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The Chemistry of Tetranitromethane

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Information on the methods of preparation, physical and chemical properties, and toxicity of tetranitromethane that appeared in print up to 1974 is reviewed systematically. Considerable attention is paid to the diverse reactivity of tetranitromethane with unsaturated compounds that has been discovered during recent years. A list of 317 references is included.

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I. INTRODUCTION

Several research workers have paid close attention to tetranitromethane during the past fifteen years. Thus, whereas around 100 publications appeared during the century after its discovery (Shishkov, 1857), this number had been doubled by 1973. Such vigorous progress in the chemistry of nitromethane is due to the discovery of fundamentally new types of chemical reactions leading to the synthesis of various nitro- and polynitro-compounds. The need therefore arose to summarise the accumulated experimental results, especially as reviews on the chemistry of tetranitromethane are lacking both in the Soviet and in the foreign literature.

Tetranitromethane is a unique nitro-compound, in which a regular tetrahedral structure, absence of polarity, and hence equivalence of all the nitro-groups are combined with great mobility of one of the nitro-groups in chemical reactions, resulting in formation of a nitryl cation NO_2^+ and the dually reactive conjugate trinitromethanide anion $(NO_2)_3C^-$ or the corresponding radical-anions or radical pairs depending on the conditions. Perhaps the most characteristic feature of tetranitromethane—a strong π-acid—is its ability to form with π- or p-electron systems (substituted aryls, alkenes, arylalkenes, dienes, vinyl ethers and esters, etc.) donor–acceptor or charge-transfer complexes which, depending on the structure of the donor and the reaction conditions, are converted into nitroaryls, arylnitroalkenes, α-nitro-ketones, tetranitroalkanes, or dinitroisoxazolidines. The diversity of these transformations constitutes the synthetic value of tetranitromethane.

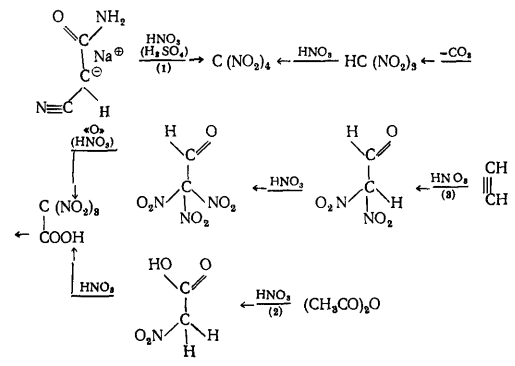
By varying the structure of the donor and the conditions of the reaction we can change the mechanism from heterolytic to radical or radical-ion in photochemical processes, thus changing the direction of the reaction and the structure of the final products, and accomplishing controlled syntheses by means of tetranitromethane.

II. METHODS OF PREPARATION OF TETRANITROMETHANE

Tetranitromethane was first obtained by Shishkov[1,2] in 1857 by the action of a mixture of nitric and sulphuric acids on sodium 2-cyanoacetamide (1), converted further into trinitroacetonitrile, which was then hydrolysed to ammonium trinitromethanide, this being subsequently nitrated with fuming nitric acid to give tetranitromethane. This was the sole method until 1903, when a 10% yield of tetranitromethane was obtained from acetic anhydride and diacetylorthonitric acid[3]. During subsequent years acetic anhydride, acetylene, ethylene, and products of the pyrolysis of natural gas were used as starting materials. Acetic anhydride was nitrated with acetyl nitrate[4], nitrogen pentoxide alone[5] and mixed with nitrogen peroxide[6], and with nitric acid alone[7] and in the presence of glacial acetic acid[8-10] and catalysts (orthophosphoric, sulphuric, and hydrochloric acids, phosphorus pentoxide, phosphoryl chloride, phosphorus pentachloride, sulphuryl chloride, acetyl chloride, and boron triacetate[11]).

A semi-industrial, convenient, and safe laboratory process giving yields up to 65% was accomplished by nitrating acetic anhydride with nitric acid[12,13]. Nitration takes place in several stages: the nitroacetic acid formed is further nitrated to trinitroacetic acid, which is decarboxylated to trinitromethane, and this is nitrated to tetranitromethane (2).

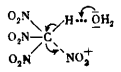
The use of acetylene and ethylene (Orton, 1918)[14,15] broadened considerably the raw-materials base for the production of tetranitromethane. The nitration of acetylene with 90–97% nitric acid in the presence of oleum or phosphorus pentoxide and mercury nitrate as catalyst also involves trinitroacetic acid and trinitromethane as intermediate species[16] (13).



In 1949 a semi-industrial plant was described for the production of tetranitromethane by the nitration of acetylene[17]. Small industrial plants have been described also for continuous production from pure acetylene[18] and from natural gas by preliminary pyrolysis in an electric

arc followed by nitration with a mixture of nitric and sulphuric acids[19].

A study of the kinetics[20] and the mechanism[21] of the final stage in most methods of preparation—the nitration of trinitromethane by nitric acid—showed that, in the presence of 87.5–100% sulphuric acid, the reaction is represented by a third-order equation (containing the concentrations of the nitryl ion, trinitromethane, and water or sulphuric acid) and results from a concerted attack by the nitryl ion at the carbon atom and by the base at the hydrogen atom



The formation of a small quantity of tetranitromethane (up to 1%) in the manufacture of trinitrotoluene stimulated a search for methods of obtaining the former from aromatic hydrocarbons and their derivatives[22–26]. However, such methods have not found application because of poor yields.

Treatment of keten with 100% nitric acid gives a 90% yield of tetranitromethane[27]. A low yield can be obtained by nitrating acetone with nitric acid[5,28]. The production of tetra- and tri-nitromethanes from malonamide has been patented[29]; a 58% yield of the latter is formed when this diamide is nitrated with 90% nitric acid in the presence of concentrated sulphuric acid, and a 45% yield of the former in the presence of oleum. The interaction of picrylpyridinium nitrate and nitromethane gives a nearly theoretical yield of tetranitromethane[30]. Rather theoretical interest attaches to the Hantzsch method[31], consisting in the reaction of iodotrinitromethane with silver nitrite in aqueous–alcoholic solution, and the analogous action of nitryl chloride on trinitromethane or its silver and potassium salts (yields 65%, 20%, and 94% respectively)[32].

Among the many processes only the nitration of acetic anhydride and that of acetylene have found industrial application. However, the first of these methods has the disadvantage of using large quantities of strong acids, which corrode the equipment, and the second involves the formation of large quantities of gases. The economics of these methods depends on the degree of utilisation and recovery of byproducts.

III. PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

Physicochemical constants determined for tetranitromethane by different workers differ significantly[33], so that it is difficult to use them to describe the structure of the compound or to assess its purity. The values given below have been adopted by the International Bureau of Physicochemical Standards.

