273. S.N.Ananchenko, A.V.Platonova, V.N.Leonov, and I.V.Torgov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1074 (1961).
274. S.N.Ananchenko, V.M.Rzheznikov, V.N.Leonov, and I.V.Torgov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1913 (1961).
275. V.M.Rzheznikov, S.N.Ananchenko, and I.V.Torgov, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 463 (1962).
276. N.N.Gaidamovich and I.V.Torgov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1162 (1961).
277. N.N.Gaidamovich and I.V.Torgov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1803 (1961).
278. S.I.Zav'yalov, G.V.Kondrat'eva, and L.F.Kudryavtseva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 529 (1961).
279. J.F.Collins and H.Smith, J.Chem.Soc., 4308 (1956).
280. A.J.Birch and H.Smith, J.Chem.Soc., 4909 (1956).
281. A.J.Birch, G.A.Hughes, and H.Smith, J.Chem.Soc., 4774 (1958).
282. W.S.Johnson, H.C.Dehm, and D.J.Chinn, J.Org.Chem., 19, 670 (1954).
283. A.J.Birch and J.A.K.Quartey, Chem.and Ind., 489 (1953).
284. W.F.Johns, J.Amer.Chem.Soc., 80, 6456 (1958).
285. G.Stork, H.N.Knastgir, and A.J.Solo, J.Amer.Chem. Soc., 80, 6457 (1958).
286. A.J.Solo, Diss.Abs., 20, 511 (1959).
287. A.J.Birch and H.Smith, J.Chem.Soc., 1882 (1951).
288. N.A.Nelson and R.B.Garland, J.Amer.Chem.Soc., 79, 6313 (1957).

Zelinskii Institute of Organic Chemistry,
Academy of Sciences of the USSR

U. D. C. 547.87

2,4,6-TRICHLORO-1,3,5-TRIAZINE (CYANURYL CHLORIDE) AND ITS FUTURE APPLICATIONS

V. I. Mur

CONTENTS

I. Introduction 92
II. Reactivity of cyanuryl chloride and of triazine 93
III. Reactions of cyanuryl chloride 94
1. Hydrolysis 95
2. Reactions with amines 96
3. Reactions with alcohols and phenols 98
4. Reactions with sulphur-containing compounds 99
5. Reaction with formation of a C–C bond 99
6. Various substitution reactions 100
7. Reduction of cyanuryl chloride and other chlorinated triazines 100
8. Reactions with transformation of the ring 101

I. INTRODUCTION

The chemistry of 2,4,6-trichloro-1,3,5-triazine† (cyanuryl chloride)[1-5] formed the subject of a section in the comprehensive monograph "s-Triazines and Derivatives"[6], which reviewed work, published up to 1954, on the preparation, reactions, and applications of the compound. The problem of the reactivity of cyanuryl chloride and other halogenated derivatives of triazine was not discussed in the monograph.

Although the chemistry of cyanuryl chloride has been intensively developed since then, only one review paper in Japanese, covering the literature up to 1956, has dealt with this question[7]. It describes the synthesis of triazine derivatives from cyanuryl chloride, and examines some relations between the nature of the reactants and their reactivity. This review does not cover the practical application of cyanuryl chloride and the products obtained from it.

The chemistry of cyanuryl chloride has not been reviewed in the Soviet literature, and it is therefore opportune and useful to report progress in this field.

A great achievement is the production of a new type of dyes — the reactive dyes[8-28] — based on cyanuryl chloride. Their molecules contain active chlorine atoms combined with the triazine ring, and during dyeing react with the hydroxy- or amino-groups of the fibre. This results in the formation of a chemical compound between the fibre and the dye, which is of ether type in the case of cellulose and of amide type with wool and other fibres containing primary or secondary amino-groups. The resulting dyeings are distinguished by their brightness and purity of colour and by exceptionally high fastness to wet treatments, and the dyes themselves by simplicity of application and relative cheapness, which gives them an advantage over other groups of dyes.

Cyanuryl chloride is of great value for agricultural needs: especially during recent years numerous derivatives have been synthesised which act as insecticides, fungicides, and week-killers[29-37], some of which have already been used in agriculture. The most effective are compounds containing active chlorine atoms combined with triazine, in particular 2-chloro-4,6-bisdimethylaminotriazine, and also dichloro-derivatives of triazine.

Recently compounds have been obtained from cyanuryl chloride which inhibit the growth of tumors, and this may prove invaluable in the treatment of cancer[38-41]. Other drugs required in medicine are synthesised on the same basis, for example antitubercular[42,43] and trypanocidal[44-49] preparations.

Cyanuryl chloride is of equal value for the synthesis of many other substances required in various branches of the economy. Thus certain sulphur-containing triazine derivatives obtained from cyanuryl chloride act as antioxidants[50], plasticisers[51], and vulcanisation accelerators[53] in the rubber industry. Other preparations have great importance as textile auxiliaries, especially as finishing[54] and brightening[55,56] agents. In the synthetic dye industry cyanuryl chloride is employed not only for the synthesis of reactive dyes, on which more than a hundred patents have been taken

† Since the present review is concerned only with derivatives of 1,3,5-triazine, the numerical locants will be omitted, and the molecule referred to simply as "triazine".

out (during 1957–1961)[57], mainly by Ciba and I. C. I., but also in the manufacture of direct (especially green)[58,59], vat (Ref. 59, p. 1021), and several other dyes[52,60-62].

The diversity of the fields of application of cyanuryl chloride is due to its distinguishing feature — the presence in its molecule of three active chlorine atoms, which can be replaced one by one. The successive substitution of the chlorine atoms when cyanuryl chloride reacts with various compounds enables a multitude of the most diverse substances to be obtained.

II. REACTIVITY OF CYANURYL CHLORIDE AND OF TRIAZINE

The ease of replacement of the chlorine atoms in cyanuryl chloride and its partial substitution products, *i.e.* di- and mono-chlorotriazines, is determined both by the nature of the nucleophilic reagent and by the number and nature of the substituents linked to the triazine ring. Thus the reactivity of cyanuryl chloride itself and of many of its monosubstituted derivatives is roughly equal to that of oxychlorides[63] or acid chlorides of certain carboxylic acids[64]; in disubstituted derivatives it in general approximates in reactivity to the alkyl halides, although reactivity depends on the nature of the substituents.

The reactivity of cyanuryl chloride and of other chlorinated triazines is governed also by the specific structure of the ring, which is usually represented as a six-membered cyclic system (I) consisting of alternating nitrogen and carbon atoms linked by alternating single and double bonds, resembling formally the benzene ring



(I)

While comprising a six-membered ring with a closed system of π electrons, triazine is distinguished from the benzene system by the characteristic presence of six unpaired electrons on the nitrogen atoms, which form part of the general system. It is probably this which is responsible for the peculiarities of the triazine system, and distinguishes it from the usual aromatic system of benzene. The increased electron density on the nitrogen atoms compared with the carbon atoms‡ in the triazine ring destroys the electronic symmetry, resulting in diminished stability compared with benzene and the capacity for addition reactions, while *C*-halogenated triazines, especially cyanuryl chloride, can undergo substitution reactions. The instability of the unsubstituted symmetrical triazine ring is shown, for example, in its hydrolysis, especially in the presence of mineral acids, when reaction is almost instantaneous, formic acid and ammonia being produced[66,67]. Ring-opening occurs also on treatment of triazine with sodamide or a primary or secondary amine, the products being in the first case sodium cyanide and ammonia, and in the second a substituted formamidine[6]. Weakening and rupture of a C–N bond in triazine occur also on treatment with aluminium chloride[6].

The instability of triazine has prevented it from being obtained by the removal of substituents from the triazine ring by the usual methods[6]. This also constitutes an important distinction from benzene and other aromatic hydrocarbons, which can be prepared[68] in this way.

In contrast to benzene, triazine can undergo addition reactions. With hydrogen chloride, for example, it yields the addition product $2C_3H_3N_3.3HCl$,[67] and with silver[67] and mercury[69] salts the compounds $AgNO_3.2C_3H_3N_3$, $AgNO_3.C_3H_3N_3$, and $HgCl_2.C_3H_3N_3$. Even halogen adds on at 0° in carbon tetrachloride[70].

Triazine does not undergo catalytic hydrogenation[70]. It is a catalyst poison, even traces of it poisoning the catalyst in the hydrogenation of cyclohexene.

Owing to the diminished electron density on the carbon atoms, triazine is incapable of the electrophilic substitutions — nitration and sulphonation — characteristic of benzene. For the same reason it has not proved possible to prepare *C*-nitro-derivatives by replacing a chlorine atom in cyanuryl chloride by a nitro-group or by oxidising amino-derivatives of triazine[7].

The diminished electron density of the carbon atoms in triazine explains the great mobility of the halogen atoms in its halogenated derivatives, in particular of chlorine in cyanuryl chloride, which distinguishes the latter fundamentally from chlorobenzenes. Replacement of one or two chlorine atoms in cyanuryl chloride by electron-donor groups should increase the electron density on the triazine carbon atoms, and thereby diminish the activity of the remaining chlorine atoms, as actually occurs.

Thus replacement of the chlorine atoms in cyanuryl chloride by amino- or hydroxy-groups takes place in stages[64,71,72], and this is a consequence of the levelling out of electron density in the triazine, *i.e.* of its increase on the carbon atoms due to entry of an electron-donor substituent. A similar phenomenon is observed when one or two chlorine atoms are replaced by alkoxy-groups[73], as a result of which the C–Cl bond becomes more stable, and the chlorine atoms become less active. A CHN_2 group has a similar but less clearly defined effect[74].

