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THE CHEMISTRY OF THE HALOGEN AZIDES

K. DEHNICKE

Fachbereich Chemie der Universität Marburg, Marburg, Federal Republic of Germany

I. Introduction

Although more than 80 yr have passed since the discovery of iodine azide by A. Hantzsch and M. Schümann (*59*), and the other halogen azides have been known for a long time [chlorine azide: 1908 by F. Raschig (*115*); bromine azide: 1925 by D. A. Spencer (*126*); fluorine azide: 1942 by J. F. Haller (*58*)], it is only in recent years that these azides have found use in preparative chemistry. Increasing knowledge of the properties has brought about a better understanding of the reaction pathways and improvement in the synthesis of the halogen azides and has facilitated their application in synthetic chemistry. In the field of organic chemistry, the work of A. Hassner *et al.* has shown the importance of iodine azide and bromine azide in olefinic addition, as the reaction products undergo numerous subsequent reactions. These topics were reviewed in 1971 (*76*). In inorganic chemistry, chlorine azide and iodine azide are predominant. The preferred type of reaction is the substitution of a halide ligand or an organic group by the azide

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group; however, oxidative additions and, for iodine azide, donor–acceptor complexes are also known. A summary of the properties of halogen azides was published in 1967 (*20*), followed in 1979 by a review of the development of iodine azide chemistry (*21*).

II. Preparation and Modes of Formation

A. FLUORINE AZIDE

Fluorine azide is best prepared from dry hydrazoic acid and fluorine in the gas phase (*2, 58*).

$$4HN_3 + 2F_2 \rightarrow 3FN_3 + N_2 + NH_4F$$

Decomposition reactions of the fluorine azide are avoided when the reactants are diluted with N_2 (*54*). [FN_3 is also formed as an intermediate product in the synthesis of N_2F_2 from fluorine and solid sodium azide, moistened with traces of water (*119*) and diluted with CaF_2 to avoid local rise in temperature (*111*).] At 35 to 45°C the reaction mixture yields N_2F_2, NF_3, and N_2, as well as FN_3 (*110*). For papers reviewing N—F compounds see (*17, 109*).

B. CHLORINE AZIDE

According to F. Raschig (*115*), chlorine azide is formed upon acidification of aqueous solutions of alkali hypochlorite and sodium azide with boric acid or acetic acid.

$$N_3^- + ClO^- + 2H^+ \rightarrow ClN_3 + H_2O$$

Because in this reaction chlorine azide is produced in high concentrations locally, explosions can occur. Later, Frierson *et al.* (*52*) obtained ether solutions of ClN_3 by passing gaseous chlorine through a suspension of silver azide in ether. For preparative purposes, the most convenient method is the reaction of chlorine gas, diluted with nitrogen, with an aqueous solution of sodium azide (*22*).

$$N_3^- + Cl_2 \xrightarrow[H_2O]{0°C} ClN_3 + Cl^-$$

After being dried with phosphorus pentoxide, the resulting chlorine azide can be used directly for further reactions (*8*). The process requires careful avoidance of pressure variations, as otherwise explosions are inevitable (*8*).

Apart from NF_2Cl, chlorine azide is also formed in the reaction of fluorine with a mixture of sodium chloride and sodium azide (*1*). Possibly ClN_3 exists in aqueous solutions of $NaN_3/FeCl_3/H_2O_2$, which are applied in radical addition of $Cl\cdot$ and $N_3\cdot$ to olefinic double bonds (*81*); (see Section IV,A). The complex C_6H_5—$I(Cl)N_3$, accessible by a reaction of $C_6H_5I(OAc)_2$ with trimethylsilyl azide and acetyl chloride in several steps, can be interpreted as an adduct of chlorine azide, which however decomposes, even at 0°C. It is also used for the addition of ClN_3 to olefinic double bonds (*141*) (see Section IV, A).

C. BROMINE AZIDE

Bromine azide was first prepared by D. A. Spencer (*126*), by passing a stream of bromine diluted with nitrogen over dry sodium azide. It is obtained as an orange-red and very explosive fluid.

$$NaN_3 + Br_2(g) \rightarrow NaBr + BrN_3$$

Even today this is the best method of preparing pure bromine azide; however, the slow reaction rate necessitates a long zone of contact. Caution is necessary, as violent explosions are apt to occur wherever liquid bromine comes into contact with powdered sodium azide (*37*)!

Solutions of bromine azide in hexane, carbon tetrachloride, and other inert solvents are obtained from silver azide and bromine when the suspension contains some dry sodium sulfate, to avoid decomposition of the BrN_3 by traces of water (*37*). For preparative purposes, solutions of bromine azide in dichloromethane or pentane can be prepared by addition of bromine to an agitated two-phase system held at 0°C, the aqueous phase of which consists of sodium azide and 30% HCl (*60*). It can be assumed that the hydrazoic acid formed here primarily is brominated.

$$HN_3 + Br_2 \rightarrow BrN_3 + HBr$$

D. IODINE AZIDE

Iodine azide has been known since 1900, from a paper by A. Hantzsch and M. Schümann (*59*), who obtained IN_3 in an ether suspension of silver azide with iodine.

$$AgN_3 + I_2 \rightarrow AgI + IN_3$$

The ether solutions are very unstable, especially when they contain traces of water. Higher stability is achieved by dry solutions of iodine azide in carbon tetrachloride, dichloromethane, benzene, and similar solvents. They are prepared from an excess of moist silver azide, which can be handled without risk, and iodine, in the presence of a drying agent like sodium sulfate (*23*). Evaporation of solutions in solvents with high vapor pressure, like CH_2Cl_2 and $CFCl_3$, yields pure iodine azide as golden, sublimable crystals (*21, 23*). For many preparative purposes it is convenient to use solutions in acetonitrile and other polar solvents, like pyridine or dimethylformamide; these are produced by heterogenous reaction of suspensions of NaN_3 with iodine chloride (*76*).

$$NaN_3 + ICl \xrightarrow{CH_3CN} NaCl + IN_3$$

III. Properties

A. Handling of the Halogen Azides and Chemical Properties

The gaseous halogen azides are very hazardous to handle—it is advisable to dilute them with an inert gas. Explosions can occur upon sudden variations of pressure (*20*). Appropriate use of gaseous chlorine azide in preparative operations has been described by Brauer (*8*). Especially dangerous are the pure halogen azides in the condensed phases. Thus fluorine azide inevitably explodes on attempting to evaporate the condensate (*58*), whereas the controlled thermal cleavage in the diluted gas phase results in N_2F_2 (*58, 110, 111, 119*).

$$2FN_3 \rightarrow N_2F_2 + 2N_2$$

On the other hand, dilute solutions of bromine azide and iodine azide in dichloromethane, hexane, and other nonpolar solvents can be handled safely and used for preparative purposes (*23, 37, 60*); the same is true for solutions of iodine azide in acetonitrile (*76*). Only in water does chlorine azide dissolve without decomposition, whereas bromine azide and iodine azide slowly dissociate to the elements. Anhydrous solutions in nonpolar solvents are more stable; for example, iodine azide solutions can be kept in the dark at 0°C for several days. Pentane slowly reacts with chlorine azide, undergoing substitution (*52*).

$$C_6H_{12} + ClN_3 \rightarrow C_6H_{11}Cl + HN_3$$

Contact with strong reducing agents like sodium, zinc, magnesium, or white phosphorus causes violent explosions (*52, 59, 126*).