Tetranitromethane is a highly volatile, mobile liquid boiling at 127.5°C under normal pressure[34] and melting at 13.9°C.[35] Experimental values of the vapour density have been given[34,36–39] over the range 0–127.5°C, and it can be calculated by means of the equation $\lg p = 7.23 - 2130/T$.[37] The vapour pressure of tetranitromethane has been determined close to its melting point[40]. The density d is respectively 1.64837, 1.63944, and 1.62178 g cm^{-3} at 15, 20, and 30°C. The change in density per degree is 0.00174 g cm^{-3}, and the coefficient of expansion is 0.00109.

The refractive index[41] at 15°C is given by

$He_\gamma = 1.43655$, $dn/dt = 0.00045$; $H_\alpha = 1.43709$, $dn/dt = 0.00045$; $D_{Na} = 1.44066$; $He_\delta = 1.44076$, $dn/dt = 0.00046$; $He_\nu = 1.44768$; $dn/dt = 0.00046$; $H_\beta = 1.44937$, *Veviol* = 1.45593.

The dispersion $H\beta - H\alpha = 0.01228$. Molecular refractions[41] are listed in Table 1. The refraction for the nitro-group in tetranitromethane is 7.20 [42] ($MR_D = 31.40$) and 7.248.[43]

Table 1.

	H_α	D	H_β	H_γ
Found	31.16	31.39	31.65	—
Calculated	29.01	29.30	29.72	30.07
Difference	+2.15	+2.09	+1.93	—

Viscosity has been determined experimentally at 15, 20, 30, and 40°C,[35,41,44], and surface tension at 15, 20, 25, 30, and 50°C.[41,54] The parachor of tetranitromethane has also been calculated[45]. The speed of sound in the liquid is 1039 m s^{-1} at 20°C, with a temperature coefficient in the range 4–6 m s^{-1}.[46]

Both the pure compound[47] and its solution in liquid sulphur dioxide[48] showed negligible electrical conductivity. On the other hand, a solution of tetranitromethane in liquid ammonia was very highly conducting[49], probably because of interaction with the solvent. The dielectric constant of tetranitromethane at 5, 20, and 25°C is respectively 2.15, 2.317, and 2.521 s^2 cm^{-2}.[42,47–54] Birefringence has been reported in an electric field, with a molar Kerr constant of 2.98×10^{-12} cm V^{-2}.[55] Experimental dipole moments[52,55–58] lie in the range $(0.19–0.71) \times 10^{-18}$ D at 25°C. Actually, however, the dipole moment of tetranitromethane is zero[6]: the observed values lie within the limits of experimental error, and have been determined on impure samples. One cause of the high value was determination of the dipole moment in solvents (e.g. benzene) capable of forming donor–acceptor complexes with tetranitromethane.

The magnetic susceptibility and the magnetic permeability have been investigated[59–61]. The magnetic refraction and the Cotton–Moulton effect have been examined[62]. Several nuclear magnetic resonance studies have been made[63–69].

The ultraviolet spectrum of tetranitromethane was first obtained by Zelinskii[70], and was later analysed[38,71–75]. The main absorption band in dichloromethane has $\lambda = 280$ nm and $\epsilon = 135$. Discussion of the infrared spectrum[73,76–84] led to the assignments—asymmetric and symmetric stretching vibrations of nitro-groups at 1618 and 1266 cm^{-1} respectively (both very strong); and other bands at 1645 (medium), 1439 (weak), 1370 (m), 990 (w), and 973 (m) cm^{-1} [73]—and interesting studies were made[78,85] of the infrared spectra of the vapour at 25°C, the liquid at 18°C, and the crystalline state at −40, −88, −104, and −126°C. Tetranitromethane can exist in two crystalline forms, with an isomorphous transition at −99.8°C. The Raman spectra obtained in three different states—solid, liquid, and dissolved in tetrachloromethane—indicate that the molecule possesses the symmetry $D_2 = S_{4u} = V_d = 42m$.[86] The main lattice parameters have been determined by

means of X-rays[87-93] (see Fig. 1). The diffraction of X-rays has been studied in the liquid and in its solutions[94-96].

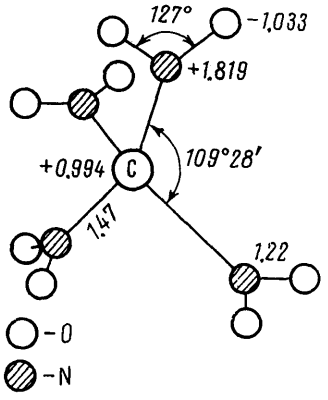


Figure 1. Model of the tetranitromethane molecule.

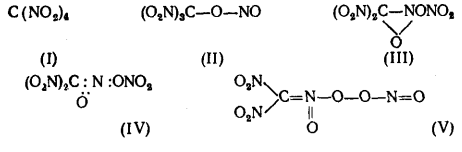
Heats of formation and combustion were determined[8]:

$$C(\text{diamond}) + 2N_2(\text{gas}) + 4O_2(\text{gas}) = C(NO_2)_4 + 4.7 \text{ kcal mole}^{-1}$$
$$C(NO_2)_4 = CO_2 + 3O_2 + 2N_2 + 89.6 \text{ kcal mole}^{-1}.$$

More recent papers have given more accurate values for the heat of formation (8.9 [97] and 8.8 ± 0.7 [98] kcal mole^{-1}) and the heat of combustion (102.9 kcal mole^{-1} [97,99,100]). Determinations have been made of the latent heat of evaporation[37], the entropy of evaporation[38], and the entropy of vaporisation[101,102]. The energy of dissociation of the carbon–nitrogen bond in tetranitromethane has been estimated as 38.2 [103,104] and 39.3 [105] kcal mole^{-1}. The enthalpy of formation of the compound is 18.5 kcal mole^{-1}.[105,106]

Tetranitromethane is highly toxic[107-112], attacking the respiratory tracts and the central nervous system[112-116]. The threshold concentration is 0.003 mg litre^{-1}, and the permissible limit in air 0.001 mg litre^{-1}.[113-117] Various methods have been worked out for its determination—spectrophotometrically in air and in solutions[113,118,119], calorimetrically in water[120], volumetrically in concentrated nitric acid[121], oscillopolarographically in nitromethane[122], and polarographically in the presence of *m*-dinitrobenzene and 1,3,5-trinitrobenzene[123]—and its use for analytical purposes has been reported[124,125]. Tetranitromethane possesses fungicidal[126,127] and insecticidal[128] properties; data have been published on its biochemical activity[128-131].

Because of the great mobility of one nitro-group in chemical reactions, many investigators suggested that the four nitro-groups were not equivalent. As a consequence, a structure was in various cases attributed to the compound that explained only the particular reaction, without taking into account the great diversity of its chemical and physicochemical properties.



In a study of the aci-form of the nitro-group Hantsch[132] suggested the equivalence of all four true nitro-groups (I). Investigation of the behaviour of the compound as a nitrating agent led Schmidt[133] to the nitrite structure (II), adopted by Macbeth[134] on the basis of the similarity in appearance of the ultraviolet spectra of mixtures of tetranitromethane and unsaturated hydrocarbons to those of complexes of alkyl nitrites and unsaturated compounds. Willstätter[135] had deduced the existence of the "cyclic form" (III). Claisen[136] and subsequently Auwers[137] suggested a "nitrone" type of structure (IV) from a study of the physical properties. Finally, examination of the oxidising properties of the compound enabled the "peroxide" structure (V) to be attributed to it[138]. Several investigators assumed[71,139,140] that an equilibrium was established between undissociated and ionic forms.