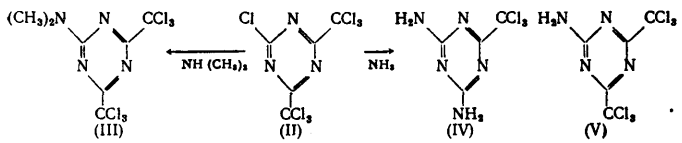
Study of the hydrolysis of 6-alkylamino-, 6-alkoxy-, and 6-alkylthioderivatives of 2,4-dichlorotriazine showed the alkylamino-derivatives to be the most stable; in the other groups of derivatives the chlorine atoms were more mobile[75]. The hydrolysis rate constants for these derivatives show that a compound is more stable (the chlorine is less mobile) the more readily the XAlk group donates electrons.

If, on the other hand, we assume that one or two chlorine atoms in cyanuryl chloride have been replaced by groups which can attract electrons no less strongly than does chlorine, *i.e.* by groups capable of diminishing the electron density on the carbon atoms in triazine and thereby promoting nucleophilic substitution, in this case substitution would have no deactivating influence on the reactivity of the remaining one or two chlorine atoms.

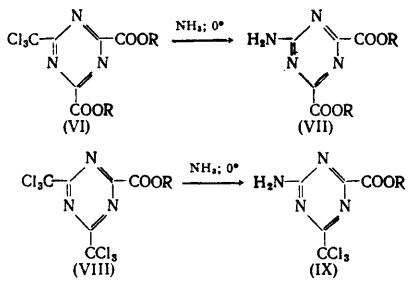
In fact, if two chlorine atoms in cyanuryl chloride are replaced by CCl_3 groups, which can be readily exchanged for nucleophilic substituents[76,77], deactivation of the remaining chlorine is not observed. Thus when the compound (II) reacts with dimethylamine, the chlorine is replaced even

‡ The non-uniform distribution of electron density is confirmed by calculation, which gives relative values of 1.179 and 0.821 on nitrogen and carbon respectively[65].

at 0°, with formation of (III).[78] Reaction of (II) with ammonia yields (IV), but (V) is not formed; this indicates that a group can readily undergo substitution if it itself exerts no deactivating influence on the other substituent:



It is probable that the ester group likewise does not deactivate substitution in the triazine ring[7]. Ammonia acts on (VI) to give (VII) even at 0°, and in the same way (VIII) yields (IX).



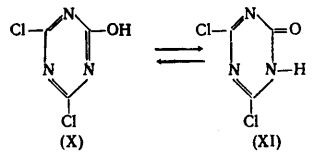
Replacement of a chlorine atom in cyanuryl chloride by a cyano-group probably does not diminish the activity of the remaining chlorine atoms, for, being linked to triazine, the cyano-group itself develops sufficient mobility. 2,4,6-Tricyanotriazine hydrolyses readily[79], and even in the cold is rapidly decomposed by water into hydrogen cyanide and cyanuric acid.

It follows that the nature and extent of the influence of substituents in the triazine ring on the activity of chlorine depend on their electronegativity. However, few data are yet available on this point, and the influence of substituents in the triazine ring can be assessed only qualitatively, by analogy with systems which have been studied more thoroughly, for example substituted bromobenzene. In the reaction of piperidine with *para*-substituted *o*-bromonitrobenzenes the substituent groups arrange themselves in the following sequence of diminishing deactivating effect on replacement of the bromine: $NH_2 > OH > N(CH_3)_2 > > OC_2H_5 > OCH_3 > CH_3 > C_4H_9^t > H > COOH > Cl, Br$.[80]

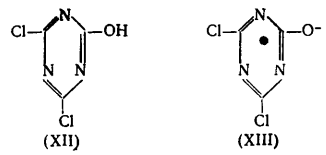
The activity of chlorine attached to a triazine carbon atom is influenced not only by the degree of electronic saturation of the substituent but also by whether or not it contains a reactive hydrogen atom.

Thurston *et al.*[72] noted that chlorine atoms in 2,4-dichlorotriazines are more active when a 6-monoalkylamino--group rather than a 6-dialkylamino-group is present. They explain this phenomenon by the fact that, if the substituent contains hydrogen, it can act as a hydrogen-donor in the triazine or the tautomeric dihydrotriazine. The attacking molecule, for example water (in hydrolysis), forms a hydrogen bond with the latter, thereby facilitating attack on an adjacent C–Cl bond. Hydrogen-bond formation is impossible in molecules of 2,4-dichloro-6-dialkylamino--1,3,5-triazines.

Precise data are lacking for hydroxy-derivatives. Wegmann[81] has reported the preparation of 2,4-dichloro-6-hydroxytriazine (X), which exhibits very little activity, undergoing reaction only at high temperatures, with the participation of only one chlorine atom. It is assumed that the low reactivity of this compound is due to its ability to pass into the tautomeric form (XI) with loss of its "aromatic" properties. As a result, the chlorine atoms which it contains differ in activity.



Matsui and Sakamoto[63] made a careful study of the hydrolysis of cyanuryl chloride in alkaline medium, and concluded that 2,4-dichloro-6-hydroxytriazine is fairly reactive: one of its chlorine atoms is very readily hydrolysed, and both chlorine atoms can be replaced by aniline under mild conditions. The sodium salt of this compound is stable, and is not hydrolysed at 0–5° even in the presence of strong alkali; its chlorine atoms cannot be replaced by aniline in alkaline medium. The diminished reactivity of the sodium salt of dichlorohydroxytriazine is explained by the difference in electron density on the triazine ring in the compounds (XII) and (XIII), *i.e.* by the different effects of the substituents OH and O^- on the activity of the chlorine.



As a result of the lack of agreement between observations made by different investigators, we may regard the reactivity of 2,4-dichloro-6-hydroxytriazine as an open question, especially in view of the fact that the Japanese workers did not succeed in isolating either the compound (XII) or 2-chloro-4,6-dihydroxytriazine. When an attempt was made to obtain these compounds by acidifying solutions of their sodium salts, only cyanuric acid was formed. The compound obtained by Wegmann was not characterised, nor was its mode of synthesis described.

The activity of chlorine atoms in triazine derivatives is affected by various substituents even when the latter are not directly linked to the triazine but are present in an aromatic ring combined with the latter[75,82]. Koopman[75] found that *para*-substituents in 2,4-dichloro-6-phenyltriazines could be arranged in the following sequence according to their acceleration of hydrolysis: $OCH_3 < SCH_3 < < H < SO_2CH_3 < NO_2$. The results do not contradict Hammett's rule if Jaffé's values[83] of σ are accepted for the above substituents.

Other investigators[84,85] have observed the effect of substituents, as a function of their polarity, on the reactivity of arylaminochlorotriazines.

III. REACTIONS OF CYANURYL CHLORIDE

Cyanuryl chloride is characterised mainly by reactions involving substitution by nucleophilic reagents. In contrast to triazine itself, reactions involving cleavage of the ring are not characteristic of cyanuryl chloride, and addition reactions are quite unknown.

Although many reactions involving substitution in cyanuryl chloride and other chlorinated triazines have been described, little work has been done on their mechanism. Only in a few cases has it been shown that the main reaction of cyanuryl chloride with nucleophilic reagents takes place by an S_N2 mechanism. [7,85]

1. Hydrolysis

Interest in the hydrolysis of cyanuryl chloride and of its partial conversion products is due mainly to its being a side-reaction in the preparation of several products of practical importance. Sometimes the hydrolysis of these derivatives is utilised for the preparation of triazine derivatives containing hydroxy-groups. For example, a quantitative yield of ammelide (2-amino-4,6-dihydroxytriazine) is obtained[87] by the hydrolysis of 2-amino-4,6-dichlorotriazine, which is readily prepared from cyanuryl chloride and ammonia[72,86]. Ammeline (2,4-diamino-6-hydroxytriazine) is obtained[88] in a similar manner from 2,4-diamino--6-chlorotriazine[72]. Complete hydrolysis of cyanuryl chloride itself yields cyanuric acid (2,4,6-trihydroxytriazine $\rightleftharpoons$ 2,4,6-trihydro-2,4,6-trioxotriazine). The most convenient method for its preparation is to boil cyanuryl chloride with glacial acetic acid[6] for 1 h, when the yield is 95%.

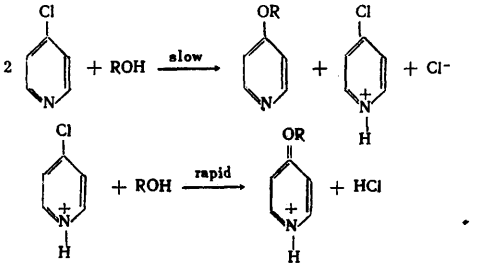
The hydrolysis of cyanuryl chloride and other chlorinated triazines, which usually takes place in aqueous medium or in a mixture of water with an organic solvent, is considerably accelerated by elevated temperatures and the presence of alkali. Opinions differ concerning the effect of acids. Only cyanuric acid has been isolated among the products of the acid hydrolysis of cyanuryl chloride[63,89,90].

Fierz-David and Matter[64] found that cyanuryl chloride was stable in water at 0° for 12 h, but it was rapidly hydrolysed even at room temperature. The experiments were made in the presence of calcium carbonate in an apparatus which enabled the course of hydrolysis to be followed from the amount of carbon dioxide evolved. These workers gave no data on the complete hydrolysis of cyanuryl chloride or its intermediate products.