In an aqueous, alkaline medium the halogen azides are hydrolyzed, forming hypochlorite (*59, 115*).

$$XN_3 + 2OH^- \rightarrow XO^- + N_3^- + H_2O$$
$$X = Cl, Br, I$$

The reaction with arsenite is suitable for titrimetric analysis (*57*).

$$XN_3 + AsO_3^{3-} + 2OH^- \rightarrow N_3^- + X^- + AsO_4^{3-} + H_2O$$

Because the redox potential of iodine azide is similar to that of iodine, an iodometric titration is equally possible (*21*).

$$IN_3 + 2S_2O_3^{2-} \rightarrow I^- + N_3^- + S_4O_6^{2-}$$

Therefore, iodine azide can be used as a mild oxidizing agent for the formation of S—S bonds (*12*).

$$2Na[4\text{-}NO_2C_6H_4S] + IN_3 \rightarrow (4\text{-}NO_2C_6H_4)_2S_2 + NaI + NaN_3$$

The toxicity of the halogen azides has not yet been investigated, but it can be supposed that they are at least as toxic as the halogens and hydrazoic acid, respectively. Chlorine azide smells somewhat like dichlorine monoxide or nitrogen trichloride, whereas the odor of the other halogen azides resembles rather that of the free halogens.

B. PHYSICAL PROPERTIES

1. *Thermodynamic and Kinetic Data*

Some physical data of the halogen azides are listed in Table I. Most physical investigations have been carried out on chlorine azide. The determination of the heat of decomposition (Table I) refers to the reaction

$$XN_3(g) \rightarrow \tfrac{3}{2}N_2(g) + \tfrac{1}{2}X_2(g)$$
$$X = Cl, Br$$

which was carried out calorimetrically as well as mass spectroscopically (*45*). The overall activation energy for BrN_3 is approximately

TABLE I

PROPERTIES OF HALOGEN AZIDES

Azide	Melting point (°C)	Boiling (sublimation) point (°C/Torr)	Heat of decomposition ΔH°_{293} (kcal mol^{-1})	Maximum flame temperature (K)
FN_3	−154 (*58*)	−82/760[a] (*58*)		
ClN_3	−100 (*52*)	15/760 (*52*)	−93.2 (±1.5) (*44, 107*)	3380 (20 Torr) (*107*)
BrN_3	−45 (*126*)	—	−92.0 (±2.0) (*45*)	4013 (20 Torr) (*45*)
IN_3	Solid	~20/760 (*23*)		

[a] Could only be determined as condensation temperature.

15–18 kcal mol^{-1} (*45*). In the thermal decomposition of ClN_3 in a flow reactor between 600 and 850 K under isothermal conditions, NCl was found by mass spectroscopy (*18*). The study of the kinetics of the reaction of Cl atoms with ClN_3 at pressures near 1 Torr in a discharge-flow reactor coupled with a quadrupole mass spectrometer gave the rate constant for the initial step

$$Cl + ClN_3 \rightarrow N_3 + Cl_2$$

as $k_1 = 2.3 \times 10^{-11} \exp(-1100/RT)$ cm^3 mol^{-1} sec^{-1} between 300 and 675 K (*18*). The kinetics of chemiluminescent reactions of the gaseous azide radical produced in the same rapid reaction have been studied (*14*). The rate constants of the following reactions of N_3 and NCl free radicals have also been determined, using a simulation technique (*68*).

$$\begin{gathered} Cl + N_3 \rightarrow NCl + N_2 \\ N_3 + N_3 \rightarrow 3N_2 \\ NCl + NCl \rightarrow N_2 + Cl_2 \end{gathered}$$

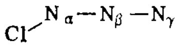
Critical quenching pressures P_C and velocities of the flame front D_L near detonation limits have been measured in capillary tubes of radius r for gaseous ClN_3; P_C has been found to be proportional to $1/r$ for $r >$ 0.25 mm (*105*). General characteristics of the decomposition flame of ClN_3 (*108*) and detonation velocities of ClN_3 in cylindrical tubes (*106*) have also been given. The explosion of chlorine azide produces a continuous spectrum, extending from the ultraviolet to the red, with a maximum intensity at 500–550 nm (*112*); the emission of blue light can be seen at all pressures above 0.1 Torr (*113*).

The very high rate of explosion of chlorine azide allows it to be used in gas lasers mixed with various gases, to transform its chemical energy into laser radiation (*117*). Thus, HF lasing has been produced by a Xe flash-lamp initiation of an explosion in ClN_3–NF_3–H_2 (1 : 1 : 2; 12–24 Torr) and ClN_3–SF_6–H_2 (24 : 19 : 57) mixtures (*67*). Also, ClN_3 serves as a Cl source to produce HCl laser action from H_2–ClN_3 gas mixtures containing less than 20 mol % ClN_3 (*118*). The sequence of reactions that lead to population inversion is as follows (*118*).

$$\begin{aligned} ClN_3 &+ h\nu \rightarrow Cl + N_3 \\ Cl &+ H_2 \rightarrow HCl + H \\ H &+ ClN_3 \rightarrow HCl^* + N_3 \end{aligned}$$

2. *Microwave Spectrum and Structure of Chlorine Azide*

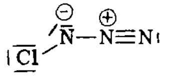
The structure determination of ClN_3 was carried out by R. L. Cook and M. C. L. Gerry on the basis of the microwave spectrum (*19*).



The bond distances (pm) and angles are

$Cl—N_\alpha$	174.5(5)	$Cl—N_\alpha—N_\beta$	108°40′ (30)
$N_\alpha—N_\beta$	125.2(10)	$N_\alpha—N_\beta—N_\gamma$	171°56′ (30)
$N_\beta—N_\gamma$	113.3(10)		

All atoms are coplanar; the deviation from the linearity of the NNN axis is surprising, but it can be explained by slight Cl=N double bonding (**III**) (*19*). The molecular structure can be described by **I** rather than by **II**.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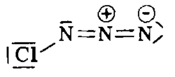
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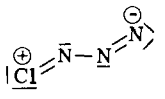

(III)

Values for the Cl quadrupole coupling constants have been obtained for all isotopic species, and for the most abundant, $^{35}Cl^{14}N_3$, they were transformed into the principal field gradient axis system. The values obtained were consistent with the proposed structure (*19*).

3. *Vibrational Spectra*

Information about the vibrational spectroscopy of the halogen azides XN_3 exists in the form of IR spectra in an Ar matrix for X = F, Cl, and Br (*80*), in solution for ClN_3 (*70*), and for IN_3 in solution (*23*), in the

TABLE II

VIBRATIONAL SPECTRA OF THE HALOGEN AZIDES[a]

Azide	Reference	Conditions	νN—X	$\nu_{as}N_3$	ν_sN_3	δN_3	$2 \times \nu_sN_3$	$\nu_sN_3 + \nu_{as}N_3$
FN_3	(*80*)	IR, Ar matrix	869	2034	1086	503, 654		
ClN_3	(*79, 80*)	IR, Ar matrix	721 (^{37}Cl) 724 (^{35}Cl)	2060, 2072	1144	520		
	(*70*)	CH_2Cl_2 solution	719	2070	1134	518, 539		
BrN_3	(*80*)	IR, Ar matrix	687	2053, 2070	1160	530		
IN_3	(*21*)	IR, gas phase, 10 Torr IN_3/750 Torr N_2		2055, 2065	1170, 1180		2325	3190
	(*23*)	IR, benzene solution	338	2058	1176	578		3242
	(*23*)	IR, solid, Nujol	338	2045	1240	580, 648	2460	3242
	(*48*)	Raman (6471 Å) CH_2Cl_2, liq. N_2	410	2052	1207	583, 628		
	(*48*)	IR, CH_2Cl_2 143K	400	2050	1222	595, 623		

[a] All data in cm^{-1}.

gas phase (*21*), as the low-temperature matrix spectrum in CH_2Cl_2 (*48*), as well as in the solid state (*23*). The Raman spectrum of iodine azide could only be measured in a CH_2Cl_2 matrix due to its decomposition in the laser beam (6741 Å). The results are given in Table II. The spectra correspond to the molecular symmetry C_s, this also being found for ClN_3 from the microwave spectrum (*19*). In the series of the halogen azides from FN_3 to IN_3, the I—N stretching vibration appears shifted to surprisingly long wavelengths. This fact can be explained by the high polarity of the I—N bond according to $I^+—N^-$ (*23*), as well as by coupling with the in-plane bending vibration of the N_3 group (*3*). This interpretation is supported by the electron spectra of the halogen azides (see Section III,B,4), as well as by the chemical reactions of iodine azide (see Section IV). Therefore, among the halogen azides, iodine azide is the only species the halogen atom of which has acceptor qualities (see Section IV,B,3). Nevertheless, even the Cl atom in the ClN_3 molecule, according to LCAO–SCF–MO calculations, exhibits a weak positive charge (*72*), which corresponds to the values of the Cl quadrupole coupling constants (*19*).