Later determinations of the dipole moment[56,57,141] and the parachor[45], as well as study of X-ray diffraction patterns[87,94], and the Raman and infrared spectra in the gaseous state[85,142-144] have shown that the molecule has the form of a regular tetrahedron with S_{4u} symmetry.

Quantum-chemical calculation based on the Slater treatment shows[145] that the electron density is considerably raised on the oxygen atoms of the nitro-groups, but significantly lowered on the nitrogen and carbon atoms (Fig. 1).

IV. DONOR–ACCEPTOR (CHARGE-TRANSFER) COMPLEXES

Tetranitromethane is a strong acceptor of electrons and, like Lewis acids, a powerful complexing agent. Its electron affinity has been estimated as 1.7 eV (similar to the value of 1.8 eV for iodine), which is responsible for its great tendency to form complexes with donors[146]. Indeed, one of the most interesting reactions of the compound with alkenes, dienes, arylalkenes, and aryls, yielding a wide range of organic compounds, begins with the formation of charge-transfer complexes, as will be shown below.

The ability of tetranitromethane to form coloured complexes was discovered almost simultaneously by Ostromyslensky[147,148] and by Werner[149] as early as 1909. It is evident as an instantaneous yellow to dark red coloration on addition to a solution of an unsaturated compound. This qualitative test, termed the Ostromyslenskii reaction, is widely used to distinguish tautomeric forms of organic compounds[147,148,150,151] and to detect ethylenic hydrocarbons[152,153], dienes[154], terpenes[155,156], steroids[157], unsaturated ketones[158], dimethylcyclohexanedione derivatives of aldehydes[159], fats and higher unsaturated aliphatic acids[160,161], and aromatic hydrocarbons[150,162-164]. At the same time, this colour reaction is not universally applicable: thus no coloration is observed with benzoic, maleic, and fumaric acids[151], $\alpha\beta$-unsaturated aliphatic acids and their derivatives, $\alpha\beta$-unsaturated aldehydes[154], and halogenated unsaturated compounds[165], owing to the inability of tetranitromethane to form complexes with compounds containing electrophilic groups at the multiple bond. On the other hand, coloured complexes are formed with compounds containing no multiple bond, e.g. cyclopropane[166,167], diethyl sulphide, iodoethane, triethylphosphine, 1,4-dioxan, 1,4-dithian[168-170], dimethyl sulphoxide[171], and various amines[133,172,173]. Not long ago it was proposed that tetranitromethane should be used in the development of chromatograms as a qualitative reagent for organic compounds of bivalent sulphur[174].

Study of the relation between the structure of the unsaturated compound and the colour produced by mixing with tetranitromethane indicated that the intensity of the coloration increased with the basicity of the unsaturated compound[140,175-177]. The ultraviolet spectra of mixtures of aromatic hydrocarbons showed that the colour intensity varied linearly with the concentration of the hydrocarbon and with the number of methyl groups in the benzene ring[178,179].

The mechanism of formation and the structure of the complexes with unsaturated compounds have been discussed since the time of their discovery. Hypotheses involved isomerisation of one or more true nitro-groups into nitrite groups, which form the coloured complex with the alkene[134]. It was assumed also that the coloured complexes were polarised particles retained by electrostatic forces[179,180], or ion-pairs comprising a carbonium ion and a trinitromethanide anion[140,181-183].

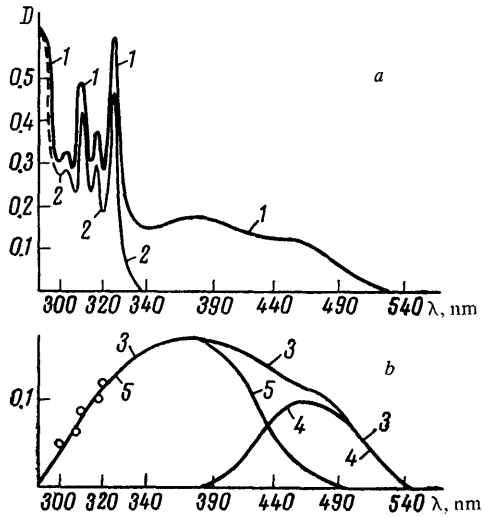


Figure 2. (*a*) Electronic absorption spectrum of 0.80 M tetranitromethane + 0.05 M 2,6-dimethylnaphthalene in heptane: 1) spectrum of tetranitromethane in heptane; 2) long-wavelength region of spectrum of dimethylnaphthalene in heptane. (*b*): 3) spectrum of charge-transfer complex; 4) long-wavelength absorption band of charge-transfer complex; 5) short-wavelength band of charge-transfer complex.

Perekalin et al.[184-189] used electron spectroscopy to study the spectra of the ternary systems formed with a donor and a solvent, in which they detected new bands absent from the initial components, which they ascribed to absorption by the complex. Detailed examination of the charge-transfer spectra with donors, e.g. 2,6-dimethylnaphthalene (Fig. 2), revealed two bands, which were assigned to the same complex[189]. The substantial solvatochroism of the bands due to the complexes, together with their bathochromic displacement with decrease in the ionisation potential of the donor (Table 2), indicated that those at longer wavelengths were intermolecular charge-transfer bands. A modified method of isomolar series throughout the band envelope indicated that the composition of all the charge-transfer complexes was equimolecular[189].

Table 2. Positions of absorption band maxima for charge-transfer complexes in heptane and in nitromethane ν_h and ν_n, extinction coefficients ϵ_{max}, and ionisation potentials *I*.

Donor	ν_h, cm^{-1}	ν_n, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	*I*, eV
Anethole	20 400	21 900	720	—
Hexamethylbenzene	20 600	21 850	1 200	7.8
Tetraphenylethylene	20 750	22 950	4 000	—
Mesitylene	25 800	27 350	3 000	8.4
α-Methylstyrene	25 800	28 050	1 100	—
Benzene	31 300	33 000	10 000	9.2

Table 3. Association constants, products $K_c\epsilon_{max}$, and thermodynamic functions of tetranitromethane complexes in heptane.