Matsui and Sakamoto[63] studied the hydrolysis of cyanuryl chloride in aqueous acetone medium at 15° with and without addition of acid, but were unable to follow the different stages in the process owing to the rapid breakdown of the intermediate compounds to cyanuric acid. Previous addition of hydrochloric acid was found to slow down the initial stage of hydrolysis, but to increase the rate of hydrolysis of the intermediate compounds, which for this reason could not be isolated. Their presence was established only from the shape of the hydrolysis curve.

In a study of the hydrolysis of dichlorotriazines in aqueous acetone medium Koopman[75] found the same rate constant for hydrolysis of the first chlorine atom in 2-butoxy-, 2-butylthio-, and 2-phenyl-4,6-dichlorotriazines, whether or not the original mixture had first been acidified with nitric or sulphuric acid to pH 1. From this he concluded that hydrogen ions do not influence the rate of hydrolysis of chlorinated triazines.

However, Koopman's views are at variance with the concept of the acid catalysis of nucleophilic substitution reactions in nitrogeneous heterocyclic compounds (containing halogen attached to a carbon atom conjugated with the ring nitrogen atom)[47,48,91], a particular case of which is provided by the autocatalysis of hydrolysis and alcoholysis[92,93]

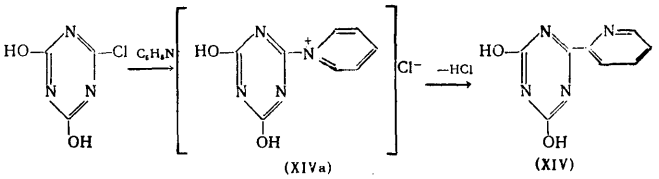


As a result of this, halogenated "aromatic" heterocycles are extremely sensitive to moisture, hydrolysis yielding the hydrogen halide, which accelerates further decomposition. A similar phenomenon is observed with halogenated triazines.

In contrast to acid hydrolysis, for which occurrence of the reaction in stages has not been established, with alkaline hydrolysis the existence of intermediate compounds has been shown, and they have been isolated. Fierz--David[64] was the first to report the formation of 2-chloro--4,6-dihydroxytriazine, a product of the incomplete hydrolysis of cyanuryl chloride with 10% caustic soda at 100°. The third chlorine atom is replaced only when the temperature is raised to 125°. These results have since been repeated many times and reported in the literature[6,7,63].

Wegmann reported[81] that the structure of 2,4-dichloro--6-hydroxytriazine — a product of the incomplete hydrolysis of cyanuryl chloride — had been established analytically, and that the substance was extremely unstable, liable to explosive decomposition when dry, but no information on its method of preparation or its properties has yet been published.

The presence of 2-chloro-4,6-dihydroxytriazine among the products of the partial alkaline hydrolysis of cyanuryl chloride was proved by Saure[71], who converted this compound into 2,4-dihydroxy-6-2′(or 4′)-pyridyltriazine (XIV), the reaction being assumed to proceed as follows



(XIVa) (XIV) (or γ-isomer)

Japanese workers[63] have made the most detailed study of alkaline hydrolysis. They have been the first to isolate and analyse the sodium salts of 2,4-dichloro-6-hydroxytriazine and 2-chloro-4,6-dihydroxytriazine. In contrast to the hydroxy-compounds themselves, these salts are characterised by stability to alkalis. In the presence of acids, they are first converted into the hydroxy-compounds, which are rapidly hydrolysed to cyanuric acid.

The sodium salt of 2,4-dichloro-6-hydroxytriazine was obtained by the hydrolysis of cyanuryl chloride at room temperature with solutions of sodium bicarbonate or carbonate in the proportion of at least 2 moles per mole of cyanuryl chloride, as well as in the presence of a slight excess of sodium hydroxide at 0–5°. This salt is stable, and when

dry can be stored for a long time; in aqueous solution at room temperature no change in acidity is observed for several days.

The monosodium salt of 2-chloro-4,6-dihydroxytriazine has been obtained by the hydrolysis of cyanuryl chloride or its monohydroxy-derivative in the presence of excess of caustic soda at 15–40°. This salt is still more stable to the prolonged action of alkali. Its hydrolysis in the presence of caustic soda begins at 80–90°. On hydrolysis in the presence of an insufficient quantity of neutralising reagent, the solution gradually becomes acid, with the formation of cyanuric acid.

The hydroxy-derivatives themselves could not be isolated. Their existence was proved by the formation of 2,4-dianilino-6-hydroxytriazine (XV) and 2-anilino-4,6-dihydroxytriazine (XVI) by the action of aniline on the sodium salts of the hydroxy-derivatives in faintly acid medium. Since (XVI), in contrast to (XV), is soluble in aqueous alkali, the amounts of the original hydroxy-compounds could be determined in the mixtures formed by hydrolysis under various conditions.

2. Reactions with Amines

The interaction of cyanuryl chloride with amines shows a stepwise course still more clearly than does its hydrolysis. However, the generally accepted empirical rule, according to which the first chlorine atom in cyanuryl chloride is replaced at 0°, the second at 30–50°, and the third at 90–100°, cannot be regarded as of general validity, although it is applicable to many reactions occurring in aqueous medium[42,44–46,64,94,95].

In several cases the second chlorine atom can be replaced even at 0°.[64] This occurs, for example, with sulphanilic acid and several other amino-sulphonic acids of the benzene and naphthalene series. Several amines can react with all three chlorine atoms at 0°.[96] Relatively inactive amines, for example those of the anthraquinone series, which do not contain sulphonato-groups, react in anhydrous solvents (usually nitrobenzene) above 100°, when a stepwise course of the reaction is not observed, and sometimes only two chlorine atoms can be replaced[64]. In such cases reaction must be carried out in boiling phenol in order to substitute the third chlorine atom (Ref. 59, p. 1021). Several amines do not react at all with cyanuryl chloride at 100°.[6]

The complete reaction of cyanuryl chloride with primary and secondary aliphatic and aromatic amines yields substituted melamines; melamine itself (2,4,6-triaminotriazine) is obtained by the action of ammonia on cyanuryl chloride. The reaction can take place in stages depending on the conditions: 2-amino-4,6-dichlorotriazine is formed in cold ethereal solution[72,87], 2,4-diamino-6-chlorotriazine in aqueous solution at room temperature[72], and melamine at 100° under pressure[97,98].

The possibility of stepwise reaction between cyanuryl chloride and ammonia was shown long ago by Diels[87] in the synthesis of trisubstituted triazines by various methods. Three different amines — NH_3, CH_3NH_2, and $C_2H_5NH_2$ — were made to react successively with cyanuryl chloride at 0°, then at 20–60°, and finally at 100°. Changes in the sequence in which the reagents were made to react yielded in all cases the same substance, which proves the stepwise character of the process.

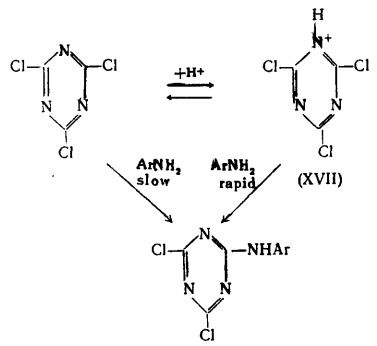
The reaction between cyanuryl chloride and amines occurs in stages, as does hydrolysis, as a result of the influence of the substituent in the triazine on the activity of the chlorine atoms which are present. Substituents having a greater tendency to donate electrons increase the electron density of the triazine ring, the C–Cl bond becomes more stable, and as a consequence the chlorine becomes less mobile.

Apart from substituents, the nature of the amine, determined both by its basic strength and by the steric factor, affects its reaction with chlorinated triazines. Of course, amines which are weak bases, for example aromatic amines containing negative substituents (2,4-dinitroaniline), react less vigorously than do stronger bases with chlorinated triazines. The ease of reaction with such amines as ethyleneimine[96], morpholine[38,39,99], and piperidine[71] is due to the absence of steric hindrance[6]. With these amines all the chlorine atoms can be replaced after a short time at 0–25°. Nevertheless, amines with even slight steric hindrance, such as diethylamine and iminodipropionitrile, form only monoamino- and diamino-derivatives at 25°.

Substitution of chlorinated triazines by amines is greatly affected by the nature of the solvent. The reaction is accelerated in polar solvents, especially in water, if the solubility of the amines permits their use. Reaction is more rapid in acetonitrile than in benzene[96], and the third chlorine atom in triazine can sometimes be replaced only in phenol (Ref. 59, p. 1021), as already mentioned.

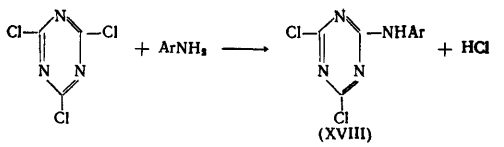
The reaction between chlorinated triazines and amines is usually carried out in the presence of an acid-binding agent, for example caustic soda, sodium carbonate or bicarbonate, or a tertiary amine, sometimes the amine used for the reaction.