4. *Ultraviolet–Visible Spectra*

The UV spectra have been measured in the gas phase for ClN_3 (*15*) and in a hexane solution in the case of ClN_3, BrN_3, and IN_3 (*38*). All halogen azides exhibit three absorption bands (Table III), one of which lies in the visible range of the spectrum and corresponds to an electron

TABLE III

UV–VISIBLE SPECTRA OF THE HALOGEN AZIDES ClN_3, BrN_3, AND IN_3

Azide	Solvent	λ_{max} (nm)	ε ($l\ mol^{-1}\ cm^{-1}$)	Half width (nm)	Assignment	Reference
ClN_3	(Gas)	210–220	~2000			(*15*)
		249	455 ± 70			(*15*)
ClN_3	Hexane	211	815	13	$sp_x \rightarrow \pi_y^*$	(*38*)
		252	240	25	$\pi_y \rightarrow \pi_x^*$	(*38*)
		380	8	40	[a]	(*38*)
BrN_3	Hexane	235	366	30	$sp_x \rightarrow \pi_y^*$	(*38*)
		289	106	32	$\pi_y \rightarrow \pi_x^*$	(*38*)
	CCl_4	420	32	75	[a]	(*38*)
IN_3	Hexane	209	870	11	$sp_x \rightarrow \pi_y^*$	(*38*)
		243	615	26	$\pi_y \rightarrow \pi_x^*$	(*38*)
		350	40	60	[a]	(*38*)

[a] See text for assignment.

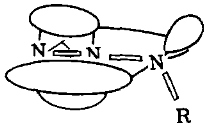


FIG. 1. Schematic representation of the bonding π orbitals of covalent azides according to Müller (*89*).

transition of the halogen components. The weak intensity of this band in chlorine azide (380 nm) is supported by its pale yellow-green color. In the case of bromine azide (red-brown) this band is at 420 nm, very near to the absorption maximum of Br_2 [417 nm (*38*)], whereas the absorption maxima of Cl_2 [332 nm (*114*)] and I_2 [517 nm (*9*)] clearly differ from the characteristic values of the halogen azides. In the case of IN_3 (gold colored) this band (341 nm) lies at shorter wavelengths than that of I_2. On the other hand, the opposite is true of chlorine azide and Cl_2.

In the UV, the halogen azides each show two band maxima, which, according to their position and the extinction values, correspond to other covalent monomeric azides, for example, alkyl azides [~285 and ~215 nm (*134*)]. In compliance with the bonding of these azides, which can be described by two N—N σ bonds, one localized π bond N_β—N_γ, one delocalized π bond N_α—N_β—N_γ, and two more lone electron pairs at the N_α atom and the N_γ atom (Fig. 1), these bands have been assigned by W. D. Clossen and H. B. Gray (*16*) to transitions of the electrons in the two highest occupied orbitals π_y and sp_x to the antibonding π^* orbitals (Fig. 2). In the free azide ion these transitions are degenerate, so that only one band is observed (*134*). In the series IN_3–BrN_3–ClN_3, the energy difference of these bands is the smallest in iodine azide (Δ = 34 nm), which is in agreement with a high polarity of the $I^{\delta+}$—$N^{\delta-}$ bond. Thus, IN_3 is in an intermediate position between the covalent alkyl azides and the azide ion, whereas BrN_3, probably due to its weak electronegativity, most closely resembles the alkyl azides (Δ = 54 nm). In chlorine azide this difference becomes smaller (Δ = 41 nm), an explanation being a reversal of the polarity according to $Cl^{\delta-}$—$N_3^{\delta+}$ (*38*), which was deduced from IR data some time ago (*20*). Ab initio calculations (Section II,B,3), however, indicate a charge distribution $Cl^{\delta+}$—$N_3^{\delta-}$ (*72*), which corresponds to nuclear quadrupole moment measurements (*19*). On the other hand, the ^{15}N-NMR spectrum (Section II,B,6) has also been interpreted; it suggests electron suction to the Cl atom (*85*). This question must probably remain unanswered until exact measurements of the electron distribution can be

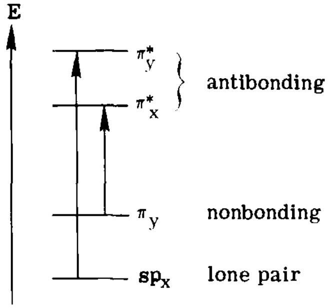


FIG. 2. Energy-level diagram of electron transitions of covalent azides according to Closson and Gray (*16*).

obtained. However, it is certainly not possible to derive a polarity $Cl^{\delta+}—N_3^{\delta-}$ from chemical reactions, as suggested occasionally (*13, 72*), because reversal of this polarity is quite common here (see Section III,B).

5. *Photochemical Decomposition*

By UV irradiation of an argon matrix containing the halogen azides FN_3, ClN_3, and BrN_3, D. E. Milligan and M. E. Jacox obtained FN, ClN and BrN (*79, 80*), the stretching vibrations of which were measured by IR. They are given in Table IV, together with the stretching-force constants, and are supplemented by information about IN, which was produced by glow discharge from the elements (*82*). The course of the force-constant values is as expected, showing maximum π bonding in NF. This species is isoelectronic with the O_2 molecule (f = 11.4 N cm^{-1}); however, its bonding should rather be compared with that of the O_2^- ion (KO_2, f = 6.2 N cm^{-1}) (*136*). So a correct description is provided by the following formulation.

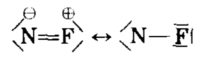

$$\overset{\ominus}{N}=\overset{\oplus}{F} \leftrightarrow N-F$$

TABLE IV

IR ABSORPTIONS AND FORCE CONSTANTS FOR THE HALOIMIDO SPECIES XN

	NF (*80*)	NCl (*80*)	NBr (*80*)	^{14}NI (*82*)	^{15}NI (*82*)
ν (cm^{-1})	1115	819	689	590	573
f(N—X) (N cm^{-1})	5.9	4.9	3.35	2.58	—

TABLE V

^{15}N-NMR SPECTRUM OF ClN_3[a]

	N_α		N_β[b]		N_γ
δ (ppm)	−269.556		−120.207		−110.582
J (Hz)		24.0		7.8	

[a] At −80°C in CH_2Cl_2 solution (*85*).

[b] The isotope shift of the β N atom is 0.12 ppm (α ^{14}N, γ ^{14}N), 0.07 ppm (γ ^{14}N), and 0.02 ppm (α ^{14}N).

6. ^{15}N-NMR Spectra

A ^{15}N-NMR spectrum is known only in the case of chlorine azide (*85*). It was measured on a sample with 50% abundance of ^{15}N for the β N atom and with 90% abundance for the α and γ N atoms in dichloromethane at −80°C (Table V). The values of the chemical shift refer to $^{15}NO_3^-$ in D_2O, externally. Noteworthy is the change in the order of the signals N_β—N_γ—N_α to N_γ—N_β—N_α, in agreement with the smallest shielding of the N_γ atoms, as observed in the case of covalent azides, for example, HN_3 and RN_3 (*85*). It can be explained by the electronegativity of the Cl atom and the resulting electron displacement toward the Cl atom (*85*).

