prior to the formation of the isonitrile and the selenophosphorus compounds, such a mechanism may be proved possible by stereochemical studies as has been shown by Bodkin and Simpson [50] for alkylation reaction of cyclic six-membered phosphites. The presence of penta-covalent species in the reaction between tervalent amine oxides and tervalent phosphorus compounds has not been confirmed in stereochemical studies.[51]

EXPERIMENTAL

Acetonitrile and cyclohexane were purified as previously reported.[52] Mid-fractions from the final distillations, carefully flushed with nitrogen, were used in crystallization and for the kinetic studies. Benzene, toluene, diethyl ether, and various petroleum ethers were dried with sodium prior to use.

Methyl diphenylphosphinite, b.p. 102°C (0.75 mm), ethyldiphenylphosphinite, b.p. 157°C (10 mm), and dimethylphenylphosphonite, b.p. 86 – 87°C (10 mm) were made, according to standard procedures, from the corresponding chloro compounds and distilled under nitrogen until their UV spectra in cyclohexane were constant. Trimethyl phosphite, b.p. 110°C (760 mm), and 2-methyl-1,3-dioxaphospholane, $(CH_2O)_2P-OMe$, b.p. 38°C (8 mm) were treated several times with sodium, a large volume petroleum ether (40 – 60°C) was added, and the solutions were stored at – 20°C for 24 h prior to filtration and final distillation. Tris(morpholino)phosphine, m.p. 156°C, was made according to Michaelis[53] or Burgada,[54] crystallized from toluene and finally from acetonitrile. Great care was exercized to exclude moisture from these compounds and their solutions. Triphenyl phosphine, triphenyl arsine, and tributyl phosphine were commercial products and purified by standard methods.

Trityl isoselenocyanate was prepared according to Pedersen [55] from trityl chloride and potassium selenocyanate in acetone. As traces of trityl carbinol could not be removed from the isoselenocyanate by crystallization, the trityl chloride and the ionic selenocyanate were carefully purified and dried prior to the synthesis. The compound was finally crystallized from low-boiling petroleum ether and cyclohexane, dried in vacuum and stored in a dark bottle in the refrigerator. M.p. 129 – 130°C, $\lambda_{max}(CCl_4) = 2100$ cm^{-1}, $\Delta\lambda_{\frac{1}{2}} = 110$ cm^{-1}, $A = 17 \times 10^4$M^{-1}cm^{-2}.

Trityl isonitrile, m.p. 136°C, was prepared from trityl chloride and tetramethylammonium dicyanoargentate.[56] Tetraphenylarsonium cyanide was made as reported.[52]

Reaction between triphenyl phosphine and trityl isoselenocyanate. To 17.4 g trityl isoselenocyanate, 0.050 mol, in 100 ml diethyl ether, was added 13.1 g triphenyl phosphine, 0.050 mol, in 25 ml diethyl ether. After stirring for a few min, a white crystalline compound started to separate. The reaction mixture was stirred for 2 h at room temperature and then set aside overnight. Yield of crystalline product, triphenyl phosphine selenide, 17.5 g; calculated 17.0 g. After one crystallization from ethanol with close to quantitative yield, the phosphine selenide was obtained pure, m.p. 188 – 189°C (187 – 188°C [25]).

The mother liquor from the reaction was evaporated to dryness and the residue, 12.5 g, was crystallized from cyclohexane yielding 8.9 g trityl isonitrile, 67 %, in the first crop. The melting point and the IR spectrum was the same as that of the isonitrile formed from trityl chloride and tetramethyl dicyanoargentate.[56] However, even after repeated purification, this sample of trityl isonitrile attained a pink colour when exposed to daylight, suggesting it to be contaminated by traces of triphenyl phosphine selenide or trityl isoleselenocyanate and preventing it being used as a UV standard.

As the synthesis of the various selenophosphorus compounds from trityl isoselenocyanate and the corresponding tervalent phosphorus compounds was rather tedious, these compounds were generally made using grey selenium as selenating agent in toluene. After the exothermic reactions were over, the reaction mixtures were refluxed until all the selenium had reacted. Methyl and ethyl diphenyl selenophosphinate were alternatively easily obtained by alcoholysis of chloro diphenyl phosphine selenide, b.p. 215°C (8 mm).

In those reactions where metallic selenium was applied as reagent and the products, the selenophosphorus compounds, had to be purified by distillation, it was necessary to use a small excess of the tervalent phosphorus compounds to obtain pure products. If selenium was used in excess, the products were slightly yellow-greenish and deposited selenium on standing, even after repeated distillations. Unreacted tervalent phosphorus compounds, on the other hand, were easily separated from the products due to the large differences in boiling points. The products were usually obtained in from 80 to 90 % yield. The selenophosphorus compounds from 2-methoxy-1,3-dioxophospholane decomposed on attempted distillation, but as the rate of the reaction between this cyclic phosphite and trityl isoselenocyanate was determined by the IR technique, the rates of reaction could be obtained in this case without the use of a pure product.

The following selenophosphorus compounds were synthesized.

Triphenylphosphine selenide. M.p. 188 – 189°C (187 – 188°C [25]).