Sometimes the reaction is catalysed by acids, as with other nitrogen-containing heterocyclic systems[47,48,91,100]. For example, the reaction of 2,4-diamino-6-chlorotriazine with aniline is accelerated by the presence of hydrochloric acid, but slowed down on addition of caustic soda[91]. In the presence of a large excess of acid, however, hydrolysis takes place at the same time. A similar phenomenon is observed with other aromatic amines and chlorinated triazines[47], sulphuric and tartaric acids also having a catalytic effect[91]. This phenomenon is explained by the diminution in electron density on the carbon atom of triazine caused by formation of an "ammonium"[91] or a triazinium ion[22] (XVII), which facilitates attack on the carbon atom by nucleophilic reagents:



Bitter and Zollinger[101,102] studied the kinetics of the reaction between cyanuryl chloride and nucleophilic reagents (aromatic amines) in a non-polar medium (benzene), and found that in the case of primary amines the reaction

does not follow a simple second-order law. Owing to autocatalysis, an induction period appears, the final reaction product (XVIII) accelerating the process:

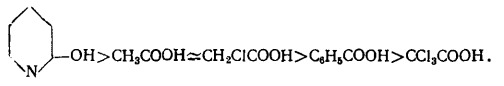


(XVIII)

The catalytic action of (XVIII) is due to the presence of the hydrogen atom in the NHAr group, as a result of which this compound functions as an acid. If the substituent group does not contain hydrogen, as in the case of *NN*-dialkylamino-derivatives, the reaction is not accelerated. This explains the absence of autocatalysis in substitution by secondary amines.

Other workers[103] have also observed autocatalysis in reactions of various 2-amino-4,6-dichlorotriazines with primary aromatic amines.

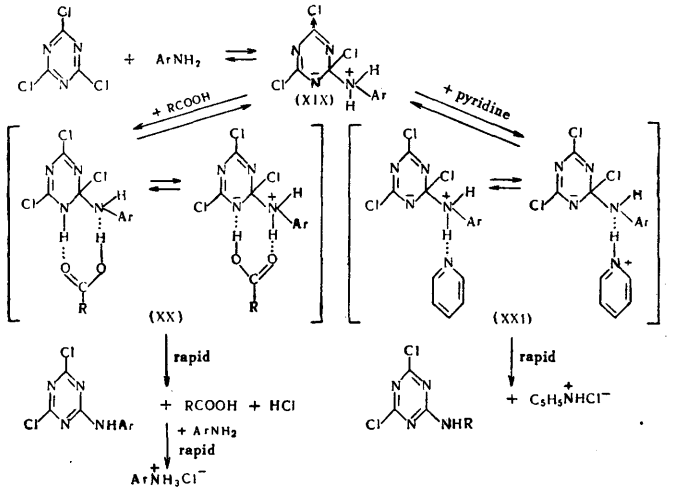
Several organic acids also catalyse the reaction between chlorinated triazines and amines in non-polar solvents[102]. Their effect is not directly related to their dissociation constant. These acids can be arranged in the following sequence according to the magnitude of their effect on the reaction velocity



Phenol, *o*- and *p*-nitrophenols, and picric acid show practically no catalytic effect.

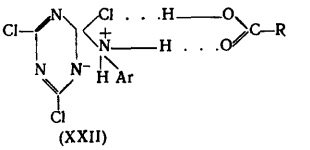
The reaction of cyanuryl chloride with arylamines is accelerated also by bases such as pyridine and triethylamine[22].

Bitter and Zollinger have shown[22] that substitution is rather more rapid with *NN*-dideuteroaniline than with aniline in the presence of acetic acid [$k_H/k_D = 0.95$] and rather slower in the presence of pyridine [$k_H/k_D = 1.04$].



All of these results suggest that an intermediate product (XIX) is formed, the breakdown of which is accelerated both by pyridine or the amine (proton–acceptors) and by bifunctional catalysts such as carboxylic acids and pyrid-2-one[104]. Reaction proceeds via the complexes (XX) and (XXI). The bifunctional compounds then act, on the one hand, as Brønsted acids (proton–donors), activating the nitrogen in the α position of the heterocycle, and on the other hand as proton–acceptors (the carbonyl oxygen or the nitrogen in the pyrid-2-one), drawing off hydrogen from the amine[22]).

The hypothetical formation of an intermediate complex ion

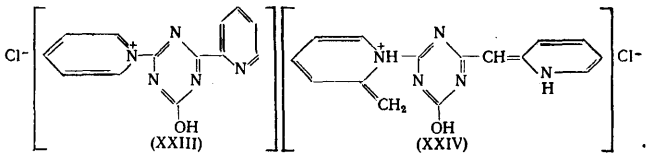


(XXII)

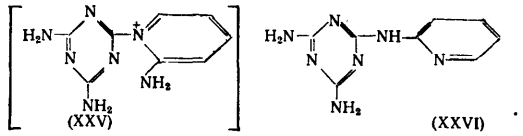
is improbable, for the hydroxy-proton of the acid would then facilitate the elimination of chlorine. However, this is inconsistent with the fact that replacement of the chlorine atom in 1-chloro-2,4,6-trinitrobenzene, which is similar in reactivity to cyanuryl chloride, is not catalysed by carboxylic acids.

Cyanuryl chloride and other chlorinated triazines react not only with aliphatic and aromatic primary and secondary amines containing one functional group[35,38,39,72,99,105] but also with aminophenols[106], arylsulphonylarylamines[43], and aminoarenesulphonamides[107]. Similar behaviour is shown by compounds in which the amino-group is not attached to carbon, such as arenesulphohydrazides.[108], sulphonamides[109], and hydrazines[110], salts of urea[51] and its derivatives, as well as thiourea and its derivatives[51]. Heterocyclic amines have also been employed in this reaction, such as 8-amino-6-methoxyquinoline[42], 4,6-diamino-2-methylquinoline[111], *N*-3-aminopropylpiperidine[112], 2-aminopyridone[113], and 4,6-diaminoquinaldine[49], as well as piperazine, piperidine, and morpholine[38,39,99,113].

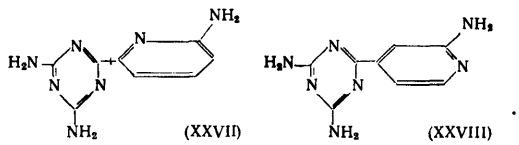
Tertiary amines, although usually employed as neutralising agents in reactions between chlorinated triazines and compounds containing a mobile hydrogen atom, react in several cases with chlorotriazines to form quaternary ammonium salts[114]. Analogous compounds are formed also with pyridine (see XIVa)[71]; under different conditions (XXIII) is formed[71]. If pyridine is replaced by 2-methylpyridine, the compound (XXIV) is obtained[115].



Reaction of 2-aminopyridine with 2,4-diamino-6-chlorotriazine involves the intermediate formation of a quaternary ammonium salt (XXV), the final product of the reaction being 2,4-diamino-6-2′-pyridylaminotriazine (XXVI)[113].



The isomeric compounds (XXVII) and (XXVIII) are formed as byproducts



Numerous reactions of cyanuryl chloride and other chlorinated triazines with more complicated amines are known, the latter including aminoazo-compounds, aminoanthraquinones, and other cyclic compounds of practical value [52,57].

3. Reactions with Alcohols and Phenols

Cyanuryl chloride can react with alcohols [73] in stages. Owing to the weaker deactivating influence of the OAlk group in comparison with NHAlk, NHAr, and NAlkAr, however, the stepwise character of the process is less clearly marked than in the reaction with amines. The stepwise character of the reaction with phenols [116] is still less strongly developed, for the same reason.

Replacement of chlorine by OAlk is easily accomplished by treating cyanuryl chloride with alkoxides [117-119] or with alcohols in the presence of bases [117]. Depending on the amount and nature of the alkaline reagent, the process can occur in stages [73]; it is preferable to use sodium bicarbonate, carbonate, or hydroxide. However, in the presence of caustic soda the reaction may be accompanied, even on cooling, by replacement of all the chlorine atoms. For example, the gradual addition of a concentrated solution of sodium hydroxide to a cooled suspension of cyanuryl chloride in allyl alcohol [120] may yield triallyloxytriazine.

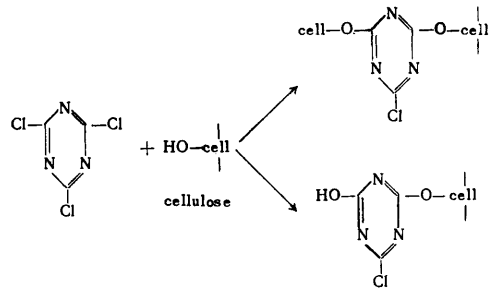
The stepwise interaction of cyanuryl chloride with various alcohols has been studied [121] in the presence of calcium carbonate between 0° and 35°, and the successive formation of mono-, di-, and tri-alkoxy-derivatives of triazine has been established. Measurement of the quantity of carbon dioxide evolved gave the rate of the process, and showed that reaction is more rapid with the lower alcohols. The sequence of alcohols according to their ability to replace the chlorine atom in chlorotriazine is (increasing from left to right) — isopropanol, n-propanol, n-butanol, ethanol, and methanol.

Primary alcohols containing negative substituents, such as trifluoro-, tribromo-, and trinitroxy-methylethanol, and 2-methyl-2-nitropropanol, are also able, in the presence of an alkaline reagent, to replace the chlorine atoms in cyanuryl chloride with formation of the corresponding ethers. Substitution does not take place with nitroethanol and 2-nitrobutan-1-ol, probably because primary and secondary nitro-compounds exist in alkaline medium as *aci*-forms; these react with cyanuryl chloride at the *aci*-hydrogen atom to form an unstable ester, which cannot be isolated [122].

In several cases the presence of an alkaline reagent is insufficient for the reaction to succeed, and considerably better results are obtained by using 2,6-dialkylpyridines to combine with the acids [123], especially good results being obtained with 2,4,6-trimethylpyridine [36].

Alkali-metal alkoxides, even in equivalent proportions, usually yield with cyanuryl chloride only the triethers [117,124-126]. Cases are known in which the three chlorine atoms are substituted in the presence of an alkali metal. This occurs with cyanuryl chloride and 2,3-epoxypropanol [127] in the proportions 1 : 3 (in the presence of sodium) in anhydrous medium (for example benzene) at 0–15°, the yield of 2,4,6-trisepoxypropyltriazine being 95%. The reaction with 1-chloro-2,3-epoxypropane is similar; the mechanism of the reaction is not indicated.