7. Photoelectron Spectra

The helium [He(I)] photoelectron spectra of ClN_3 and BrN_3 have been recorded and the results compared with ab initio and semiempirical calculations (*53*). The spectra provide an interesting investigation into how the orbitals of a linear pseudohalide grouping are perturbed by an off-axis halogen atom. An important conclusion is that bending the linear 16-valence electron ion N_3^- removes the π degeneracies and stabilizes the out-of-plane orbital (a″) more than the in-plane orbital (a′). This is in contrast to the HN_3 molecule, in which the a′ orbital is preferentially stabilized, because this orbital has the required symmetry to interact with the H 1s atomic orbital. The net result is a substantial splitting of the π-bonding N_3 orbitals, the extent of the perturbation depending upon the nature of the halogen (*53*).

8. Magnetic Susceptibility

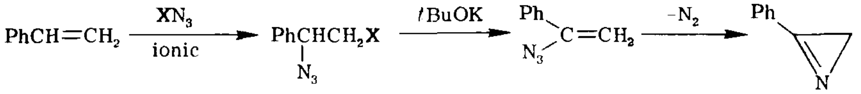
The determination of the magnetic susceptibility of chlorine azide, dissolved in carbon tetrachloride, shows at 20°C a weak paramagnetism of $\chi_{mol} = 16.5 \times 10^{-6}$ emu (*74*).

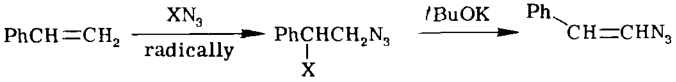
IV. Applications in Synthetic Chemistry

A. ORGANIC CHEMISTRY

The use of halogen azides, especially bromine azide and iodine azide, in synthetic organic chemistry mainly originates from work of A. Hassner *et al.*, who found a method of adding halogen azides to olefinic double bonds. A review of this work was published in 1971 (*76*); for a summary in Japanese see Ota and Yoshida (*102*). In this chapter only the most essential aspects of their investigations can be mentioned and some selected new work cited.

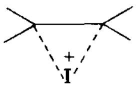
The addition of halogen azides to olefinic double bonds can occur both ionically and radically, depending on the polarity of the solvent among other things (*76, 116*). By addition of styrene, it is possible to obtain, for example, both regioisomeric azides, from which vinyl azides can be produced (*76*), which in their turn serve in the synthesis of azirines (*64, 66, 125*).





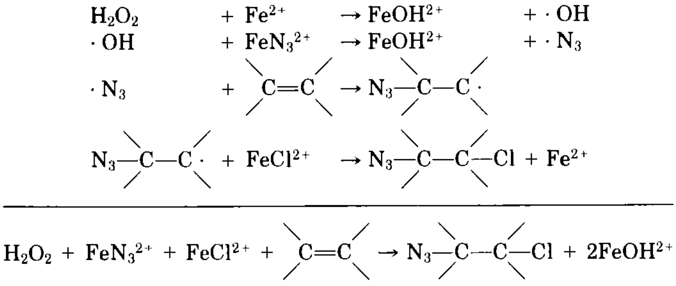
In this way, the first synthesis of a 2-vinylazirine was accomplished by the reaction of iodine azide with diphenyl butadiene and basic cleavage of HN_3, from the primary diazide (*61*).

In the ionic addition of iodine azide to olefins, an intermediate formation of a halogenium ion complex was proved (*51, 62*).



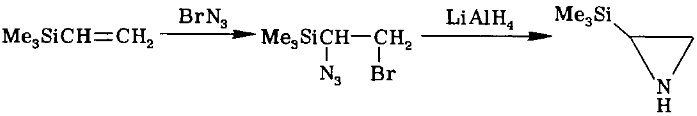
The tendency to homolytic cleavage increases in the sequence $IN_3 < BrN_3 < ClN_3$ (*76*), which is in accordance with the electronic spectra of halogen azides (*38*) as well as the IR spectra (*20–23, 48, 80*).

The radical addition of chlorine azide, which was produced *in situ* in the system $H_2O_2/FeCl_3/NaN_3$ in the presence of an olefin, can be described by the following sequence of reactions.



It is interesting that the easily decomposable $PhI(Cl)N_3$, which can be seen as an adduct of chlorine azide with iodobenzene, reacts differently from chlorine azide itself; for example although the stereoisomeric *cis*- and *trans*-2-chloro-1-azido-1-phenylcyclohexene are formed by treating phenyl-1-cyclohexene with ClN_3, the reagent $PhI(Cl)N_3$ yields the stereoisomeric mixture 1-chloro-2-azido-1-phenylcyclohexane (*141*).

Some new results are as follows. The reaction of iodine azide with cyclopentadiene in acetonitrile produces 2,4-diazidocyclopenten-1,2 (*122*), the addition of iodine azide to *trans*-1-azido-4-iodocyclooctene, 1-(4-iodocyclooctyl)-5-methyltetrazole and 5-azidocyclooctene (*63*). The synthesis of vicinal iodoazides can be carried out by using phase-transfer reagents in the system H_2O, $NaN_3/CHCl_3$, and I_2 in the presence of cyclohexene (*140*). The synthesis of *C*-silyl-substituted aziridine can be effected by the reaction (*43*)



An easy synthesis of 2-bromo-Δ^1-unsaturated 3-ketosteroids has been carried out by addition of BrN_3, for example, to 5α-cholest-1-en-3-one, leading to 2-bromo-5α-cholest-1-en-3 one (*69*). A new synthetic route to 9,10-iminophenantrene was found by sequential treatment of phenanthrene with BrN_3 and $LiAlH_4$ (*40*). The addition of IN_3 to 3-*t*-butylcyclohexene and 3-methoxycyclohexene has been studied with respect to stereochemical addition (*11*), and general aspects of the addition of IN_3 to alkenes have also been published (*10*). The synthesis of 3-azidoindolenines by treatment of indoles with IN_3 or BrN_3 have been described (*132*), as well as the reaction of benzo[*b*]furan and 1-oxylindoles with IN_3 (*131*). Other authors have dealt with the reaction of IN_3 with vinyl sulfones (*133*), with tryptophols and *N*-acyltryptamines (*65*), and with the reactions of IN_3 and BrN_3 with triacetylgalactal in the presence of mercury acetate, forming azidogalactopyranose (*7*).

B. INORGANIC CHEMISTRY

Most preparative applications in inorganic chemistry are based on iodine azide and chlorine azide; some reviews on this subject have already appeared (*20, 21, 49*). On the other hand, only two examples are known of the use of FN_3, which, in view of electronegativities, would better be called "azidium fluoride" (see Section III,B, concerning ClN_3).

The synthesis of NF_3 has been described as being achieved by passing FN_3 into liquid NOF or ClF_3, in a tubular Ni reactor at −70 to −60°C (*55*). In a similar way, $ClNF_2$ can be obtained by reaction of FN_3 with excess chlorine at −85 to −50°C (*56*).

$$4FN_3 + Cl_2 \rightarrow 2ClNF_2 + 5N_2$$

The reasons for the few examples of application of bromine azide in inorganic chemistry are, on the one hand, the difficult preparation of BrN_3 that is free of traces of bromine and, on the other, the fact that its behavior in reactions is of no advantage compared to ClN_3 and IN_3.