Donor	K_c	$K_c\epsilon_{max}$	$-\Delta H_c$, kcal mole^{-1}	$+\Delta G_c$, kcal mole^{-1}	$-\Delta S_c$, cal mole^{-1} deg^{-1}
1,1-Di-*p*-methoxy phenylethylene	0.170	93	1.2	1.0	7.5
Anethole	0.114	81	0.9	1.3	7.5
α-Methylstyrene	0.080	88	0.8	1.5	7.8
β-Methylstyrene	0.045	68	0.7	1.9	8.9
Tetraphenylethylene	0.015	60	0.6	2.5	10.6
Hexamethylbenzene	0.153	180	1.5	1.1	8.8
Mesitylene	0.060	180	1.2	1.6	9.7
Benzene	0.020	190	0.9	2.3	11.0

Thermodynamic parameters calculated for several charge-transfer complexes (Table 3) from a spectrophotometric study of the effect of temperature on the association constants[189,190] reveal the weakness of the complexes ($\nu_c \ll 1$, $\Delta H_c \simeq 1.0$ kcal mole^{-1}, $\Delta G_c > 0$). A definite parallelism is evident between the equilibrium constant and the heats of complex formation, with increase in K_c corresponding to increase in the enthalpy[184,190]. The comparatively slight differences in entropy are evidently due to significant polarisation of the charges accompanying formation of the charge-transfer complexes. The closeness of the product $K_c\epsilon_{max}$ (Table 3) to values characteristic of the homologous series of alkenes ($K\epsilon_{max} \simeq 80$),[184] not to those for alkylbenzenes (~180),[187] shows that π-electrons of the multiple bond, not those of the benzene ring, form the centre of coordination in the charge-transfer complexes of arylalkenes.

The complexes become significantly less stable with increase in the dielectric constant of the medium (Table 4). A clear parallelism is evident between K and $(\epsilon - 1)/(\epsilon + 2)$.[189] Determination of the dipole moments of the charge-transfer complexes with various hydrocarbons, by the method of spectral shifts (Table 5), was extremely important in establishing the structure of the complexes. From the dipole moments at 20°C and the spectroscopic characteristics a quasi-ionic structure with separated charges (Fig. 3) was attributed to the charge-transfer complexes in the ground state.

Table 4. Association constants of tetranitromethane complexes of anethole and of isodurene in various solvents at 20 ± 0.1 °C.

Solvent	$(\varepsilon-1)/(\varepsilon+2)$	Anethole	Isodurene
Heptane	0.234	0.114	0.122
Tetrachloromethane	0.292	0.092	0.065
Diethyl ether	0.530	0.018	0.030
Chloroform	0.560	0.012	0.020
Dichloromethane	0.720	0.006	0.008

Table 5. Calculated individual constants C_1^a and dipole moments of complexes.

Donor	α-Methylstyrene	β-Methylstyrene	Anethole	Benzene	Naphthalene
C_1^a av	2700	2500	1700	2000	3000
μ_g, D	6.0	6.0	5.0	5.0	6.5

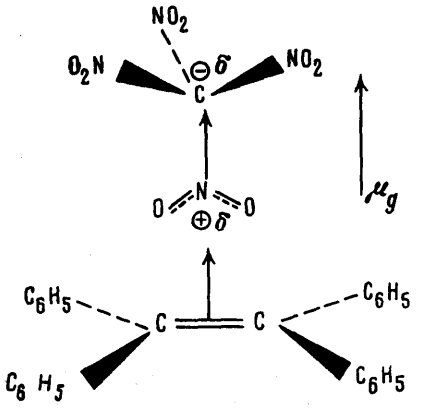


Figure 3. Model of complex of tetranitromethane with tetraphenylethylene.

Existing information on the properties and the structure of the complexes enables us to represent the interaction of unsaturated compounds with tetranitromethane by the scheme

$$D + C(NO_2)_4 \rightleftarrows D^{+\delta} \ldots {}^{-\delta}C(NO_2)_4 \underset{\text{(VI)}}{\overset{300\,^\circ K}{\rightleftarrows}} [D \ldots NO_2]^{+\delta} \ldots {}^{-\delta}C(NO_2)_3 \underset{\text{(VII)}}{}$$

$$\rightarrow \text{Transition state} \rightarrow \text{Reaction products}$$

Mixing an alkene with the nitro-compound produces initially charge-transfer complexes of type (VI), which are converted by further interaction of donor and acceptor into charge-transfer complexes with separation of charges (type VII). Redistribution of electron density and change in the steric configuration then convert the latter complexes into a reactive transition state, subsequently settling into the final products depending on its structure and the reaction conditions.

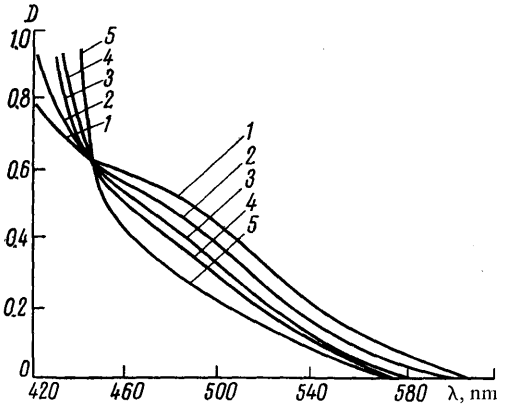


Figure 4. Dependence of electronic absorption spectra on time elapsed from start of reaction (min): 1) 3; 2) 6; 3) 20; 4) 60; 5) 120.

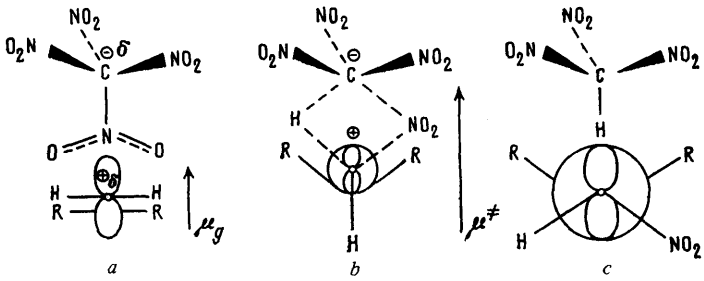
Table 6. Thermodynamic activation parameters for the reaction between tetranitromethane and 1,1-di-*p*-methoxyphenylethylene and electrical characteristics of the transition state.

Solvent	$\frac{\varepsilon-1}{\varepsilon+2}$	$-\ln K_2$		$\Delta H^{\neq}$,	$-T\Delta S^{\neq}$,	$\Delta F^{\neq}$,	$\ln A$	$\mu^{\neq}$, D	Q
		20° C	30° C	kcal mole^{-1}					
Heptane	0.235	6.58	5.35	21.4	0.5	20.9	31.3	12	0.60
Tetrachloromethane	0.292	8.09	7.50	9.5	12.2	21.7	9.3	11	0.55
Tetrachloroethylene	0.302	7.62	6.84	5.8	15.6	21.4	3.4	11	0.55
Tetrachloroethane	0.702	6.19	5.57	10.0	10.6	20.6	12.0	12	0.60
Dichloroethane	0.757	5.53	6.41	13.9	6.4	20.3	16.7	12	0.60
Nitromethane	0.926	0.27	1.07	20.8	3.8	17.0	37.0	15	0.80

This process was studied experimentally on the reaction with 1,1-di-*p*-methoxyphenylethylene leading to the formation of 1,1-di-*p*-methoxyphenyl-2-nitroethylene (95%). The presence of a sharp isobiestic point in the electronic spectra in different solvents (Fig. 4) confirmed the hypothetical intermediate formation of a charge-transfer complex. Treatment of experimental kinetic results yielded[189] thermodynamic parameters of the limiting stage and dipole moments of the transition state in various solvents (Table 6). The variation from 0.55 to 0.8 in the degree of charge transfer Q, defined as the ratio of the dipole moment μ of the transition state to the maximum value $\mu^{\neq}$ for the ion-pair (~20 D), shows that the transition state occupies an intermediate position between the charge-transfer complex and the ion-pair, approaching the latter.