In the presence of alkalis cyanuryl chloride and other chlorotriazines are able to react with cellulose. The reaction is analogous to benzoylation or acetylation, and takes place both in organic solvents [128,129] and in water [81]. In the latter case the main reaction is accompanied by hydrolysis. In aqueous medium such hydrolysis has prevented the replacement of only one chlorine atom with formation of a cellulose ether and the dichloride of cyanuric acid.



In the absence of acid-binding reagents, heating cyanuryl chloride with alcohols yields cyanuric acid and hydrogen chloride, the degree of etherification being slight. At low temperatures, however, cyanuryl chloride reacts with methanol to form the triether, reaction being more rapid than in the presence of such reagents as $NaHCO_3$ and $CaCO_3$. The difference in reaction velocity is due to the catalytic action of the hydrogen chloride evolved [130].

In contrast to alcohols, phenols react with cyanuryl chloride and other chlorinated triazines with greater difficulty. Reaction requires a fairly high temperature or the use of alkali-metal phenoxides. Thus when cyanuryl chloride (1 mole) reacts with sodium phenoxide (3 moles) in aqueous acetone at 25°, all three chlorine atoms are replaced to give a 95% yield of the triether [116]. In order to obtain the same compound from phenol, the temperature must be raised to 170–200°. [116,131]

Although the stepwise character of the reaction of cyanuryl chloride with phenols is smoothed out, owing to the weaker deactivating influence on the remaining chlorine atoms of the OAr group compared with OAlk and to the lower reactivity of phenols, it is possible by suitable choice of the reaction conditions to replace the chlorine atoms in cyanuryl chloride successively by phenoxy-groups [116,117,132]. The Cl atoms in 2-amino-4,6-dichlorotriazine can also be replaced successively by OAr [116]. When the reaction is first carried out with phenol and sodium carbonate at 65°, 2-amino-4-chloro-6-phenoxytriazine is obtained; when this is treated with sodium phenoxide at 100°, 2-amino-4,6-diphenoxytriazine is formed. The latter is obtained also when 2-amino-4,6-dichlorotriazine is treated with sodium phenoxide at 100°. 2,4-Diamino-6-phenoxytriazine can be prepared in a similar manner from the corresponding monochloro-derivative; when an amino-derivative of chlorotriazine is treated with phenol itself, substitution takes place only at 200°, the amino-group being partly replaced by the phenoxy-group [116].

The best results in stepwise substitution of the chlorine atoms are achieved in the presence of pyridine, 2,6-dimethylpyridine, 2-methylquinoline, and 2,4,6-trimethylpyridine [75].

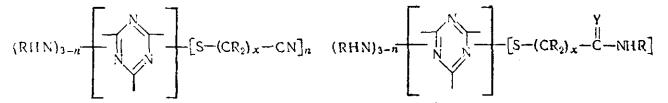
Phenols containing an aldehyde group react smoothly. Thus gradual addition of an alcoholic solution of *o*-, *m*-, or *p*-hydroxybenzaldehyde to cyanuryl chloride in acetone yields the 2,4,6-trisformylphenoxytriazine. This latter compound reacts in acid medium with 4-oxo-2-thiothiazolidine and its 3-ethyl and 3-phenyl derivatives to form the

corresponding 2,4,6-tris-(4-oxo-2-thiothiazolidin-5-ylidenemethylphenoxy)triazines, which possess strong fungicidal properties[37].

4. Reactions with Sulphur-Containing Compounds

Cyanuryl chloride and other chlorinated triazines react with thiols or their alkali-metal derivatives to form sulphides. The chlorine atoms are exchanged for alkylthio- and arylthio-groups still more readily[75] than for alkoxy- and aryloxy-groups. For example, one chlorine atom in cyanuryl chloride is exchanged at -25° to -30° by the action of methanethiol, and at 0° by the action of ethanethiol. Owing to the great activity of thiols, reaction takes place more readily with substituted chlorotriazines too[75].

Various thiol derivatives — mercapto-nitriles[133], mercapto-amides[134], and their salts — have been used in reactions with cyanuryl chloride, when compounds of types (XXIX) and (XXX) are formed depending on the conditions.



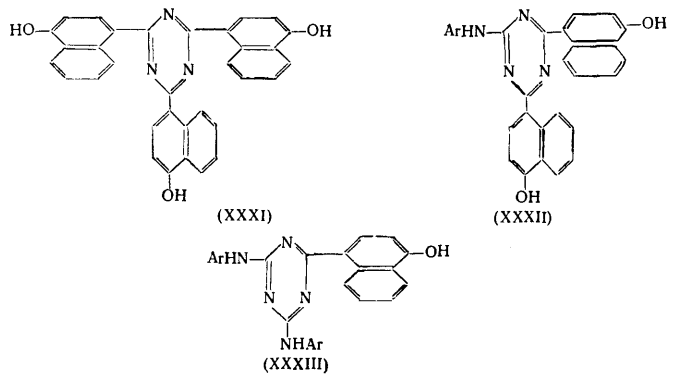
(XXIX) (XXX)

Cyanuryl chloride and other chlorinated triazines react also with the following compounds — thiocyanic acid and its salts[135], thiourea[136], 5-substituted 4-methyl-2-mercaptothiazoles[137], ethyl 2-mercaptothiazol-4-ylacetate[138], dialkyldithiocarbamates[34,139], the sodium derivative of 2-mercaptobenzothiazole[140], thioglycollic acid[141], and mercaptoalkanesulphonates[142]. The reaction products obtained from cyanuryl chloride and many of the above compounds exhibit the properties of insecticides, fungicides, and weed-killers. An especially active fungicide is 6-chlorotriazine-2,4-diyl bisdimethyldithiocarbamate, which is prepared from cyanuryl chloride and sodium dimethyldithiocarbamate[34].

Sodium hydrogen sulphide reacts similarly to thiols and their metallic derivatives with cyanuryl chloride[143], the monosodium salt of trithiocyanuric acid being formed.

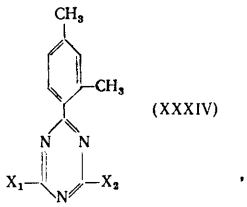
5. Reactions with Formation of a C–C Bond

Cyanuryl chloride can undergo the Friedel–Crafts, Wurtz, and Grignard reactions, with formation of aryl- and alkyl-triazines. For example, cyanuryl chloride and other chlorotriazines can be condensed with phenols[7,64], in particular with 1-naphthol to give the compounds (XXXI)–(XXXIII).



(XXXI) (XXXII) (XXXIII)

Interaction between cyanuryl chloride, benzene, and aluminium chloride has been reported[144]. However, no success was achieved[64] in obtaining a phenyl- or triphenyl-triazine derivative in this way. Later the reaction of cyanuryl chloride with benzene or its homologues in the presence of aluminium chloride and a small quantity of water (at the boiling point) has been patented in the German Federal Republic[145]; 2,4,6-triphenyltriazine and 2,4,6-tri-*o*(and *p*)-tolyltriazines have been obtained in this way. In the absence of water, without the temperature being raised, a compound of general formula



(XXXIV)

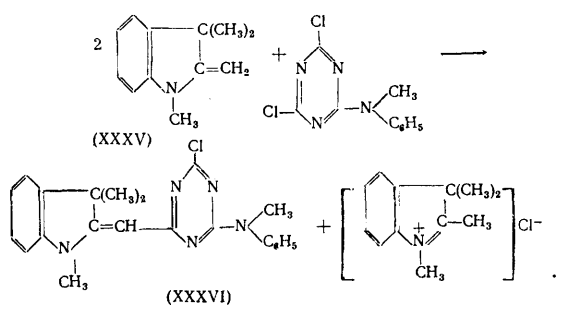
could be obtained in which X_1 represents chlorine and X_2 represents chlorine or 2,4-dimethylphenyl. The reaction is carried out in the presence of aluminium chloride and in an inert solvent; depending on the quantity of xylene, the products are 2,4-dichloro-6-(2,4-dimethylphenyl)triazine and 2-chloro-4,6-bis-(2,4-dimethylphenyl)triazine, which are intermediates for vat dyes[146].

Cyanuryl chloride undergoes the Wurtz–Fittig reaction with iodobenzene and bromophenetole, to form the corresponding triaryltriazines[147–149].

Reaction of cyanuryl chloride with a Grignard reagent can yield, depending on the reaction conditions, mono-, di-, or tri-alkyl or -aryl derivatives containing either identical or different radicals[150–153].

Carbon–carbon bonds are formed in the reaction of cyanuryl chloride with diethyl malonate. Only one chlorine atom is replaced if the ester is used in the base-catalysed reaction. With sodiomalonic ester, all three chlorine atoms can be replaced[6].