1. Substitution Reactions

a. Reactions with Element Halides. The dominating type of reaction of halogen azides in inorganic chemistry is the substitution of a halide ligand X (X = Cl, Br, or I) by the azide group.

$$M^{\delta+}{-}X^{\delta-} + X^{\delta+}{-}N_3^{\delta-} \rightarrow M{-}N_3 + X_2$$

These types of reactions proceed more rapidly the more polar the M—X bond and the more polar the X—N_3 bond of the halogen azide. Therefore, iodine azide exhibits the highest reactivity in the series $Cl{-}N_3 \leqq BrN_3 \ll IN_3$. Thus tungsten hexachloride reacts with chlorine azide in CCl_4 suspension within several hours, whereas the same reaction takes only a few seconds when iodine azide is used (*34, 99*).

$$WCl_6 + ClN_3 \rightarrow WCl_5N_3 + Cl_2$$

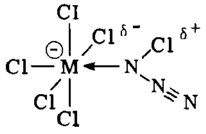
$$WCl_6 + IN_3 \rightarrow WCl_5N_3 + ICl$$

Chlorine azide also reacts extremely quickly when the metal halide is a Lewis acid; examples are the reactions with molybdenum pentachloride (*34*) and antimony pentachloride (*94*).

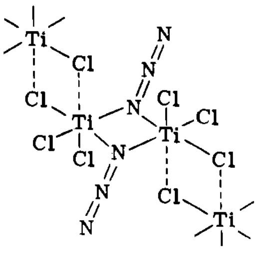
$$MoCl_5 + ClN_3 \rightarrow MoCl_5N_3 + \tfrac{1}{2}Cl_2$$

$$SbCl_5 + ClN_3 \rightarrow SbCl_4N_3 + Cl_2$$

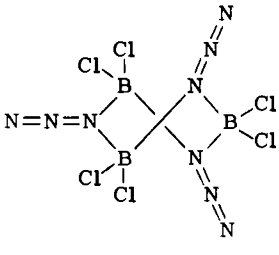
Presumably, a donor–acceptor complex (I) is formed here primarily, which makes the halogen atom of the halogen azide positive so that charge compensation Cl^+/Cl^- and cleavage of the Cl_2 are effected in a secondary step (*20*). In favor of this mechanism is the large electron density of the N_α atoms, as concluded for ClN_3 from the structure (*19*) and the ^{15}N-NMR spectrum (*85*), the latter proving that the N_γ atom of ClN_3 has the lowest electron density, so that it cannot be considered for a donor function. This concept is also in agreement with all structural data, according to which only the N_α atom of covalent azides is capable of donor activities (*89*). Finally, it must be pointed out that halides of low polarity, for example, CCl_4, $SiCl_4$, and $GeCl_4$, do not react with chlorine azide. Table VI contains the results of reactions of halogen azides with element halides. Most of the azido halogeno complexes obtainable in this way are explosive as solids; nevertheless, some of them can be structurally investigated. They show very clearly the tendency to associate via the N_α atom.



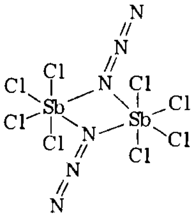
(I)



$[TiCl_3N_3]_\infty$ (*138*)



$[BCl_2N_3]_3$ (*90*)



$[SbCl_4N_3]_2$ *(91)*

The use of iodine azide also allows the synthesis of metal bromide azides and iodide azides, as well as the preparation of halogeno azido complexes.

$$TiBr_4 + 2IN_3 \rightarrow TiBr_2(N_3)_2 + 2IBr \quad (75)$$

$$MoBr_4 + IN_3 \rightarrow MoBr_3N_3 + IBr \quad (29)$$

$$AlI_3 + IN_3 \rightarrow AlI_2N_3 + I_2 \quad (30)$$

$$PPh_4[NbCl_6] + IN_3 \rightarrow PPh_4[NbCl_5N_3] + ICl \quad (42)$$

Many of these azido complexes are highly energetic starting substances for the formation of nitrido halides, which are produced in high purity in thermal dissociation reactions in inert solvents like CCl_4.

$$TiCl_3N_3 \rightarrow [TiNCl]_x + N_2 + Cl_2 \quad (22)$$

$$VOCl_2N_3 \rightarrow [VON]_x + N_2 + Cl_2 \quad (22)$$

$$MoCl_5N_3 \rightarrow \tfrac{1}{4}[MoNCl_3]_4 + N_2 + Cl_2 \quad (34, 127)$$

$$MoBr_3N_3 \rightarrow MoNBr_3 + N_2 \quad (29)$$

$$ReCl_4N_3 \rightarrow ReNCl_3 + N_2 + \tfrac{1}{2}Cl_2 \quad (28)$$

A review article on the occurrence of transition metal–nitrogen multiple bonds in the products has appeared in 1981 *(35)*. Table VII summarizes the results of secondary products of the metal azides with preparative importance.

The thermolysis of the trimeric azidodichloroboron has been known for a long time. It leads to hexachloroborazine by migration of a Cl ligand from boron to nitrogen *(92, 103)*. A similar mechanism can be assumed in the decomposition of vanadium tetrachloride azide, obtained from VCl_4 and chlorine azide *(130)*.

$$VCl_4N_3 \rightarrow Cl_3V{\equiv}N{-}Cl + N_2$$

TABLE VI

SUBSTITUTION REACTIONS OF THE HALOGEN AZIDES WITH METAL HALIDES AND WITH ORGANOMETALLIC COMPOUNDS

Starting materials	Reagent	Solvent	Reaction products	Color	Remarks	Reference	Crystal structure
BCl_3	ClN_3	—	$[BCl_2N_3]_3$	White	[abd]	*(104)*	*(90)*
BBr_3	BrN_3	—	$[BBr_2N_3]_3$	White	[abd]	*(104)*	
BI_3	IN_3	CH_2Cl_2	$[BI_2N_3]_n$	Yellow	[abcd]	*(31)*	
AlI_3	IN_3	C_6H_6	$[AlI_2N_3]_n$	Yellow	[ceg]	*(30)*	
GaI_3	IN_3	C_6H_6 suspension	$[GaI_2N_3]_n$	Yellow	[ceg]	*(30)*	
$SnCl_4$	ClN_3	—	$[SnCl_3N_3]_n$	White	[abe]	*(22)*	
$SbCl_5$	ClN_3	—	$[SbCl_4N_3]_2$	White-yellow	[abe]	*(94)*	*(91)*
$TiCl_4$	ClN_3	—	$[TiCl_3N_3]_n$	Yellow	[abe]	*(22)*	*(138)*
$TiBr_4$	IN_3	CCl_4	$[TiBr_2(N_3)_2]_n$	Orange-red	[abe]	*(75)*	
TiI_4	IN_3	C_6H_6	$[TiI_3N_3]_n$	Black	[abce]	*(75)*	
$ZrCl_4$	IN_3	CCl_4 suspension	$[ZrCl_3N_3]_n$	White	[abe]	*(46)*	
VCl_4	ClN_3	CCl_4	$[VCl_4N_3]_n$	Black-brown	[ab]	*(130)*	
VCl_4	NaN_3/Cl_2	—	$[Cl_3V{\equiv}N{-}Cl]_2$	Red	[bde]	*(50)*	*(129)*
VCl_4	IN_3	CCl_4	$[Cl_3V{\equiv}N{-}I]_2$	Black	[bce]	*(27)*	*(4)*
$VOCl_3$	ClN_3	—	$VOCl_2N_3$	Orange	[abe]	*(22)*	
$NbCl_5$, $TaCl_5$	ClN_3	CCl_4 suspension	$[MCl_4N_3]_2$	White	[abe]	*(128)*	*(128)* M = Ta
$CrCl_3$	IN_3	CCl_4 suspension	$[CrCl_2N_3]_n$	Violet	[ae]	*(47)*	
CrO_2Cl_2	ClN_3	—	CrO_2ClN_3	Dark green	[abe]	*(34)*	
$MoCl_5$	ClN_3	CCl_4 suspension	$MoCl_5N_3$	Red	[abd]	*(34)*	
$MoCl_5N_3$	ClN_3	CCl_4	$MoCl_4(N_3)_2$	Black	[ab]	*(34)*	
$MoCl_5$	IN_3	CCl_4 suspension	$[MoNCl_4]_2$	Brown	[be]	*(78)*	
$MoBr_4$	IN_3	CCl_4 suspension	$[MoBr_3N_3]_n$	Black-brown	[abe]	*(29)*	
MoI_3	IN_3	CCl_4 suspension	MoI_2N_3	Black	[bch]	*(75)*	