Conversion of the charge-transfer complex via the transition state into the reaction product (the nitroalkene) is shown diagrammatically in Fig. 5. In the complex the π-electron cloud of the double bond of the donor fits into the electron gap of one of the nitro-groups (Fig. 5*a*), which entails weakening of one of the carbon–nitrogen bonds and strengthening of interaction between the cationoid nitro-group and a carbon atom of the multiple bond. The tendency to $sp^2 \rightarrow sp^3$ rehybridisation of the carbon atoms forming the double bond creates favourable steric conditions (rotation about the carbon–carbon bond) for the quasi-carbonium cation (Fig. 5*b*) to settle into the

nitroalkene (Fig. 5*c*). Because of the eclipsed configuration and further weakening of the π-bond, state (*b*) has the highest energy content and hence is the decisive transition state. The stage of detachment of a proton is not rate-determining, as is indicated by the absence of a kinetic isotope effect.



R = *p*-$CH_3OC_6H_4$

Figure 5. Models of: *a*) charge-transfer complex; *b*) transition state; *c*) reaction products.

Exposure to monochromatic light of wavelength 405 or 436 nm changes the mechanism of conversion of the charge-transfer complexes and initiates complete transfer of an electron from donor to acceptor with formation of radical-ion species recorded by electron-spin resonance[191-198]. Under the influence of a light quantum the tetranitromethane molecule, by capturing the electron from the donor, passes into an unstable radical-anion, which then breaks down into a trinitromethanide anion and a nitro-radical $\cdot NO_2$. The radical-cation $D^{\cdot+}$ is stabilised as the nitrocarbonium cation D^+NO_2 by addition of the paramagnetic nitro-radical:

$$D + C(NO_2)_4 \rightleftarrows D^{\oplus\delta}\cdots{}^{\ominus\delta}C(NO_2)_4 \xrightarrow{h\nu} D^{\oplus\cdot} + {}^{\cdot}C(NO_2)_4 \rightarrow$$
$$\rightarrow D^{\oplus\cdot} + {}^{\cdot}NO_2 + \overset{\ominus}{C}(NO_2)_3 \rightarrow D^{\oplus}NO_2 + \overset{\ominus}{C}(NO_2)_3 \ .$$

The subsequent course of the reaction is determined by the changes undergone by the trinitromethanide–nitrocarbonium ion-pair.

A radical-ion mechanism is improbable for the reaction with 1,1-di-*p*-methoxyphenylethylene at 300 K), for photoexcitation by a light quantum in the intermolecular charge-transfer band does not influence the rate of transfer, and no induction period is detected even in the presence of oxygen. One-electron transfer may be possible for the reaction with alkenes, terminating in the synthesis of other products, but this mechanism has not been confirmed experimentally.

The alternative of a free-radical decomposition of the charge-transfer complex, leading to a paramagnetic trinitromethyl radical with a subsequent chain reaction, has also been discussed[193-197]. In the absence of illumination at 300 K and of high concentrations of the initial components, however, paramagnetic species are not directly generated by tetranitromethane for alkenes[198]. The nitro-radical and other paramagnetic species sometimes recorded result from thermal decomposition of the nitronic ester of trinitromethane.

Steric rearrangement of the charge-transfer complex by a free-radical mechanism to reaction products is permissible for the reaction with 1,1-di-*p*-methoxyphenylethylene, but the dipole moment of the transition state will then be determined by that of the $(p\text{-}CH_3OC_6H_4)_2C(CH_2NO_2)\cdot$ radical. Comparison of its dipole moment with that of the transition state (~5 and ~15 D) excludes a chain reaction mechanism under the given conditions.

V. CHEMICAL PROPERTIES

1. Nucleophilic Substitution

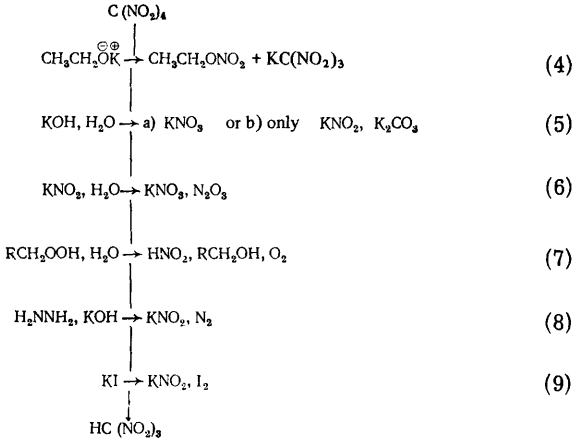
The sterically strained arrangement of the four electrophilic nitro-groups in the molecule lowers the activation energy of the carbon–nitrogen bond, enhances the electrophilic character of the carbon atom, usually through the charge-transfer complex stage, and makes it the centre of attack by nucleophilic reagents.

Hantzsch and Rinckenberger[199] found that tetranitromethane is smoothly converted in almost theoretical yield into its salt by the reaction (4) which has remained to the present time the most convenient laboratory method for obtaining trinitromethane (by the action of an alcoholic solution of potassium hydroxide or ethoxide). However, aqueous potassium hydroxide, depending on its concentration, either gives the same results with the formation of potassium nitrate or causes complete degradation to potassium nitrite and carbonate[133,200] (reaction 5). The potassium salt of trinitromethane can be obtained also by the reaction of tetranitromethane with potassium hydroxide dissolved in aqueous glycerol[201].

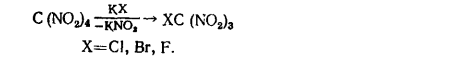
A patented process of obtaining trinitromethane and its salts is based on the hydrolysis of tetranitromethane in the presence of nitrites of light metals, the consumption of which is diminished by conducting the reaction in the presence of a base—potash, potassium hydroxide, potassium or sodium acetate, etc. (reaction 6).[202] At the same time a detailed kinetic study was made of the reaction of tetranitromethane with hydroxide and nitrite ions[203,204]. The rate-determining stage is formation of a charge-transfer complex in the first case, and in the second case the reaction is of the first order with respect to both tetranitromethane and the nucleophile. Alkyl hydroperoxides are a thousandfold as effective as hydroxide ions in accelerating the reaction[204] (7).

