Kinetic Studies of the Reactions of Hexachlorocyclotriphosphazene and Octachlorocyclotetraphosphazene with t-Butylamine

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The rates of the reactions of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) with t-butylamine in methyl cyanide were determined at three temperatures in the range 273—308 K. The reaction of $N_3P_3Cl_6$ was also studied in tetrahydrofuran. Rigorous purification of the chlorophosphazenes and the solvents was essential to obtain reproducible results. An $S_N2(P)$ mechanism involving the formation of a five-co-ordinate phosphorus intermediate is in accord with the kinetic data. The greater reactivity of $N_4P_4Cl_8$ compared to that of $N_3P_3Cl_6$ arises entirely from the lowering of the enthalpy of activation. The effects of ring size and the solvent on the rates are discussed in terms of the activation parameters.

NUCLEOPHILIC substitution reactions at a phosphorus centre continue to be a live subject of research in view of their mechanistic significance and biochemical relevance.[1-6] Cyclophosphazenes constitute an important class of inorganic heterocyclic compounds containing four-co-ordinate phosphorus(v) centres. The regio- and stereo-selectivity frequently found in the nucleophilic displacement reactions of halogenocyclophosphazenes is not clearly understood in mechanistic terms.[7] Kinetic data for the reactions of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) with amines have been obtained only recently.[8-10] Although brief kinetic reports have mentioned the enhanced reactivity of the oligomeric octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) towards amines, activation parameters have not been evaluated.[11,12] In this paper, we report the results of a kinetic study of the reactions of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with t-butylamine in methyl cyanide. The reaction of $N_3P_3Cl_6$ has also been investigated in tetrahydrofuran (thf). A preliminary note on some aspects of the work has appeared.[13]

EXPERIMENTAL

Materials.—Hexachlorocyclotriphosphazene (m.p. 113 °C) and octachlorocyclotetraphosphazene (m.p. 124 °C) were repeatedly recrystallized from light petroleum (b.p. 60—80 °C). For each kinetic run, a freshly recrystallized sample of the chlorophosphazene was sublimed ($N_3P_3Cl_6$: 95 °C/3 mmHg; † $N_4P_4Cl_8$: 110 °C/3 mmHg) and the sublimate was removed in a dry-box filled with dry nitrogen. The sublimed sample was stored in a desiccator and used within 24 h. All subsequent sampling operations were carried out in a dry-box filled with dry nitrogen.

t-Butylamine (BDH) was heated under reflux over KOH pellets for 6 h and distilled. It was redistilled (b.p. 41 °C/680 mmHg) over sodium just before use. Methyl cyanide (E. Merck) was dried over anhydrous sodium sulphate, boiled under reflux with phosphorus pentoxide (5—10 g l^{-1}) for 2 h, and distilled. The middle fraction was redistilled over molecular sieves (BDH, type 4A) prior to use and stored over molecular sieves. Tetrahydrofuran (BDH) was heated under reflux with KOH pellets until a negative peroxide test resulted. In view of the enhanced sensitivity of pure thf towards light and oxygen,[14] the amount required for each kinetic run was redistilled over KOH pellets just before the experiment. An atmosphere of dry nitrogen was maintained during the distillation and transfer of the solvent. Benzene and light petroleum (b.p. 60—80 °C) were purified by standard procedures.[15] Nitric acid (BDH, AR) was diluted with chloride-free water to obtain a 0.1 mol dm^{-3} solution. The solution was boiled to expel oxides of nitrogen, cooled, and used for quenching the kinetic runs.