WCl_6	ClN_3	CCl_4	WCl_5N_3	Red	[a,b,d]	(*34*)	
WCl_6	IN_3	CCl_4 (0°C)	$[WNCl_4]_n$	Brown	[b,e]	(*120*)	
WCl_6	IN_3	CCl_4 (20°C)	$[WNCl_3]_n$	Ocre	[b,e]	(*99*)	
WBr_6	BrN_3, IN_3	CH_2Br_2	$[WNBr_3]_n$	Black-brown	[b,e]	(*121*)	
$ReCl_5$	ClN_3	CCl_4 suspension (0°C)	$ReCl_4N_3$	Black	[a,b]	(*28*)	
UCl_6	ClN_3	CH_2Cl_2	UCl_5N_3, $UCl_4(N_3)_2$	Black	[a,b]	(*71*)	
$PPh_4[NbCl_6]$	IN_3	CH_2Cl_2	$PPh_4[NbCl_5N_3]$	Orange	[f]	(*42*)	(*90*)
$PPh_4[NbBr_6]$	IN_3	CH_2Cl_2	$PPh_4[NbBr_5N_3]$	Maroon	[f]	(*96*)	
$PPh_4[TaCl_6]$	IN_3	CH_2Cl_2	$PPh_4[TaCl_5N_3]$	White	[f]	(*42*)	
$PPh_4[TaBr_6]$	IN_3	CH_2Cl_2	$PPh_4[TaBr_5N_3]$	Yellow	[f]	(*96*)	
AlR_3 (R = Me, Et)	ClN_3	C_6H_6	$[AlR_2N_3]_3$	Colorless	Liquid[b,c,d]	(*36*, *86*, *87*)	
$AlClEt_2$	ClN_3	C_6H_6	$[AlClEtN_3]_3$	White	[b,c,d]	(*73*)	
GaR_3 (R = Me, Et)	ClN_3	C_6H_6	$[GaR_2N_3]_3$	Colorless	Liquid[d]	(*87*, *88*)	
$InEt_3$	ClN_3	C_6H_6	$[InEt_2N_3]_2$	White	[b,c,d]	(*87*)	
$TlEt_3$	ClN_3	C_6H_6	$[TlEt_2]N_3$	White	[e,h]	(*87*)	
ZnR_2 (R = Me, Et,Ph)	ClN_3	Hexane	$[ZnRN_3]_n$	White	[a,b,c,e]	(*36*, *83*)	
CdR_2 (R = Me, Et)	ClN_3		$[CdRN_3]_n$	White	[a,b,c,e]	(*36*, *84*)	
CdEt(OEt)	ClN_3	Hexane	$[Cd(OEt)N_3]_4$	White	[b,e]	(*84*)	
HgR_2 (R = Me, Et, *i*Pr, *c*Pr, *n*Pr, *n*Bu, Ph)	ClN_3	CCl_4, C_6H_6	R—Hg—N_3	White	[a](R = Me)[d]	(*33*, *36*, *124*)	

---

[a] Explosive.

[b] Sensitive to moisture.

[c] Sensitive to oxygen.

[d] Soluble in nonpolar solvents.

[e] Soluble in polar solvents like $POCl_3$, pyridine, etc.

[f] Soluble in CH_2Cl_2.

[g] Soluble in benzene in the presence of AlI_3.

[h] N_3 group ionic.

TABLE VII

SECONDARY PRODUCTS OF THE AZIDO COMPLEXES WITH PREPARATIVE IMPORTANCE

Starting materials	Conditions	Products	Remarks†	Reference	Crystal structure
$[BCl_2N_3]_3$	(200°C, pressure)	$[ClBNCl]_3$	[b]	*(103)*	*(92)*
$[BI_2N_3]_n$	CH_2Cl_2 (20°C)	$[IBNI]_n$, BN	[bc]	*(31)*	
$[SbCl_4N_3]_2$	CCl_4, boiling	$C(N_3)_3^+$ $SbCl_6^-$	[ab]	*(95)*	*(93)*
$[TiCl_3N_3]_n$	CCl_4 (20°C)	TiNCl	Polymeric[b]	*(22)*	
$VOCl_2N_3$	CCl_4 (20°C)	VON	Polymeric[b]	*(22)*	*(137)*
VCl_4N_3	CCl_4 (20°C)	$[Cl_3V{\equiv}N{-}Cl]_2$	[b]	*(130)*	*(129)*
$MoCl_5N_3$	CCl_4, boiling	$[MoNCl_3]_4$	[b]	*(34)*	*(127)*
$MoBr_3N_3$	CCl_4, boiling	$[MoNBr_3]_n$	[b]	*(29)*	
WCl_5N_3	CCl_4, boiling	$[WNCl_3]_n$	[b]	*(99)*	
UCl_5N_3	CCl_4 (20°C)	$C(N_3)_3^+$ UCl_6^-	[ab]	*(71)*	
UCl_5N_3	CH_2Cl_2 (20°C)	NH_4UCl_6		*(71)*	
$PPh_4[NbCl_5N_3]$	PPh_3, CH_2Cl_2 (20°C)	$PPh_4[NbCl_5(NPPh_3)]$	[f]	*(42)*	
$PPh_4[NbBr_5N_3]$	PPh_3, CH_2Cl_2 (20°C)	$PPh_4[NbBr_5(NPPh_3)]$	[f]	*(96)*	
$PPh_4[NbCl_5N_3]$	$AsPh_3$, CH_2Cl_2, $h\nu$ (65°C)	$PPh_4[NbCl_5(NAsPh_3)]$	[f]	*(96)*	
$PPh_4[TaCl_5N_3]$	PPh_3, CH_2Cl_2, $h\nu$ (65°C)	$PPh_4[TaCl_5(NPPh_3)]$	[f]	*(42)*	
$PPh_4[TaBr_5N_3]$	PPh_3, CH_2Cl_2, $h\nu$ (65°C)	$PPh_4[TaBr_5(NPPh_3)]$	[f]	*(96)*	

† See Table VI for footnotes.

On the other hand, the preservation of an I—N bond is observed in the reaction of vanadium tetrachloride with iodine azide (*27*).

$$VCl_4 + 2IN_3 \rightarrow Cl_3V{\equiv}N{-}I + 2.5N_2 + ICl$$

The compounds can be visualized as nitrene complexes; their crystal structures reveal a linear $V^-{\equiv}N^+{-}X$ axis (X = Cl, I) and a very short VN bond length of 165 pm (*4, 101, 129*). The N—I compound undergoes halogen exchange with chlorine or bromine (*27*).

$$Cl_3VNI + X_2 \rightarrow Cl_3VNX + IX$$

$$X = Cl, Br$$

A review article about nitrene complexes of transition metals was published in 1980 (*100*).