Attempts to obtain the sodium salt of trinitromethane by the action of sodium methoxide on tetranitromethane were unsuccessful[205]. Compounds used as denitrating agents were potassium sulphite and phosphite, hydrazine[206], hydrogen peroxide[24], potassium hexacyanoferrate(II),[207] potassium iodide[208], etc. The reaction with hydrazine can be used for the quantitative determination of tetranitromethane from the nitrogen evolved (8).[206] Phenylhydrazine in the presence of caustic potash converts tetranitromethane into the potassium salt of nitromethane[201]. The reaction of tetranitromethane with sodium sulphite underlay a method for purifying crude trinitrotoluene by washing it with 3–5% sodium sulphite solution[209]. Iodometric[210] and spectrophotometric[211] methods of determining tetranitromethane are based on its reaction with potassium iodide (9) in

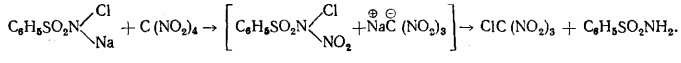
aqueous alcohol; overall the reaction has the second order, and the first order with respect to each of the components[211,212].



The action of lithium, potassium, rubidium, and caesium halides on tetranitromethane in dimethylformamide can be used for the separation of halogenotrinitromethanes[213,214]:



The next two reactions are essentially non-nucleophilic, but yield substitution products. In dimethylformamide and dimethyl sulphoxide tetranitromethane reacts readily with chloramine B to form chlorotrinitromethane via a stage involving *N*-chloro-*N*-nitrobenzenesulphonamide and sodium trinitromethanide[215,216]:

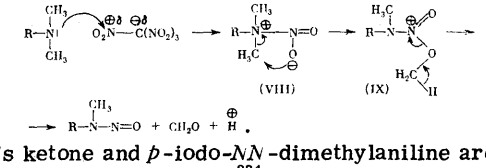


Recent reports[217,218] that a nitro-group in tetranitromethane can be replaced by an alkyl in a medium comprising acetone and Hexametapol or dimethylformamide have aroused interest in connection with a discussion of the reaction mechanism[214,219].

2. Nitrosation of Tertiary Amines

Schmidt[133,220-222] accomplished by means of tetranitromethane the nitrosation of aliphatic and aromatic tertiary amines in pyridine and of ring-halogenated aromatic tertiary amines in acetic acid.

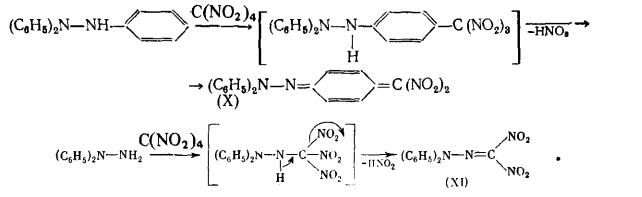
The nitrosation of ethylbenzylamine yields 14% of *N*-nitrobenzylamine and 70% of nitrosoethylbenzylamine[223]. The conversion of tertiary amines into nitrosamines probably involves intermediate formation of a nitroammonium ion (VIII); four-centre transfer leads to rupture of the nitrogen–carbon bond with formation of a nitronic ester (IX), which dissociates into a nitrosamine and an aldehyde[140]:



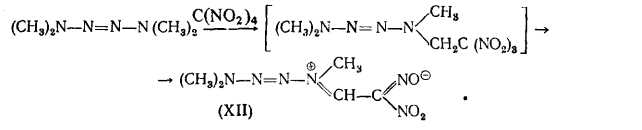
Michler's ketone and *p*-iodo-*NN*-dimethylaniline are probably nitrosated similarly[224]. However, the mechanism of the nitrosation of tertiary amines by tetranitromethane requires further elaboration.

3. *gem*-Dinitromethylation

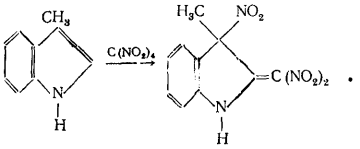
In several cases tetranitromethane acts as a *gem*-dinitromethylating agent as well as an oxidant. Thus with triphenylhydrazine it forms (X),[225] and with $\alpha\alpha$-diphenylhydrazine it gives (XI).[226] In all cases initial trinitromethylation of the nucleophilic compound (as a result of a four-centre transfer) is followed by elimination of one nitro-group, leaving a *gem*-dinitromethylene derivative:



Tetramethyltetrazen is converted into the zwitterion (XII):[227]



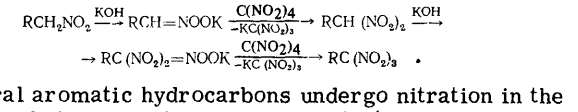
With skatole the *gem*-dinitromethylated product contains another nitro-group[228]:



In a brief communication on the reaction of tetranitromethane with cycloalkenes[229] a dinitromethane structure was incorrectly attributed to the main reaction product[230,231].

4. Electrophilic Substitution

Nitroalkanes, *gem*-dinitroalkanes, aromatic hydrocarbons, and arylalkenes having an activated multiple bond undergo mild nitration by tetranitromethane (in an alkaline medium). Mononitroalkanes and *gem*-dinitroalkanes in an alkaline medium yield trinitroalkanes[232,233]:



Several aromatic hydrocarbons undergo nitration in the presence of strong nucleophilic reagents (caustic alkalis, pyridine); e.g. *p*-cresol is nitrated to *m*-nitro-*p*-cresol[234], and naphthalene to 1-nitronaphthalene[183]. *NN*-Dimethyl-*p*-toluidine (in a neutral medium) forms with tetranitromethane a salt of trinitromethane and *m*-nitro-*NN*-dimethyl-*p*-toluidine, which on treatment with alkali is converted into *m*-nitromethyl-*p*-toluidine[234]. In the absence of alkali *N*-alkylcarbazoles are nitrated in the ring, slowly but with high yields[235]; nitration is considerably accelerated by ultraviolet irradiation. Kinetic investigation of the nitration of *para*-substituted phenols[236] in water and in 95% ethanol showed in both cases the second order with respect to the phenol, the limiting stage being dissociation of the charge transfer-complex.

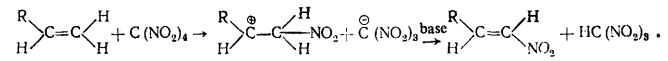
The nitration of tyrosine at pH 8.0 by tetranitromethane to 3-nitrotyrosine stimulated intensive research on proteins containing tyrosine residues[237-248]. Alkaline

nitration has been used to obtain nitro-derivatives of azulenes. Thus an 85% yield of 1-nitro-2,4,8-trimethylazulene was isolated from the nitration of 2,4,8-trimethylazulene in the presence of pyridine[249,250]. Cyclopenta[*c*]thiapyran gave with tetranitromethane the corresponding mononitro-derivative[251].