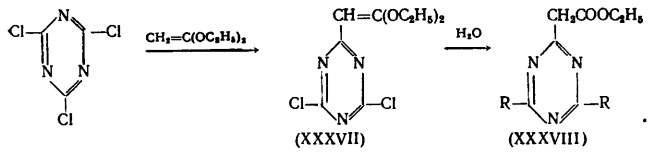
Cyanuryl chloride reacts similarly with other compounds containing an active methylene group. Thus, depending on the reaction conditions, 1,3,3-trimethyl-2-methyleneindoline (XXXV) can successively substitute the chlorine atoms to form the corresponding derivatives, for example 2,4-dichloro-6-(1,3,3-trimethylindolin-2-ylidenemethyl)triazine[154,155]. If one chlorine atom of cyanuryl chloride is first substituted by means of *N*-methylaniline, and then a second chlorine atom by means of (XXXV), the monochloro-derivative (XXXVI) is formed:



(XXXV) (XXXVI)

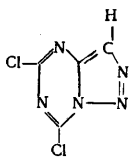
Similar behaviour to (XXXV) is shown by other heterocyclic bases containing methylene groups, for example 1,2-dihydro-1-methyl-2-methylenequinoline, 2,3-dihydro-3-methyl-2-methylenebenzothiazole, and also 1,1-bis-*p*-dimethylaminophenylethylene[156].

1,1-Diethoxyethylene also reacts at the methylene group with cyanuryl chloride[157]. The product (XXXVII) hydrolyses to the esters (XXXVIII), those in which R represents Cl or OH being formed in greater or smaller amounts depending on the conditions:



(XXXVII) (XXXVIII)

Cyanuryl chloride reacts with diazomethane[158], when only one chlorine atom is usually replaced by the α-diazoalkyl group; a second chlorine atom is replaced with difficulty. The reaction is carried out with excess of diazomethane, which also acts as a neutralising agent, being decomposed by hydrochloric acid into methyl chloride and nitrogen. The product is given the structure

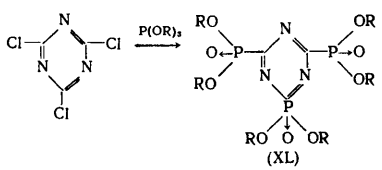


(XXXIX)

Reduction of 4,6-disubstituted 2-diazomethyltriazines with hydrogen sulphide or a thiol yields the corresponding 4,6-disubstituted triazine-2-aldehyde hydrazones, which can be converted into the free aldehydes. When 2,4-dichloro-6-diazomethyltriazine is reduced with ethanethiol in the presence of alkali, 4,6-dimercaptotriazin-2-al hydrazone is first formed, and then the corresponding aldehyde[159].

6. Various Substitution Reactions

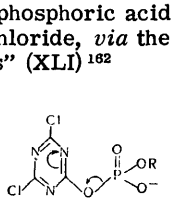
The reaction of cyanuryl chloride with trialkyl phosphites is analogous to the Arbuzov reaction for alkyl halides and results in the formation of alkylphosphonic esters. The three chlorine atoms are readily substituted, with the formation of triesters of triazinetriphosphonic acid (XL)[160]



(XL)

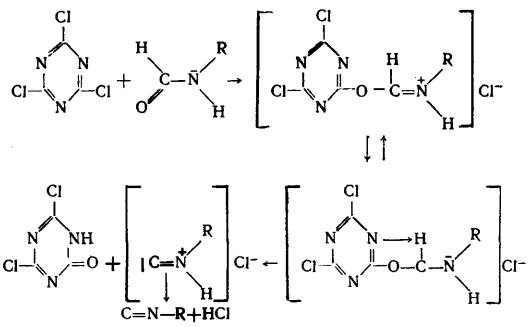
Other organophosphorus compounds derived from cyanuryl chloride have been obtained[161].

Various diesters of phosphoric acid can also be obtained by means of cyanuryl chloride, *via* the intermediate formation of "enol phosphates" (XLI)[162]



(XLI)

With sodium azide cyanuryl chloride forms the dangerously explosive cyanuryl triazide[6]. With monosubstituted formamides it forms the corresponding isocyanides, the reaction being represented by the scheme[163]



The action of hydrogen halides on chlorinated triazines results in halogen exchange. Thus reaction of 57% hydriodic acid with cyanuryl chloride in the cold yields a mixture of 2,4,6-triiodo- and 2-chloro-4,6-diiodotriazines[6]. Elimination of methoxyl from 2,4-dichloro-6-*o*-methoxyphenyltriazine with hydrogen bromide is accompanied by replacement of chlorine by bromine. In order to obtain 2,4-dichloro-6-*o*-hydroxyphenyltriazine, therefore, the bromine must subsequently be displaced by chlorine by the vigorous action of hydrogen chloride[82,164].

Replacement of the chlorine by fluorine atoms was at first accomplished by treating cyanuryl chloride with hydrogen fluoride[165], and later with potassium fluorosulphate[166]. In the latter case partial substitution products are formed as well[167]. Triazine fluorides have also been obtained by treating the corresponding chloro-derivatives with the Swarts reagent (a mixture of about 10 moles of antimony trifluoride, 1 mole of antimony trichloride, and 3 moles of chlorine[168]). The triazine fluorides are very toxic.

7. Reduction of Cyanuryl Chloride and Other Chlorinated Triazines

Cyanuryl chloride is unaffected by most strong reducing agents. It is not reduced by hydrogen iodide. On treatment with lithium tetrahydroaluminate in ether at -10°, 2,4-dichlorotriazine is obtained[169,170]. 2,4-Dichloro-6-dimethylaminotriazine is also formed owing to reductive cleavage of the triazine ring in the initially formed dichlorotriazine, and subsequent reaction of the resulting dimethylamine with unchanged cyanuryl chloride.

Under ordinary conditions reaction of cyanuryl chloride with lithium tetrahydroaluminate in ether yielded only inorganic reaction products, formed by decomposition of the initially produced triazine under the influence of aluminium chloride, which is also a product of the reaction[6].

Other chlorotriazines can be reduced to the corresponding substituted triazines. Thus 2-amino-4,6-dichlorotriazine and 2,4-diamino-6-chlorotriazine are reduced by hydrogen iodide in the presence of phosphorus to 2-amino- and 2,4-diamino-triazines[171]. 2-Amino-, 2-alkylamino-, and 2-phenoxy-triazines have been obtained by hydrogenating the corresponding chloro-derivatives in the presence of a palladium–carbon catalyst[151]; 2,4-dimethoxytriazine has been prepared in a similar manner[172].

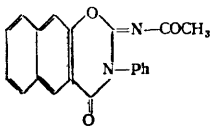
Sometimes, however, direct replacement of chlorine by hydrogen does not go well owing to poisoning of the catalyst. In these cases an indirect method of reduction is employed:

chlorine is first replaced by a methylthio-group, and the resulting derivative is then reduced in the presence of Raney nickel[173,174].

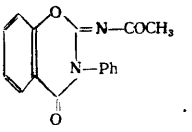
8. Reactions with Transformation of the Ring

Several of the substitution reactions of cyanuryl chloride take place under fairly severe conditions, but rupture of the triazine ring is not observed. Ring cleavage accompanying reduction of cyanuryl chloride with lithium tetrahydroaluminate is due to the intermediate formation of triazine. The cyclic system of cyanuryl chloride breaks down only on treatment with concentrated sulphuric acid at 150°.[64]

Reactions involving breakdown of the ring are known with several triazine derivatives which are obtained from cyanuyrl chloride. Thus when the products from the reaction of cyanuryl chloride with anilides of 3-hydroxy-2-naphthoic and salicylic acids are boiled with acetic anhydride in the presence of a few drops of pyridine, substances are formed which can be proved to have the structures (XLII) and (XLIII)[175]. These could result only from opening of the triazine ring.

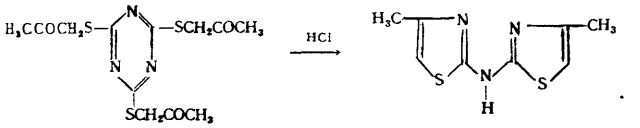


(XLII)

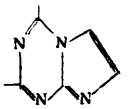


(XLIII)

Other triazine derivatives also show ring cleavage. For example, 2,4,6-triacetonylthiotriazine on treatment with hydrochloric acid undergoes the following reaction[176]



From 2,4-dichloro-6-hydroxyethylaminotriazine have been obtained, by a series of reactions, 2,4-disubstituted 6,7-dihydroimidazo[1,2-*a*]triazines[177]. Although this does not involve opening of the ring, the "aromatic" triazine system is disrupted by reaction at a cyclic double bond with formation of the bicyclic system