A noteworthy reaction takes place with molybdenum pentachloride and iodine azide at 0°C in a CCl_4 solution (*78*).

$$2MoCl_5 + 2IN_3 \rightarrow [MoNCl_4]_2 + 2ICl + 2N_2$$

The nitride chloride contains molybdenum(V) and is characterized by a direct N—N bond. Upon heating it releases chlorine and changes to $MoNCl_3$ (*78*). Some transition-metal azide complexes are capable of undergoing the Staudinger reaction with triphenylphosphine or triphenylarsine.

$$[MCl_4N_3]_2 + 2PPh_3 \rightarrow [MCl_4(NPPh_3)]_2 + 2N_2 \qquad (5, 6)$$

$$M = Nb, Ta$$

$$PPh_4[MCl_5N_3] + PPh_3 \rightarrow PPh_4[MCl_5(NPPh_3)] + N_2 \qquad (42)$$

$$M = Nb, Ta$$

$$PPh_4[NbCl_5N_3] + AsPh_3 \rightarrow PPh_4[NbCl_5(NAsPh_3)] + N_2 \qquad (96)$$

In other cases, reactions with the solvent were observed. Thus, for example, the azide complexes $[SbCl_4N_3]_2$ (*95*), UCl_5N_3 (*71*), and $[ZrCl_3N_3]_\infty$ (*46*) react with carbon tetrachloride to form the triazido carbenium cation.

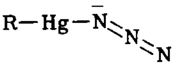
$$3SbCl_4N_3 + CCl_4 \rightarrow C(N_3)_3[SbCl_6] + 2SbCl_5$$

$[WNCl_3 \cdot 0.5HN_3]_4$ is produced in the reaction of excess iodine azide with tungsten hexachloride in dichloromethane solution, the hydrazoic acid being formed with participation of the solvent. The tungsten atoms in the $[WNCl_3 \cdot 0.5HN_3]_4$ molecule are placed at the corners of a square, the edges of which are formed by linear W≡N—W bridges of alternating WN bond lengths. The HN_3 molecules are coordinated by the N_α atoms to two diametrical tungsten atoms, and the two remaining tungsten atoms coordinate via chloro bridges to form ribbons (*135*).

b. Reactions with Organometallic Compounds. Substitution reactions in metal organic compounds have so far been exclusively carried out with chlorine azide (see Table VI). The reactions take place according to the pattern

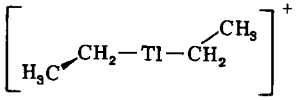
$$MR_n + ClN_3 \rightarrow MR_{n-1}N_3 + RCl$$

In contrast to the metal halide azides, in general the metal organic azides are not explosive. Exceptions to this are the monomeric organomercury azides R—Hg—N_3, which can explode upon extended heating, probably as a consequence of ligand exchange by which mercury diazide is formed. The dialkyl metal azides of aluminum (*36, 86, 87*) and gallium (*87, 88*) are colorless liquids that occur as trimeric molecules like $[R_2MN_3]_3$, in which the N_α atoms of the azide ligands link the metal atoms to planar six-membered rings (symmetry D_{3h}). On the other hand, diethyl indium azide is dimeric (*87*). The dialkylaluminum azides react very violently with water (*36, 86, 87*), whereas diethylgallium azide is affected only by concentrated sulfuric acid (*88*). The alkyl and aryl azides of zinc and cadmium form polymeric solids (*36, 83, 84*), whereas the same compounds of mercury



(*33*, *124*)

are molecular with local symmetry C_s and diethylthallium azide is ionic. Its cation



which is isosteric with diethylmercury, is only of symmetry C_2 on account of the absence of free rotation of the ethyl groups (*87*).

c. Reactions with Metal Carbonyls. The reactions of the halogen azides with metal carbonyls lead to products that vary greatly, depending on the metal carbonyl used as well as on the halogen azide (Table VIII). All reactions have in common the partial or complete substitution of carbonyl ligands and the occurrence of redox reactions.

Iron pentacarbonyl reacts even at −40 to −20°C in pentane solution with all halogen azides XN_3 (X = Cl, Br, I), yielding the yellow (X = Cl) or brown (X = Br, I) dicarbonyl azide halides (*25*, *77*).

$$Fe(CO)_5 + XN_3 \rightarrow Fe(CO)_2XN_3 + 3CO$$

The compounds are high-spin complexes. $Fe(CO)_2ClN_3$ was investigated magnetically and was found to be surprisingly strongly paramagnetic ($\mu_{eff} = 5.29$ BM, $\theta = 0°$) (*77*). The thermolysis in vacuum at 90–100°C results in mixed azide halides, free of carbonyl, for X = Cl or Br (*77*).

$$Fe(CO)_2XN_3 \rightarrow FeXN_3 + 2CO$$

The metal carbonyls of manganese and cobalt react with iodine azide in dichloromethane, yielding diazides in very high purity (*25*).

$$Mn_2(CO)_{10} + 4IN_3 \rightarrow 2Mn(N_3)_2 + 10CO + 2I_2$$

On the other hand, the reaction of nickel tetracarbonyl yields only a mixture of $Ni(N_3)_2$ and NiI_2 (*25*).

Chlorine azide reacts with the hexacarbonyls of molybdenum and tungsten in carbon tetrachloride, forming the explosive metal dicarbonyl diazides (*77*). These compounds are polymeric, with chloro bridges and via the N_α atoms of the azido groups. Upon attempting to obtain the azide chlorides free of CO by thermal degradation, the products regularly explode (*77*). In contrast, the reaction with iodine azide leads to the highly explosive dicarbonyl diazides (*25*).

$$M(CO)_6 + ClN_3 \rightarrow M(CO)_2ClN_3 + 4CO$$

$$M(CO)_6 + 2IN_3 \rightarrow M(CO)_2(N_3)_2 + I_2 + 4CO$$

$$M = Mo, W$$

Finally, the reactions of iodine azide with dirhenium decacarbonyl and triosmium dodecacarbonyl, suspended in pentane, lead to the car-

TABLE VIII

REACTIONS OF METAL CARBONYLS WITH HALOGEN AZIDES

Starting materials	Reagent	Solvent	Reaction products	Color	Remarks†	Reference
$Mo(CO)_6$	ClN_3	CCl_4	$[Mo(CO)_2ClN_3]_n$	Brown	[ab]	(77)
$Mo(CO)_6$	IN_3	Pentane (−50°C)	$[Mo(CO)_2(N_3)_2]_n$	Brown	[ab]	(25)
$W(CO)_6$	ClN_3	CCl_4	$[W(CO)_2ClN_3]_n$	Brown	[ab]	(77)
$W(CO)_6$	IN_3	Pentane (−50°C)	$[W(CO)_2(N_3)_2]_n$	Brown	[ab]	(25)
$Mn_2(CO)_{10}$	IN_3	CH_2Cl_2	$Mn(N_3)_2$	Ocre	[ab]	(25)
$Re_2(CO)_{10}$	IN_3	Pentane suspension (−25°C)	$[Re(CO)_4NCO]_2$	Ocre	[j]	(25)
$Fe(CO)_5$	ClN_3	Pentane (−20°C)	$[Fe(CO)_2ClN_3]_n$	Yellow	($\mu_{\text{eff}} = 5.29$ BM)[b,j]	(77)
$Fe(CO)_5$	BrN_3	Pentane (−20°C)	$[Fe(CO)_2BrN_3]_n$	Brown	[bj]	(77)
$Fe(CO)_5$	IN_3	Pentane (−20°C)	$[Fe(CO)_2IN_3]_n$	Dark brown	[bj]	(25)
$Co_2(CO)_8$	IN_3	CH_2Cl_2	$Co(N_3)_2$	Grey-green	[ab]	(25)
$Os_3(CO)_{12}$	IN_3	CH_2Cl_2	$[Os(CO)_2NCO]_n$	Yellow-brown		(25)
$Ni(CO)_4$	IN_3	Pentane (−25°C)	$Ni(N_3)_2$, NiI_2	Black	[ab]	(25)

† See Table VI for footnotes [a] and [b].

[j] Light sensitive.

bonyl cyanates by dissociation of nitrogen and migration of a CO group (*25*).

$$Re_2(CO)_{10} + 2IN_3 \rightarrow [Re(CO)_4(NCO)]_2 + 2N_2 + I_2$$

$$Os_3(CO)_{12} + 3IN_3 \rightarrow 3Os(CO)_2(NCO) + 3N_2 + 1.5I_2 + 3CO$$

The rhenium complex is dimeric, with the nitrogen atoms of the cyanate groups acting as bridging atoms; there are no structural data available about the osmium compound.