Procedure for the Kinetic Studies.—The rate of the reaction of $N_3P_3Cl_6$ with t-butylamine in thf or methyl cyanide was determined by estimating the amine hydrochloride formed by potentiometric titration with a standard $Ag[NO_3]$ solution. The method of ' Separate bulbs ' was employed. Cylindrical glass tubes (14 cm × 2 cm diam.) fitted with B14 ground joints were used for the kinetic runs. The required volume of a stock solution of $N_3P_3Cl_6$ in methyl cyanide was placed in 15—20 such tubes and allowed to attain the temperature of the thermostat. A solution of t-butylamine in the same solvent also ' thermostatted ' at the same temperature was then quickly added to the phosphazene solution. The total volume of methyl cyanide was 10 cm^3. After a measured time interval, the reaction mixture from each tube was poured into a separating funnel containing benzene (10 cm^3) and dilute nitric acid (10 cm^3). The chloride ion released in the reaction passed into the aqueous phase and was determined by potentiometric titration with a standard $Ag[NO_3]$ solution (0.002—0.005 mol dm^{-3}), immediately after the separation of the organic and aqueous layers. ' Blank ' experiments (without the amine solution) were carried out at the beginning and the end of each kinetic run and the blank titre value (< 0.1 cm^3 of 2.0 × 10^{-3} mol dm^{-3} $Ag[NO_3]$) was subtracted from the actual titre values obtained at various time intervals. Each kinetic run thus consisted of 15—20 such experiments and each point in the graph to determine the rate constant (see below) was obtained by an individual experiment but using the same stock solutions of the reactants. Similar experiments were also carried out in thf but in this case light petroleum–HNO_3 (10 cm^3 of each) was used for ' quenching '. The reactions were followed to an extent of 70—80% and in some cases to completion (24 h). The results are shown in Table 1.

The above procedure was not applicable for the reaction of $N_4P_4Cl_8$ with t-butylamine in methyl cyanide as an emulsion formed on quenching and this reaction was followed conductometrically. This method is possible as $N_4P_4Cl_8$ has a very low conductance [(1.0—2.0) × 10^{-6}

† Throughout this paper: 1 mmHg = (101 325/760) N m^{-2}.

TABLE 1

Kinetic data for the reactions of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with t-butylamine

Phosphazene	Solvent	Temp./°C	Second-order rate constant k_2/dm³ mol⁻¹ s⁻¹ 0	10	20	30	35	$\Delta H^{\ddagger}$/kJ mol⁻¹	$\Delta S^{\ddagger}$/J K⁻¹ mol⁻¹
$N_3P_3Cl_6$ [a]	MeCN				$(9.7 \pm 0.4) \times 10^{-3}$	$(12.5 \pm 0.2) \times 10^{-3}$	$(15.7 \pm 0.2) \times 10^{-3}$	20.3 ± 1.7	−205.7 ± 17.3
$N_3P_3Cl_6$ [b]	thf				$(1.9 \pm 0.3) \times 10^{-3}$	$(3.3 \pm 0.1) \times 10^{-3}$	$(5.7 \pm 0.1) \times 10^{-3}$	47.6 ± 2.1	−125.9 ± 6.0
$N_4P_4Cl_8$ [c]	MeCN		1.66 ± 0.09	1.89 ± 0.18	2.28 ± 0.14			8.2 ± 2.0	−201.6 ± 42.2

[a] $[N_3P_3Cl_6]_0 = (2.0—2.5) \times 10^{-3}$ mol dm⁻³; $[amine]_0 = (2.0—5.0) \times 10^{-3}$ mol dm⁻³. [b] $[N_3P_3Cl_6]_0 = (2.0—4.0) \times 10^{-3}$ mol dm⁻³; $[amine]_0 = (2.0—8.0) \times 10^{-3}$ mol dm⁻³. [c] $[N_4P_4Cl_8]_0 = (1.0—1.5) \times 10^{-4}$ mol dm⁻³; $[amine]_0 = (2.0—3.0) \times 10^{-4}$ mol dm⁻³.

Ω^{-1}] and the conductivity is linearly dependent on concentration for t-butylamine hydrochloride in methyl cyanide. Because of its low solubility,[16] stock solutions of $N_4P_4Cl_8$ were not greater than 0.005 mol dm⁻³ and because of the errors involved in weighing such small quantities and the inherently lower accuracy of the conductometric method, these kinetic data are subject to larger errors (see Table 1).