1. J.Liebig, Pogg.Ann., 15, 359, 622 (1829).
2. O.Diels, Ber., 32, 691 (1899).
3. F.Chattaway and J.Wadmore, J.Chem.Soc., 81, 200 (1902).
4. I.Klotz and T.Askonnis, J.Amer.Chem.Soc., 69, 801 (1947).
5. H.Halverson and R.Hirt, J.Chem.Phys., 19, 711 (1951).
6. E.M.Smolin and L.Rapoport, "s-Triazines and Derivatives", Interscience, New York, 1959, p.48.
7. K.Matsui, J.Soc.Org.Synth.Chem., Japan, 17, 528 (1959).
8. D.A.W.Adams, Dyer, 118 257 (1957).
9. T.Vickerstaff, Dyer, 116, 855 (1956).
10. K.A.Lunn, Chem.Rundschau, 11, 21 (1958).
11. T.Vickerstaff, J.Soc.Dyers and Colourists, 73, 237 (1957).
12. T.Vickerstaff, Melliand Textilber., 39, 765, 905 (1958).
13. T.Vickerstaff, Textil-Rundschau, 13, 267 (1958).
14. T.Vickerstaff, Tinctoria (Milano), 56, 185 (1959).
15. F.Schlaeppi, Amer.Dyestuff Reporter, 47, 377 (1958).
16. J.Wegmann, Textil-Rundschau, 13, 323 (1958).
17. J.Wegmann, Textil Praxis, 13, 1056 (1958).
18. J.Wegmann, J.Soc.Dyers and Colourists, 76, 205 (1960).
19. K.J.Bardt, Textile J.Australia, 34, 1369 (1960); Chem. Zentr., 132, 2102 (1961).
20. D.F.Scott and T.Vickerstaff, J.Soc.Dyers and Colourists, 76, 104 (1960).
21. H.Zollinger, "Chemie der Azofarbstoffe" (Translated into Russian), Goskhimizdat, Leningrad, 1960, pp.215, 299, 331.
22. H.Zollinger, Angew.Chem., 73, 125 (1961).
23. H.Hiyama and O.Manabe, J.Soc.Org.Synth.Chem., Japan, 16, 75 (1958); Ref.Zhur.Khim., 66750 (1959).
24. M.A.Chekalin, Tekstil.Prom., 21, No.1, 40 (1961).
25. A.G.Levinton, Tekstil.Prom., 18, No.5, 73 (1958).
26. A.G.Emel'yanov, Tekstil.Prom., 18, No.7, 40 (1958).
27. V.I.Mur and G.N.Vorozhtsov, Zhur.Obshch.Khim., 30, 1981 (1960).
28. A.A.Kharkharov and I.Ya.Kalantarov, "Aktivnye Krasiteli i Ikh Primenenie v Tekstil'noi Promyshlennosti" (Reactive Dyes and Their Application in the Textile Industry), Rostekhizdat, Moscow, 1961.
29. R.Kovache, R.Lévy, G.Garnier, and C.Magnouk, Chimie et Industrie, 71, 1136 (1954).
30. J.M.Harvey, Phytopathology, 45, 137 (1955); Chem.Abs., 49, 8545 (1955).
31. C.N.Wolf, U.S.P. 2720480 (1956).
32. A.Gast, E.Knüsli, and H.Gysin, Experientia, 12, 146 (1956).
33. Swiss P. 338324; Chimia (Switz.), 14, 66 (1960).
34. G.Matolcsy, J.Hamrán, and A.Végh, Magyar Kém. Folyóirat, 65, 282 (1959); Chem.Zentr., 132, 1566 (1961).
35. H.Koopman and J.Daams, Rec.Trav.chim., 77, 235 (1958).
36. H.Doopman and J.Daams, Rec.Trav.chim., 79, 83 (1960).
37. G.I.Allan and G.G.Allan, Rec.Trav.chim., 78, 375 (1959).
38. L.E.Sventsitskaya, A.A.Kropacheva, and S.I.Sergievskaya, Zhur.Obshch.Khim., 28, 1601 (1958).
39. G.I.Braz, V.K.Antonov, and K.N.Kurdyumova, Zhur. Obshch.Khim., 28, 2972 (1958).
40. J.A.Hendry, F.L.Rose, and A.L.Walpole, J.Chem.Soc., 1134 (1958).
41. F.C.Schaefer, J.Amer.Chem.Soc., 77, 5928 (1955).
42. W.Cuthbertson and J.Moffatt, J.Chem.Soc., 561 (1948).
43. R.H.Vogel, U.S.P. 2599145; Chem.Abs., 47, 2207 (1953).
44. E.A.H.Friedheim, J.Amer.Chem.Soc., 66, 1775 (1944).
45. E.A.H.Friedheim, U.S.P. 2295574; Chem.Abs., 37, 1228 (1943).
46. E.A.H.Friedheim, U.S.P. 2422724; Chem.Abs., 41, 6900 (1947).
47. C.K.Banks, O.M.Gruhzit, E.W.Tillitson, and J.Controulis, J.Amer.Chem.Soc., 66, 1771 (1944).
48. C.K.Banks and J.Controulis, J.Amer.Chem.Soc., 68, 944 (1946).
49. J.N.Ashley, S.S.Berg, and R.D.MacDonald, J.Chem.Soc., 4525 (1960).
50. B.P. 318275 (1930).

51. G.F.D'Alelio, U.S.P. 2394042; Chem.Abs., 40, 3144 (1946).
52. French P. 824940 (1938); Chem.Abs., 32, 5618 (1938).
53. U.S.P. 2061520 (1936); Chem.Abs., 31, 706 (1937).
54. L.H.Marcon, Teintex, 26, 87 (1961).
55. B.P. 796524; Chem.Abs., 53, 1762 (1959).
56. B.P. 847725, J.Soc.Dyers and Colourists, 77, 82 (1961).
57. V.I.Mur, Vestnik Tekh.Ekonomicheskoi Informatsii, No.9, 32 (1962).
58. I.M.Kogan, "Khimiya Krasitelei" (The Chemistry of Dyes), Goskhimizdat, Moscow, 1956, p.165.
59. K.Venkataraman, "The Chemistry of Synthetic Dyes" (Translated into Russian), Goskhimizdat, Leningrad, 1957, p.657.
60. W.Widmer and A.Fasciati, U.S.P. 2643996; Chem.Abs., 47, 10236 (1953).
61. K.Seitz and W.Anderau, U.S.P. 2763641; Chem.Abs., 51, 3153 (1957).
62. A.Galiezi, K.Weber, and M.Jost, Swiss P. 348547; Chem. Zentr., 132, 4712 (1961).
63. K.Matsui and I.Sakamoto, J.Soc.Org.Synth.Chem., Japan, 18, 175 (1960).
64. H.E.Fierz-David and M.Matter, J.Soc.Dyers and Colourists, 53, 424 (1937).
65. D.W.Davies, Trans.Faraday Soc., 51, 449 (1955).
66. C.Grundmann and A.Kreutzberger, J.Amer.Chem.Soc., 76, 632 (1954).
67. C.Grundmann and A.Kreutzberger, J.Amer.Chem.Soc., 76, 5646 (1954).
68. A.E.Chichibabin, "Osnovnye Nachala Organicheskoi Khimii" (Fundamental Principles of Organic Chemistry), Vol.2, Goskhimizdat, Moscow, 1958, pp.211, 212.
69. L.Hinkel, E.Ayling, and J.Beynon, J.Chem.Soc., 674 (1935).
70. C.Grundmann and A.Kreutzberger, J.Amer.Chem.Soc., 77, 44 (1955).
71. S.Saure, Chem.Ber., 83, 335 (1950).
72. J.T.Thurston, J.R.Dudley, D.W.Kaiser, I.Hechenbleikner, F.C.Schaefer, and D.Holm-Hansen, J.Amer.Chem.Soc., 73, 2981 (1951).
73. J.R.Dudley, J.T.Thurston, F.C.Schaefer, D.Holm-Hansen, F.C.Hull, and P.Adams, J.Amer.Chem.Soc., 73, 2986 (1951).
74. C.Grundmann and E.Kober, J.Amer.Chem.Soc., 79, 944 (1957).
75. H.Koopman, "Nieuwe Herbicide 1,3,5-Triazine Derivaten", Thesis, Groningen, 1957.
76. A.Kreutzberger, J.Amer.Chem.Soc., 79, 2629 (1957).
77. C.Grundmann and G.Weisse, Chem.Ber., 84, 684 (1951).
78. H.Schroeder and C.Grundmann, J.Amer.Chem.Soc., 78, 2447 (1956).
79. E.Ott, Ber., 52, 658 (1919).
80. J.F.Bunnett and R.E.Zahler, Chem.Rev., 49, 309 (1951).
81. J.Wegmann, Melliand Textilber., 39, 1006 (1958).
82. V.I.Mur, Zhur.Obshch.Khim., 29, 2267 (1959).
83. H.H.Jaffé, Chem.Rev., 53, 222 (1953).
84. K.Matsui, K.Hagiwara, and Y.Soeda, J.Soc.Org.Synth. Chem., Japan, 18, 184 (1960).
85. M.Goi, J.Soc.Org.Synth.Chem., Japan, 18, 327 (1960).
86. W.Pearlman and C.K.Banks, J.Amer.Chem.Soc., 70, 3726 (1948).
87. O.Diels, Ber., 32, 691 (1899).
88. P.Klason, J.prakt.Chem., [ii], 33, 290 (1886).
89. A.Sérullas, Annalen, 10, 43 (1834).
90. P.Klason, J.prakt.Chem., [ii], 34, 157 (1886).
91. C.K.Banks, J.Amer.Chem.Soc., 66, 1127 (1944).
92. J.Sauer and R.Huisgen, Angew.Chem., 72, 294, 301 (1960).
93. J.F.Bunnett and R.E.Zahler, Chem.Rev., 49, 273, 331 (1951).
94. E.A.H.Friedheim, U.S.P. 2390529; Chem.Abs., 40, 5070 (1946).
95. E.A.Friedheim, E.Krummenacher, H.Gubler, and O.Kaiser, U.S.P. 1625531; Chem.Abs., 21, 2193 (1927).
96. V.P.Wystrach, D.W.Kaiser, and F.C.Schaefer, J.Amer. Chem.Soc., 77, 5915 (1955).
97. A.Hofmann, Ber., 18, 2755 (1885).
98. D.W.Kaiser, J.T.Thurston, J.R.Dudley, F.C.Schaefer, I.Hechenbleikner, and D.Holm-Hansen, J.Amer.Chem. Soc., 73, 2984 (1951).
99. B.W.Horrom, J.Amer.Chem.Soc., 76, 3032 (1954).
100. C.K.Banks, J.Amer.Chem.Soc., 66, 1131 (1944).
101. B.Bitter and H.Zollinger, Angew.Chem., 70, 246 (1958).
102. B.Bitter and H.Zollinger, Helv.Chim.Acta, 44, 812 (1961).
103. M.Goi, J.Soc.Org.Synth.Chem., Japan, 18, 337 (1960).
104. C.G.Swain and J.F.Brown, J.Amer.Chem.Soc., 74, 2538 (1952).
105. D.Matolchi, L.Gereg, and A.Veg, J.Appl.Chem., 11, 136 (1961).
106. G.D'Alelio, U.S.P. 2393755; Chem.Abs., 40, 2166 (1946).
107. G.D'Alelio and H.White, J.Org.Chem., 24, 643 (1959).
108. G.D'Alelio and R.Becker, J.Org.Chem., 25, 202 (1960).
109. G.D'Alelio and R.Becker, J.Org.Chem., 25, 643 (1960).
110. R.S.Long and F.Body, U.S.P. 2679499; Chem.Abs., 49, 2083 (1955).
111. H.Jensch, German P. 606497; P.Friedländer-Fortschrittee der Teerfarbenfabrikation, 21, 539 (1937).
112. H.S.Moscher and F.C.Whitmore, J.Amer.Chem.Soc., 67, 662 (1945).
113. W.K.Detweiler and E.D.Amstutz, J.Amer.Chem.Soc., 74, 1483 (1952).
114. Austral P. 174377; Chem.Abs., 47, 12422 (1953).
115. M.C.Menon, B.Nath, and J.S.Aggarwal, Chem.and Ind., 717 (1956).
116. F.C.Schaefer, J.T.Thurston, and J.K.Dudley, J.Amer. Chem.Soc., 73, 2990 (1951).
117. A.Hofmann, Ber., 19, 2061 (1886).
118. O.Diels and M.Liebermann, Ber., 36, 3191 (1903).
119. G.I.Braz, Zhur.Obshch.Khim., 25, 1413 (1955).
120. H.Schulze, East German P. 18104; Chem.Zentr., 133, 1032 (1962).
121. K.Matsui, K.Hagiwara, and A.Hayashi, J.Soc.Org.Synth. Chem., Japan, 18, 97 (1960).
122. A.J.Matuszko and M.S.Chang, J.Org.Chem., 27, 677 (1962).
123. H.Koopman, "Nieuwe Herbicide 1,3,5-Triazine Derivaten", Thesis, Chapter II, Section I, Groningen, 1957.
124. I.Ponomarev, Ber., 15, 513 (1882).
125. I.Ponomarev, Ber., 18, 3261 (1885).
126. V.I.Mur, Zh.A.Gorbunova, and A.I.Korolev, Zhur.Vses. Khim.Obshch.Mendeleeva, 6, 586 (1961).
127. A.Wende and H.Priebe, German P. 1105875; Chem. Zentre., 132, 15930 (1961).
128. French P. 687301; Chem.Abs., 25, 812 (1931).
129. J.Warren, J.D.Reid, and C.Hamalainen, Textile Res.J., 22, 584 (1952).
130. K.Matsui and J.Semo, J.Soc.Org.Synth.Chem., Japan, 18, 105 (1960).
131. F.C.Schaefer, U.S.P. 2560824; Chem.Abs., 46, 1596 (1952).
132. R.Hirt, H.Nidecker, and R.Rechtold, Helv.Chim.Acta, 33, 1367 (1950).
133. G.D'Alelio and J.Underwood, U.S.P. 2295561; Chem. Abs., 37, 1131 (1943).
134. G.D'Alelio and J.Underwood, U.S.P. 2295562; Chem. Abs., 37, 1131 (1943).