Tri-butylphosphine selenide. B.p. 131°C (0.5 mm) [150 – 151°C (0.80 mm) [57]].

Tris(morpholino)phosphine selenide. M.p. 154 – 155°C.

(Found: C 38.96; H 6.72; N 11.29. Calc. for $C_{12}H_{24}N_3O_3PSe$: C 39.12; H 6.57; N 11.41).

O-Methyldiphenyl selenophosphinate. M.p. 88 – 89°C (89°C [58]).

(Found: C 53.34; H 4.21; Calc. for $C_{13}H_{13}POSe$: C 52.90; H 4.44).

O-Ethyl diphenyl selenophosphinate. M.p. 61 – 62°C.

(Found: C 54.68; H 4.65; P 10.09. Calc. for $C_{14}H_{15}POSe$: C 54.38; H 4.89; P 10.00).
O,O-Dimethyl phenyl selenophosphonate. B.p. 100 – 101° (0.8 mm).
(Found: C 40.04; H 4.30: Calc. for $C_8H_{11}PO_2Se$: C 38.57; H 4.45).
O,O,O-Trimethyl selenophosphate. B.p. 75 – 76°C (12 mm). The melting points are corrected.

Kinetic studies. The rates of the reactions, with the exception of the reaction between the cyclic phosphite and triphenylmethyl isoselenocyanate, were determined from the decrease of absorptions at appropriate wavelengths in the 250 – 270 nm range. The principle cause of the decrease was the disappearance of the tervalent phosphorus compounds, but the absorptions due to the other species present could not be neglected. As an example the extinction coefficients are given at 260 nm in cyclohexane for the reactants and the products for the reaction between triphenyl phosphine and triphenyl isoselenocyanate, trNCSe (in M^{-1} cm^{-1}): Ph_3P 10 720; trNCSe 2470; Ph_3PSe 3740; trNC 680.

The reactions in acetonitrile were considerably more rapid than the isomerization of trityl isonitrile to trityl cyanide in this solvent.[59] Furthermore, as the UV spectra of these two compounds were rather similar in the measured region, the effect due to the isomerization of trityl isonitrile could be neglected.

The following reaction takes place; eqn. 2:

$$\text{trNCSe} + \text{P}{\lessdot} \longrightarrow \text{trNC} + \text{SeP}{\lessdot} \qquad (2)$$

or simplified for the further calculations:

$$\text{A} + \text{B} \longrightarrow \text{C} + \text{D} \qquad (4)$$

For a second-order reaction, first order in each of the reactants, the following rate equation is obtained:

$$(a-b)^{-1} \ln[b(a-x)/a(b-x)] = k_2t \qquad (5)$$

where a and b are the concentrations of species A and B, respectively, at $t = 0$.

When ε_A, ε_B, ε_C, and ε_D are the extinction coefficients of the respective species at a given wavelength, and x is the amount of A reacted at time t, the absorption at this wavelength is given by

$$A_t = \varepsilon_A(a-x) + \varepsilon_B(b-x) + \varepsilon_C x + \varepsilon_D x \qquad (6)$$

The following general rate equation is thus readily obtained:

$$(a-b)^{-1} ln \frac{b}{a} \times \frac{A_t - a(\varepsilon_C + \varepsilon_D - \varepsilon_B) - b\varepsilon_B}{A_t - b(\varepsilon_C + \varepsilon_D - \varepsilon_A) - a\varepsilon_A} = k_2t \qquad (7)$$

When it was experimentally possible to use identical concentrations of triphenylmethyl isoselenocyanate and the phosphorus compounds, a, eqn. 7 reduces to:

$$\frac{A_t - a\varepsilon_A - a\varepsilon_B}{a(a\varepsilon_C + a\varepsilon_D - A_t)} = k_2t \qquad (8)$$

The rates of reactions were determined from runs with concentrations of reactants in the 5×10^{-4} M – 4×10^{-3} M region, depending upon the rates of reaction and, to some extent, upon extinction coefficients of the reactants used. For various concentrations of the reactants, rate plots were found to be linear up to four or five half-lives when the usual second order rate equation was applied, confirming the clean second-order kinetics, first order in each reactant. The rates of reaction were usually reproducible to within 3 to 4 % in cyclohexane, while the accuracy was considerably less for the reactions in acetonitrile due to the high rates of reactions.

The rate studies were performed on a Beckman DB spectrophotometer, using 0.1 and 1.0 cm cells. The thermostated compartments were kept at the given temperatures ±0.05°C.

As the calculations according to eqns. 7 and 8 were quite time-consuming, a Fortran N program for Watfor compiler[60] was applied for the evaluation of the rate constants.

The rate of reaction between the cyclic phosphite and triphenylmethyl isoselenocyanate was determined by measuring the disappearance of the peak at 2100 cm^{-1}

using a Unicam SP 200G Infrared Spectrophotometer. The rates of reaction in cyclohexane were in this case generally reproducible to within 5 %. The integrated extinction coefficients of triphenylmethyl isoselenocyanate in carbon tetrachloride was calculated from measurements performed with a Perkin Elmer 225 Grating Infrared Spectrophotometer.

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