The products of the reactions were isolated from the benzene or light petroleum layers by the evaporation of the solvent and identified as the mono(amino)-derivatives $N_3P_3Cl_5(NHBu^t)$ and $N_4P_4Cl_7(NHBu^t)$ by thin-layer chromatography [silica gel; eluant, benzene–light petroleum (1 : 2)] using authentic samples.[17,18]

mined accurately for the following reasons. (*a*) The mono(t-butylamino)-derivatives, $N_3P_3Cl_5(NHBu^t)$ and $N_4P_4Cl_7(NHBu^t)$, were difficult to purify because of their low melting points; [17,18] (*b*) the solubility of $N_3P_3Cl_5(NHBu^t)$ in methyl cyanide was very low and hence stock solutions of the required concentration could not be prepared owing to difficulties in accurately weighing small quantities of liquid samples; (*c*) the reaction of $N_4P_4Cl_7(NHBu^t)$ with t-butylamine yields both 2,6- and 2,4-bis(t-butylamino)-isomers of $N_4P_4Cl_6(NHBu^t)_2$.[18]

Need for Rigorous Purification of Chlorocyclophosphazenes and Solvents.—The reproducibility of the kinetic results were markedly dependent upon the purity of the chlorocyclo-

TABLE 2

Kinetic data for some typical experiments to demonstrate the need for rigorous purification of $N_3P_3Cl_6$ and the solvents [a]

Nature of $N_3P_3Cl_6$ sample	Solvent	k_2/dm³ mol⁻¹ s⁻¹	Initial concentrations/mol dm⁻³
1 Freshly recrystallized	MeCN	0.020 1	$[N_3P_3Cl_6]_0 = 2.0 \times 10^{-3}$ $[amine]_0 = 3.0 \times 10^{-3}$
2 Freshly sublimed [b]	MeCN	0.013 3	$[N_3P_3Cl_6]_0 = 2.0 \times 10^{-3}$ $[amine]_0 = 3.0 \times 10^{-3}$
3 Freshly recrystallized and sublimed	MeCN	0.009 7 [c]	*d*
4 Freshly recrystallized and sublimed	thf [e]	0.006 8	$[N_3P_3Cl_6]_0 = 3.0 \times 10^{-3}$ $[amine]_0 = 4.0 \times 10^{-3}$
5 Freshly recrystallized and sublimed	thf [f]	0.001 9 [c]	*g*

[a] The reaction involved is $N_3P_3Cl_6 + 2NH_2Bu^t \longrightarrow N_3P_3Cl_5(NHBu^t) + Bu^tNH_3^+Cl^-$; at 20 °C. [b] $N_3P_3Cl_6$ purified by recrystallization and sublimation stored in a glass weighing-bottle for 25 days and used after fresh sublimation. [c] 'Ideal' rate constant confirmed by duplicate/triplicate kinetic runs (*cf.* Table 1). [d] See footnote *a* of Table 1. [e] Purified thf stored over sodium wire (24 h). [f] Purified thf freshly distilled before the experiment. [g] See footnote *b* of Table 1.

The order of the reaction with respect to each of the two reactants was determined by the 'initial rate method'.[19,20] The rate constants and activation parameters were calculated using a least-squares curve-fitting program [21] on an IBM 360/44 computer or a DCM Microsystem 1121 calculating machine using the appropriate rate expressions.[19] The values are shown in Table 1. Error analysis was carried out by using an equation given by Binsch [22] in which the term due to temperature fluctuations was omitted.

Preliminary experiments indicated that the reactions of the mono(t-butylamino)-derivatives, $N_3P_3Cl_5(NHBu^t)$ and $N_4P_4Cl_7(NHBu^t)$, with t-butylamine were at least 10 times slower than the replacement of the first chlorine atom from the respective chlorophosphazene. Complications due to the onset of the second stage of substitution [formation of a bis(t-butylamino)-derivative] were not encountered, particularly when the initial amine concentration was equal to or less than that of the chlorocyclophosphazene. When the initial amine concentration was twice that of the phosphazene, the rate constants showed apparently increasing values after 70—75% of the reaction was over and in such cases points beyond 70% of the reaction were not included in the calculation of the rate constants. The kinetics of the second stage of chlorine replacements could not be determined accurately for the following reasons. (*a*) The mono(t-butylamino)-derivatives, $N_3P_3Cl_5(NHBu^t)$ and $N_4P_4Cl_7(NHBu^t)$, were difficult to purify because of their low melting points; [17,18] (*b*) the solubility of $N_3P_3Cl_5(NHBu^t)$ in methyl cyanide was very low and hence stock solutions of the required concentration could not be prepared owing to difficulties in accurately weighing small quantities of liquid samples; (*c*) the reaction of $N_4P_4Cl_7(NHBu^t)$ with t-butylamine yields both 2,6- and 2,4-bis(t-butylamino)-isomers of $N_4P_4Cl_6(NHBu^t)_2$.[18]