135. J.J.Roemer and D.W.Kaiser, U.S.P. 2 650 220; Chem. Abs., 48, 9412 (1954).
136. O.Manabe, H.Hiyama, *et al.*, J.Chem.Soc.Japan, Ind. Chem.Sect., 61, 1180 (1958); see K.Matsui, J.Soc.Org. Synth.Chem., Japan, 17, 528 (1959).
137. K.E.Creed, J.J.D'Amico, M.W.Harman, and R.O.Zerbe, Ind.Eng.Chem., 46, 808 (1954).
138. J.J.D'Amico and M.W.Harman, J.Amer.Chem.Soc., 77, 476 (1955).
139. J.J.D'Amico and M.W.Harman, J.Amer.Chem.Soc., 78, 5345 (1956).
140. B.P. 88 547; J.Soc.Dyers and Colourists, 78, 195 (1962).
141. B.P. 887 723; J.Soc.Dyers and Colourists, 78, 196 (1962).
142. French P. 1 194 323; Chem.Zentr., 132, 17 010 (1961).
143. A.Hofmann, Ber., 18, 2196 (1885).
144. G.Barsky and I.V.Giles, U.S.P. 1 734 029; Chem.Abs., 24, 381 (1930).
145. H.Huemer, German P. 1 009 190; Chem.Abs., 53, 18 075 (1959).
146. B.P. 884 802 (1961).
147. P.Klason, J.prakt.Chem., [ii], 35, 82 (1887).
148. F.Krafft, Ber., 22, 1759 (1889).
149. O.Diels and M.Liebermann, Ber., 36, 3191 (1903).
150. A.Ostrogovich, Chem.-Ztg., 36, 739 (1912).
151. R.Hirt, H.Nidecker, and R.Berchtold, Helv.Chim.Acta, 33, 1365 (1950).
152. U.S.P. 1 911 689; Chem.Abs., 27, 3952 (1933).
153. P.V.Laakso, R.Robinson, and H.P.Vandrewala, Tetrahedron, 1, 103 (1957).
154. German P. 825 089; Chem.Abs., 49, 11 728 (1955).
155. German P. 828 841; Chem.Abs., 50, 11 371 (1956).
156. M.Coenen, Annalen, 633, 78 (1960).
157. E.Kober, J.Org.Chem., 26, 4705 (1961).
158. C.Grundmann and E.Kober, J.Amer.Chem.Soc., 79, 944 (1957).
159. E.Kober and C.Grundmann, J.Amer.Chem.Soc., 80, 5547 (1958).
160. D.C.Marrison, J.Org.Chem., 22, 444 (1957).
161. U.S.P. 2 751 384; Chem.Zentr., 128, 4535 (1957).
162. R.Wittmann and F.Cramer, Angew.Chem., 73, 70 (1961).
163. R.Wittmann, Angew.Chem., 73, 219 (1961).
164. B.P. 691 520; Chem.Abs., 47, 12 827 (1953).
165. W.Kwasnik, Naturforsch.Med.Deutschland, 23, 243 (1949).
166. F.Seel and K.Ballreich, Chem.Ber., 92, 344 (1959).
167. D.W.Grisley, E.W.Gluesenkamp, and S.A.Heininger, J.Org.Chem., 23, 1802 (1958).
168. E.Kober and C.Grundmann, J.Amer.Chem.Soc., 81, 3769 (1959).
169. C.Grundmann and E.Beyer, J.Amer.Chem.Soc., 76, 1948 (1954).
170. A.Burger and E.Hornbaker, J.Amer.Chem.Soc., 75, 4579 (1953).
171. O.Diels, Ber., 32, 691 (1899).
172. I.Flament, R.Promel, and R.H.Martin, Helv.Chim.Acta, 42, 485 (1959).
173. C.Grundmann and E.Kober, J.Org.Chem., 21, 641 (1956).
174. C.Grundmann, H.Ulrich, and A.Kreutzberger, Chem.Ber., 86, 181 (1953).
175. B.S.Joshi, R.Srinivasan, R.V.Talavdekar, and K.Venkataraman, Tetrahedron, 11, 133 (1960).
176. A.Hantzsch, Ber., 61B, 1776 (1928).
177. R.Hinkens, R.Promel, and R.H.Martin, Helv.Chim.Acta, 44, 299 (1961).

Research Institute for Organic Intermediates and Dyes

U.D.C. 532.72

SELF-DIFFUSION AND INTERDIFFUSION IN POLYMER SYSTEMS

S.S.Voyutskii and V.L.Vakula

CONTENTS

I. Introduction 103
II. Methods for the experimental investigation of self-diffusion and interdiffusion in polymer systems 103
III. Mechanism of self-diffusion and interdiffusion of polymers 105
IV. Influence of time, temperature, and concentration on self-diffusion and interdiffusion in polymers 106
V. Influence of molecular structure and properties on self-diffusion and interdiffusion in polymers 107
VI. Importance of self-diffusion and interdiffusion in the processing and application of polymers 112

I. INTRODUCTION

During the past two decades the diffusion of substances of low molecular weight in high polymers has formed the subject of numerous researches by both Soviet and foreign investigators, among whom must be mentioned Reitlinger, Zhurkov, Ryskin, Malinskii, and Vasenin in the Soviet Union, and Barrer, Crank, Long, Park, Auerbach, Van Amerongen, McCall, Stamm, and many other workers abroad. In contrast, the phenomena of self-diffusion in polymers and of the diffusion of one polymer into another (interdiffusion) have remained little investigated because of the great experimental difficulties and the complexity of the theoretical interpretation. Nevertheless, these phenomena are of great scientific interest and immense practical importance. As we shall see below, very many properties of polymers are to some extent linked with the ability of flexible macromolecules or their segments to diffuse. The capacity for self-diffusion and interdiffusion of polymers is no less important for their processing and application.

The purpose of the present review is to summarise results on the self-diffusion and interdiffusion of polymers having flexible molecules (elastomers) and to outline directions for future research on this problem.

II. METHODS FOR THE EXPERIMENTAL INVESTIGATION OF SELF-DIFFUSION AND INTERDIFFUSION IN POLYMER SYSTEMS

The first experimental investigations of self-diffusion were based on a study of the self-adhesion of polymers, which several workers have shown[1-5] to depend on the interpenetration and intertwining of flexible macromolecules under the influence of thermal motion. The method consisted in placing two specimens of the same polymer in