2. *Oxidative Addition Reactions*

In analogy with the halogens, the halogen azides are capable of some oxidative additions. This has been examined in some examples (Table IX). The addition of halogen azides XN_3 (X = Cl, Br, I) to tin(II) chloride exclusively yields tin(IV) diazide dichloride as an almost insoluble white precipitate (*39*) yet the reaction probably proceeds via primary

$$2SnCl_2 + 2XN_3 \rightarrow SnCl_2(N_3)_2 + \text{“}SnCl_2X_2\text{”}$$

addition of an XN_3 molecule with subsequent X/N_3 ligand exchange. $SnCl_2(N_3)_2$ is interlinked by the N_α atoms of the azide bridges (*39*, *139*), so that there is no further exchange of ligands in this species. The direct addition of iodine azide to tin(II) chloride has been proved in the presence of tetramethylammonium chloride, because the octahedrally coordinated tin does not allow a secondary ligand exchange (*39*).

$$SnCl_2 + IN_3 + 2NMe_4Cl \rightarrow (NMe_4)_2[SnCl_4IN_3]$$

The oxidative addition of chlorine azide to phosphorus trichloride results in a very explosive, white azide of unknown structure, which reacts with more phosphorus trichloride, undergoing N_2 elimination according to a Staudinger reaction (*98*).

$$PCl_3 + ClN_3 \rightarrow PCl_4N_3$$

$$PCl_4N_3 + PCl_3 \rightarrow [Cl_3PNPCl_3]Cl + N_2$$

The reaction of bromine azide with antimony tribromide in bromine solution leads to the explosive, probably dimeric tetrabromo antimony azide (*32*).

$$SbBr_3 + BrN_3 \rightarrow SbBr_4N_3$$

TABLE IX

OXIDATIVE ADDITION REACTIONS OF THE HALOGEN AZIDES

Starting materials	Reagent	Solvent	Reaction products	Color	Remarks†	Reference
$SnCl_2$	ClN_3,BrN_3,IN_3	CCl_4 suspension	$SnCl_2(N_3)_2$	White	[ab]	(*39*)
NMe_4Cl, $NMe_4[SnCl_3]$	IN_3	CH_2Cl_2 suspension	$(NMe_4)_2[SnCl_4IN_3]$	Orange		(*39*)
PCl_3	ClN_3	—	PCl_4N_3	White	[abi]	(*32*)
$SbBr_3$	BrN_3	Br_2	$SbBr_4N_3$	Red-brown	[ab]	(*32*)
SbR_3	IN_3	CH_2Cl_2 (−20°C)	SbR_3IN_3	White ($R = CH_3$, C_6H_5)		(*26*)
Hg	IN_3	CH_2Cl_2 suspension (20°C)	$HgIN_3$	Yellow	[a]	(*24*)

† See Table VI for footnotes [a] and [b].

[i] Rapid decomposition, forming $[Cl_3PNPCl_3]Cl$ (*98*).

whereas trimethylantimony and triphenylantimony react with iodine azide to form the nonexplosive monomeric triorganoantimony azide iodides (*26*).

$$R_3Sb + IN_3 \rightarrow R_3SbIN_3$$

According to ^{121}Sb Mössbauer spectroscopy, methyl and phenyl groups, respectively, are coordinated equatorially, whereas I and N_3 are placed in the axial positions of the trigonal bipyramid (*26*).

The only metal that has been brought into reaction with iodine azide in a satisfactory way is mercury (*24*). It reacts in dichloromethane to

$$Hg + IN_3 \rightarrow HgIN_3$$

form mercury azide iodide: sodium, magnesium, zinc, and also white phosphorus cause violent explosions without a solvent and yield only mixtures of the halides and the azides when the reaction is moderated by a solvent (*52, 59, 115*).

3. *Donor–Acceptor Complexes of Iodine Azide*

Within the series of the halogen azides only the iodine atom in iodine azide has sufficient positive charge to act as an acceptor component with Lewis bases. Donor–acceptor complexes can be isolated when halide or pseudohalide ions in their tetramethylammonium salts, dissolved in dichloromethane, react with iodine azide, and when the solvent is evaporated (Table X) (*41*). On the other hand, the reaction of

$$IN_3 + X^- \rightarrow [X—I—N_3]^-$$

iodine azide with thiocyanate ions resulted in a spontaneous decomposition of iodine azide to the elements (*41*). Free of solvent, the complexes of iodine azide containing NMe_4^+ cations are colored, explosive solids, the IR spectra of which indicate a linear $X—I—N_\alpha$ axis. The use of the larger tetraphenylphosphonium cation yields complexes that are no longer explosive and, on account of the hydrophobic character of the phenyl groups, are no longer hygroscopic in the crystalline state (*97*). The addition of IN_3 to X^- ions causes an increase of polarity in the I—N bond, which is expressed by the longwave shift of the asymmetric N_3 stretching vibration of iodine azide from 2045 to approximately 2000 cm^{-1}, as well as by the longwave shift of both N—I—N stretching vibrations in the $[N_3—I—N_3]^-$ complex from 338 cm^{-1} in the iodine azide molecule to 285 and 269 cm^{-1} (species A and B) (*97*).

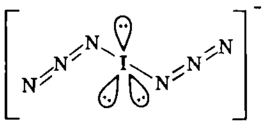
TABLE X

DONOR–ACCEPTOR COMPLEXES OF IODINE AZIDE[a]

Compound	Symmetry of the anion	Color	Remarks	ν N—X (cm^{-1})	Reference
$NMe_4[F—I—N_3]$	C_s	Yellow	[b]	403	(*41*)
$NMe_4[Cl—I—N_3]$	C_s	Orange	[b]	333	(*41*)
$NMe_4[Br—I—N_3]$	C_s	Orange-red	[b]	260	(*41*)
$NMe_4[I—I—N_3]$	C_s	Dark violet	[b]		(*41*)
$NMe_4[N_3—I—N_3]$	C_2	Orange-red	[b]	250, 237	(*41*, *97*)
$PPh_4[N_3—I—N_3]$	C_2	Orange		285, 269	(*97*)
$NMe_4[OCN—I—N_3]$	C_1	Ocre	[b]		(*41*)
$NMe_4[NC—I—N_3]$	C_s	Orange	[b]	260	(*41*)
$NMe_4[N_3—I—NC—I—N_3]$	C_1	Orange	[b]	258	(*41*)

[a] All complexes were prepared in CH_2Cl_2 solution.
[b] Explosive.

A crystal structure investigation has been carried out on $PPh_4[I(N_3)_2]$. It confirms spectroscopic data, which are in favor of an interaction of the lone electron pairs at the iodine atom with the lone pairs of the N_α atoms in the azide groups (dihedral angle 123°) (*97*). It is noteworthy that the azido groups, exhibiting a NNN bond angle of 157°, significantly deviate from the expected linearity; however, this may be a consequence of disorder, though covalent azides with NNN bond angles as small as 160° are known (*89*).



Stable, crystalline donor–acceptor complexes of IN_3 with pyridine, α,α'-dipyridyle, urotropine, and other nitrogen-containing donors have been isolated (*24*). In these complexes, $C_5H_5N(IN_3)$, $(C_5H_4N)_2(IN_3)_2$, and $(CH_2)_6N_4(IN_3)_2$, the iodine azide is coordinated via linear bridges $N^+—I^-—N_3$. The α,α'-dipyridyle–diiodine azide complex was characterized by X-ray methods; one of the IN_3 molecules is almost coplanar with the pyridyle ring to which it is bonded, whereas the other one is nearly perpendicular to the second pyridyle ring; the dihedral angle of the pyridyle rings is 63.4° (*142*).

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