Need for Rigorous Purification of Chlorocyclophosphazenes and Solvents.—The reproducibility of the kinetic results were markedly dependent upon the purity of the chlorocyclophosphazenes and the solvents. The rates of the reactions were considerably enhanced if rigorous purification methods were not adopted. There was also an increase in the 'blank' titre values (0.30—0.50 cm³ of 4.00×10^{-3} mol dm⁻³ $Ag[NO_3]$). This difficulty is highlighted by the kinetic data obtained using different samples of chlorocyclophosphazenes and solvents that were not rigorously purified. The results for some typical experiments are shown in Table 2. Although the data could be fitted into a second-order rate law and rate constants evaluated, they varied from sample to sample. Therefore, all kinetic runs were performed under identical conditions strictly following the purification procedures described above.

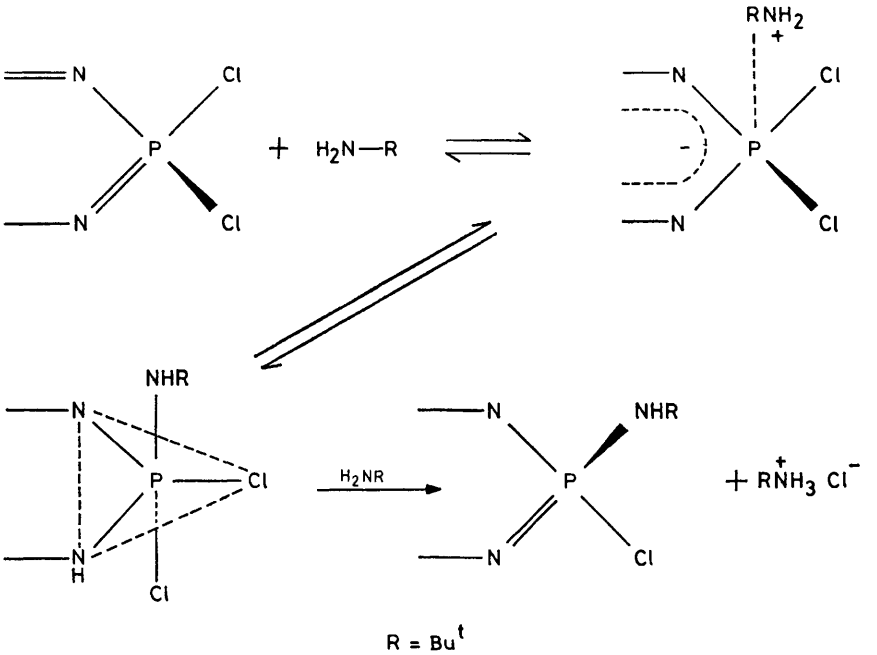
DISCUSSION

The two reactions studied, (1) and (2), follow a second-order rate law, first-order in the chlorocyclophosphazene and first-order in the amine. A bimolecular $S_N2(P)$ type mechanism involving a five-co-ordinate phosphorus intermediate is in accord with the kinetic data. According to this mechanism, the reaction takes place in two steps. In the first step, an addition complex between

the amine and the chlorocyclophosphazene is formed as an intermediate in a rapid pre-equilibrium. In the following slow step, which is rate-determining, the intermediate decomposes with the formation of a proton and a chloride ion simultaneously, resulting in the elimination of HCl. The mechanism is depicted in the Figure below.

$$N_3P_3Cl_6 + 2NH_2Bu^t \xrightarrow[\text{or thf}]{\text{MeCN}} N_3P_3Cl_5(NHBu^t) + Bu^tNH_3{}^+Cl^- \quad (1)$$

$$N_4P_4Cl_8 + 2NH_2Bu^t \xrightarrow{\text{MeCN}} N_4P_4Cl_7(NHBu^t) + Bu^tNH_3{}^+Cl^- \quad (2)$$



The $S_N2(P)$ mechanism, involving a five-co-ordinate phosphorus intermediate, for the reaction of $N_3P_3Cl_6$ with t-butylamine

Goldschmidt and Licht have studied the reactions of $N_3P_3Cl_6$ with dimethylamine [8] and methylamine [9] in thf and postulated an $S_N2(P)$ mechanism in which a solvent molecule participates in the rate-limiting step. The postulate of an addition complex between the chlorocyclophosphazene and the amine gains credence in view of a recent report which presents n.m.r. evidence for the formation of a phosphorane intermediate in the reactions of methylphosphonic difluoride ($MePOF_2$) with aniline.[6] Recently, Holmes [23] has reviewed the chemistry and structure of five-co-ordinate phosphorus.

The activation parameters presented in Table 1 can be interpreted in terms of the mechanism proposed (Figure). The overall large negative entropies of activation for these reactions are in agreement with the bimolecular mechanism.[20] Such negative entropies of activation are commonly observed in the hydrolysis reactions of phosphate esters.[24] In the two-step mechanism proposed, the first step accounts largely for the enthalpy of activation whereas the entropy of activation is primarily associated with the rate-limiting second step. The large negative values of $\Delta S^{\ddagger}$ are explained by the solvation of both proton and chloride ion being formed simultaneously in the second step.[8-10]

Enhanced rates are observed when chlorocyclophosphazene samples that are not rigorously purified are used for the kinetic studies (Table 2). Presumably the chlorocyclophosphazene undergoes mild surface hydrolysis on storage as a result of moisture adsorbed on the glass walls, and the occluded hydrogen chloride thus formed [25] rapidly reacts with the amine. Sublimation would remove this source of enhanced rate constant. If the sample of $N_3P_3Cl_6$ is not freshly recrystallized but only sublimed, it is conceivable that some of the hydrolysis products may be carried over into the sublimate and the ' hydroxychlorocyclophosphazene ' may react with the amine at a faster rate than $N_3P_3Cl_6$. No information is available on the latter point at present. Allcock *et al.*[25] have demonstrated the need for both recrystallization and sublimation of the hexachlorocyclotriphosphazene and transfer of the sample in a dry-bag without exposure to moisture, in order to obtain reproducible results in their studies on the kinetics of polymerization of the hexachloride. The higher rate constant observed when thf stored over sodium is used as the solvent is due to a ' peroxide ' effect.[26] The literature available on the kinetics of the aminolysis reactions of chlorocyclophosphazenes [8-10] does not stress the need for rigorous purification of the hexachloride, $N_3P_3Cl_6$. It may be pointed out that the rate constant reported for the reaction of $N_3P_3Cl_6$ with t-butylamine in thf [10] is *ca.* 5 times greater than our values (Table 1).

The reaction of $N_4P_4Cl_8$ with t-butylamine is 200 times faster than the analogous reaction with $N_3P_3Cl_6$. The enthalpy of activation is very much lower for $N_4P_4Cl_8$,

whereas the entropy of activation remains almost the same (Table 1). This observation strongly supports the two-step mechanism operating in both the reactions. The higher $\Delta H^{\ddagger}$ observed for the reaction of $N_3P_3Cl_6$ is due to the formation of a crowded transition state owing to the bulkiness of the t-butylamine group. Enthalpic-steric factors chiefly influence the pre-equilibrium step (*i.e.*, primarily reduce the concentration of the phosphazene–amine complex). The decrease in $\Delta H^{\ddagger}$ for the reaction of $N_4P_4Cl_8$ probably arises as a result of the greater skeletal flexibility [7] of the eight-membered ring which facilitates the molecular distortions required for the formation of the five-co-ordinate transition state.

The interaction of tetraethylammonium chloride containing radioactive ^{36}Cl with homologous chlorocyclophosphazenes, $(NPCl_2)_{3-6}$, proceeds by an $S_N2(P)$ mechanism.[16] There is a decrease in the energy of activation for the reaction of $N_4P_4Cl_8$ compared with that of $N_3P_3Cl_6$ but there is virtually no change in the frequency factor. The observations of the present study parallel the above results. However, the pentameric and the hexameric chlorocyclophosphazenes, $N_5P_5Cl_{10}$ and $N_6P_6Cl_{12}$, undergo chlorine exchange at a rate much slower than the tetrameric derivative [16] and hence factors other than ring flexibility must be considered. Paddock and Serrequi [27] have shown that the ratio of the rates of second and first fluorination steps (k_2/k_1) for $N_3P_3Cl_6$, $N_4P_4Cl_8$, and $N_5P_5Cl_{10}$ is 8, *ca.* 100, and 7 respectively and they suggested that π-inductive effects must play a significant role in determining the relative reactivity of the oligomeric chlorocyclophosphazenes. Capon *et al.*[11] have suggested that the eight-membered ring can accommodate the negative charge in the transition state more readily than the six-membered ring. It therefore appears that although the enhanced reactivity of $N_4P_4Cl_8$ can be explained on the basis of favourable steric factors, the differences in the electrophilicity of the phosphorus centre due to differences in π-bonding cannot be neglected.

The reaction of the hexachloride $N_3P_3Cl_6$ with t-butylamine in methyl cyanide is about five times faster than in thf. The decreased rate in thf largely arises as a result of the large activation enthalpy (Table 1). This observation suggests that a thf molecule is probably hydrogen-bonded to the amine in the pre-equilibrium step. Such an association will result in a crowded transition state which would account for the larger $\Delta H^{\ddagger}$.[8] The increase in $\Delta H^{\ddagger}$ is accompanied by an increase in the entropy of activation (less negative), a trend that is also observed for the alkaline hydrolysis of a series of fluoroalkoxyphosphazenes $[NP(OR)_2]_n$ (n = 3 or 4, R = CH_2CF_3 or $CH_2C_3F_7$).[28] This inverse trend can be rationalized if one realises that the greater the steric repulsion in the intermediate, the greater the steric acceleration in its decomposition, which would in turn decrease the need for the solvation of the transition state.[10]

Synthetic investigations of the reaction of the $N_4P_4Cl_8$ with t-butylamine show that the (t-butylamino)-chlorocyclotetraphosphazene derivatives $N_4P_4Cl_{8-n}(NHBu^t)_n$ (n = 1—3) possess non-geminal structures.[18] By contrast, the reaction of $N_3P_3Cl_6$ with the same amine leads to the exclusive formation of geminal products for which a proton-abstraction mechanism has been postulated.[17] The difference in behaviour has been attributed to the supposed greater reactivity of the octachloride.[18] The data reported in the present study substantiate this hypothesis. An $S_N2(P)$ reaction at a $\equiv PCl_2$ centre to yield a non-geminal product in the octachloride reactions would not be expected to be sterically hindered as the puckered eight-membered ring can readily accommodate a five-co-ordinate intermediate. In the more rigid cyclotriphosphazene system, this pathway would be impeded and hence the alternative dissociative conjugate-base mechanism [7] gains ascendency, leading to the formation of *gem*-$N_3P_3Cl_4(NHBu^t)_2$.

Both equatorial (retention of configuration) and axial (retention or inversion) attack are possible for the halogen-replacement reactions of four-co-ordinate P^V compounds.[2] Bailey and Parker [29] in their report of the kinetics of the reaction of $N_3P_3Cl_6$ with aniline in EtOH have suggested that amine attack takes place in the plane of the ring. Capon *et al.*[11] propose that the amine attack occurs from above the ring plane. However, no unambiguous evidence for or against a particular mode of attack has yet been adduced. Because the phosphorus atom is part of a ring, additional steric constraints may have to be considered. Furthermore, the importance of ligand reorganization (by Berry pseudo-rotation and turnstile rotation) [2,23] and its role in determining the geometry of the intermediates formed in these reactions are not at all understood. Another point to be reckoned with is the effect of mesomeric electron release [7] from the amino-nitrogen atom to the phosphorus centre on the ligand reorganization processes. Hence, the validity of the affirmative conclusions on the stereochemical pathways in the aminolysis reactions of chlorocyclophosphazenes [7] needs to be re-examined.

We thank the University Grants Commission, New Delhi, for generous support, Professor A. R. Vasudeva Murthy for kind interest, and Dr. M. Woods for useful discussions.

[1/541 *Received*, 6*th April*, 1981]

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