Arylalkenes in which the double bond was conjugated with the ring were nitrated by Schmidt[222,234] in the presence of pyridine and acetone to the corresponding β-nitroalkenylarenes: e.g.

$$CH_3OC_6H_4CH{=}CH_2 \xrightarrow[\text{pyridine}]{C(NO_2)_4} CH_3OC_6H_4CH{=}CHNO_2 .$$

Nitration of the same arylalkenes in methyl and ethyl alcohols yielded α-alkoxy-β-nitro-compounds[222]. Unconjugated arylalkenes[222], containing the double bond in the allyl position with respect to the ring, are not nitrated under these conditions. Bülich[181], Patterson[140], and Titov[252,253] assumed that the reaction with arylalkenes takes place by an ionic mechanism; the formation of conjugated nitroalkenes on alkaline nitration was regarded as the result of consecutive reactions involving the base—electrophilic addition to the alkene of the nitronium cation produced by heterolytic breakdown of tetranitromethane, formation of an ion-pair, nucleophilic attack by the base on the nitrocarbonium cation, and its stabilisation, with elimination of a proton, as a conjugated nitroalkene:

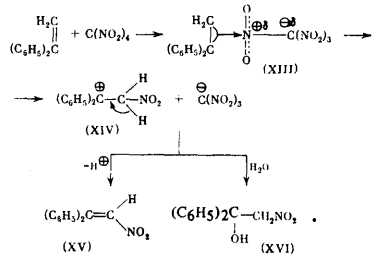


In the absence of bases addition products are formed by tetranitromethane with such alkenes, e.g. *p*-anethole[254].

5. Electrophilic Addition

A comprehensive investigation by Perekalin and Altukhov[263,264] of the reaction with substituted alkenes, arylalkenes, vinyl ethers, and dienes revealed fundamentally new reaction paths. For example, several conjugated nitroalkenes were obtained by the action of tetranitromethane on alkenes in a neutral medium.

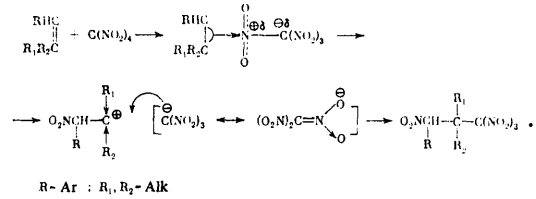
Tetraphenylethylene does not react owing to steric hindrance of the double bond and the absence of ethylenic hydrogen atoms; the behaviour of 1,1-diphenylisobutene is similar. In these cases interaction between the hydrocarbon and tetranitromethane ceases at the charge-transfer complex stage, with equilibrium displaced towards the initial components. When one or two phenyl groups attached to the same ethylenic carbon atom in tetraphenylethylene are replaced by hydrogen atoms, steric hindrance is diminished, and reaction with tetranitromethane becomes possible. Thus triphenylethylene[255], 1,1-diphenylethylene[255,256], and 1,1-di-*p*-methoxyphenylethylene[257] in the absence of basic catalysts form conjugated nitroalkenes via the stage of a charge-transfer complex (XIII), which is converted by electrophilic incorporation of a nitronium cation into a nitrocarbonium cation (XIV) (with the trinitromethanide anion as gegenion), and this is stabilised as the nitroalkene (XV) by elimination of a proton:



Intermediate formation of an ion-pair is confirmed, in particular in the case of diphenylethylene, by isolation from the reaction medium of the corresponding nitro-alcohol (XVI) resulting from attack by the hydroxide ion (in the presence of water) on the nitrocarbonium cation. The presence of an ion-pair has been established also by electron spectroscopy in the action of tetranitromethane on 1,1-di-*p*-dimethylaminophenylpropene[258]. Shielding of the cationoid carbon atom by the two phenyl groups excludes nucleophilic addition of the trinitromethanide anion. The reactivity of 1,1-diarylethylenes with tetranitromethane increases with the electron-donating power of the double bond.

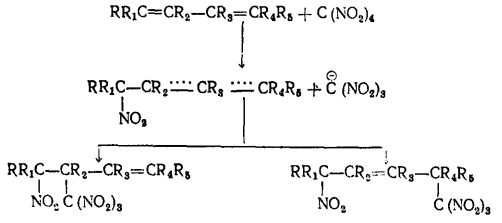
The action on alkenes in which the number of bulky phenyl rings has diminished at least to one at each carbon atom forming the double bond is more complicated and results in different final products depending on steric and electronic factors (alkyl groups adjoining the double bond and substituents in the aromatic ring). This is due to diminished steric hindrance at the cationoid carbon atom of the intermediate nitrocarbonium cation, which enables it to interact with the ambident trinitromethanide anion at its two reaction centres—an oxygen atom of the nitro-group (*O*-alkylation) and the carbon atom (*C*-alkylation)—depending mainly on the nature of the nitrocarbonium cation and to some extent on the character of the solvent.

Accumulation of nucleophilic groups in the initial alkene enhances the basic character of the double bond, increases the degree of delocalisation of the positive charge on the electrophilic centre of the nitrocarbonium cation, and causes it to react at the carbon atom of the trinitromethanide anion—the reaction centre having a smaller electron density—to form *C*-alkylated products (nitrotrinitromethylation)—1,1,1,3-tetranitroalkanes:



R = Ar ; R_1, R_2 = Alk

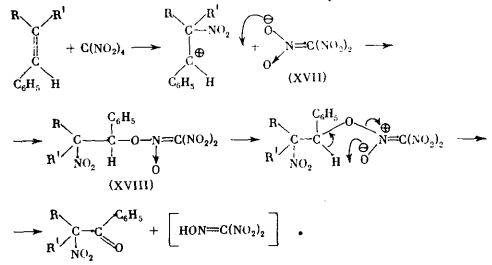
Such behaviour is exhibited by styrene derivatives alkylated at the α and β positions[259,260], arylcyclenes[231,260], and styrene derivatives *para*-substituted by electron-donating groups[254,257,261-266]. Dienes containing two or more methyl groups also undergo *C*-alkylation by tetranitromethane[267-269]:



The conjugated nitrocarbonium cation formed reacts with the trinitromethanide anion either at the 1,2-positions (2,3-dimethylbutadiene) or at the 1,4-positions (2-methylpenta-2,4-diene, 2,4-dimethylpenta-1,3-diene, and 2,5-dimethylhexa-2,4-diene) to form the corresponding tetranitroalkenes.

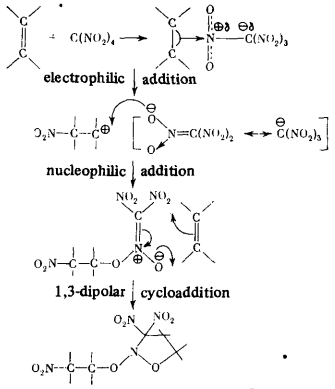
In the action of tetranitromethane on less basic unsaturated compounds the nitrocarbonium cation (XVII) appears with a considerable positive charge on the electrophilic carbon atom, and the trinitromethanide anion adds to it

at the nitro-oxygen atom having the greatest electron density (*O*-alkylation) with formation of an unstable nitroalkyl ester of aci-trinitromethane (XVIII), which is a 1,3-dipole capable of 1,3-addition of a second molecule of the alkene. However, the presence even of one substituent (phenyl or alkyl) in the β-position of the initial alkene, i.e. in the styrene derivative, makes addition of a second molecule of the alkene sterically impossible, and the resulting nitronic ester (XVIII) undergoes thermal decomposition by an intramolecular redox reaction with formation of α-nitro-ketones and dinitroformaldehyde oxime[255,257,264,270]:



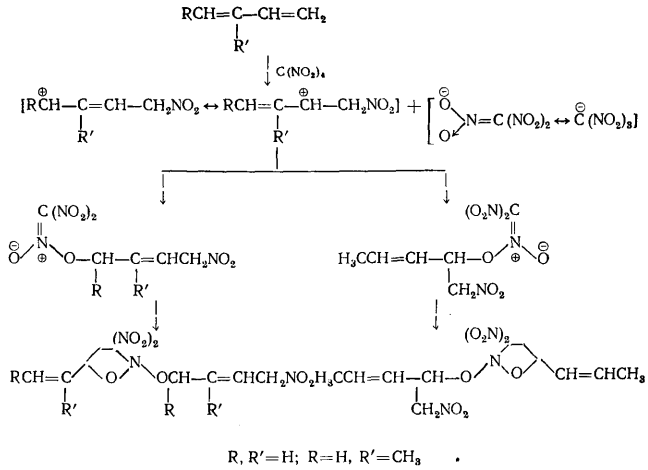
An indispensable condition for this process to occur is the presence of an α-hydrogen atom in the nitroalkyl ester (XVIII). The unstable oxime decomposes with the liberation of nitrogen sesquioxide, which nitro-nitrosates the initial alkene (yield 3–22%) and oxidises part of the oxime to trinitromethane. Formation of nitro-ketones is often accompanied by more fundamental degradative oxidation processes. Thus tetranitromethane reacts with *p*-methoxy-$\beta\beta$-dimethylstyrene[256] and with cyclohexene[270] in the absence of a solvent to give anisic and adipic acids respectively. Carboxylic acids were obtained also[160] by heating tetranitromethane with elaidic acid, stilbene, and but-2-ene. Tetranitromethane smoothly oxidises quinol to quinone, and dimethylaniline to Crystal Violet[147,151].

The action of tetranitromethane on unsaturated compounds containing adjacent to the double bond less bulky groups than phenyl (ethylene, its alkyl derivatives independently of the number and arrangement of the groups about the double bond, and also allyl and vinyl ethers), as well as styrene derivatives unsubstituted at the β-position, leads to the synthesis of 3,3-dinitroisoxazolidine derivatives[231,255,257,261,270–274]:



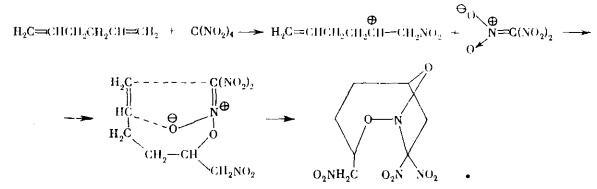
Formation of the charge-transfer complex and the ion-pair is followed by nucleophilic attack on the nitrocarbonium cation by an oxygen atom of the trinitromethanide anion to give a reactive ester of aci-trinitromethane. This reacts synchronously with a second molecule of the initial alkene, by a mechanism of 1,3-dipolar cycloaddition, to give the 3,3-dinitroisoxazolidine derivative.

With $\pi\pi$-conjugated systems tetranitromethane forms 3,3-dinitroisoxazolidine derivatives containing multiple bonds in the side-chains, as a result of 1,4-addition to butadiene and isoprene, and 1,2-addition to pentadiene; cycloaddition takes place only at the less substituted multiple bond in a diene[267,269]:

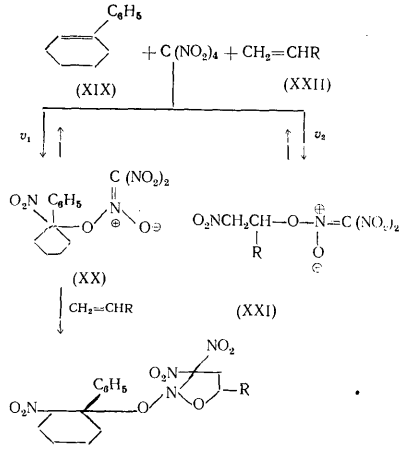


R, R′=H; R=H, R′=CH_3.

As a result of intramolecular cyclisation of the intermediate nitronic ester the reaction with hexa-1,5-diene yields a bicyclic isoxazolidine[267]:



Intermediate formation of nitronic esters of trinitromethane is supported by the controlled synthesis of substituted 3,3-dinitroisoxazolidines (of mixed composition) from tetranitromethane and two different alkenes[259,275,276]. Initially the reaction of tetranitromethane with the sterically hindered but more nucleophilic alkene (XIX) produces the nitronic ester (XX) more rapidly than the nitronic ester (XXI) is formed from the less nucleophilic and also sterically less hindered alkene (XXII); the ester (XX) then reacts with the sterically unhindered alkene (XXII), and is stabilised as the substituted dinitroisoxazolidine (XXIII) (the steric hindrance in (XIX) makes reaction of the alkene (XIX) with the nitronic esters (XX) and (XXI) impossible):



$v_1 > v_2$.

6. Acceptance of Radicals

A considerable number of studies have been made on the homolytic decomposition of tetranitromethane by the action of bases, ultraviolet radiation, or γ-rays.

Electron-spin resonance has shown that reaction with strong nucleophiles (benzidine, *NNN'N'*-tetramethylbenzidine[277], and sodium 2,4,6-tri-t-butylphenoxide[278]) begins with the appearance of charge-transfer complexes and concludes with formation of the corresponding radical-anions, which break down into anions and radicals, e.g. the 2,4,6-tri-t-butylphenoxyl radical and the trinitromethanide anion. Similar results were obtained for the action of tetranitromethane on 1,3-dicarbonyl compounds in alkaline media or under ultraviolet irradiation[279,280].

A radical-dianion of trinitromethane has been detected in the electrochemical reduction of tetranitromethane in dimethylformamide, acrylonitrile, and water[281]. Photolysis of tetranitromethane by ultraviolet radiation in water and methanol[282], in the presence of ketones, $\alpha\beta$-unsaturated ethers and esters, cyclohexene, styrene[283], and benzene derivatives[198], generates NO_2· radicals. The trinitromethyl radical was not detected owing to its great activity and rapid interaction with the solvent. The fragmentation of tetranitromethane has been studied mass-spectroscopically[284,285].

The radiolysis of tetranitromethane by γ-rays at 77°K is accompanied[286] by its breakdown into $\cdot NO_2$ and $\cdot C(NO_2)_3$ radicals. The latter is represented in the e.s.r. spectrum by a sextet having relative intensities 1 : 3 : 6 : 6 : 3 : 1. However, it is not recorded in solution or in the presence of organic compounds[286-288]. The main products of radiolysis in aqueous solution by cobalt-60 γ-rays are the $\cdot NO_2$ radical and trinitromethane in yield $I = 3.75/100$ eV, which is increased by the presence of small quantities of organic compounds (ethanol, benzene, ethyl acetate, etc.)[289-295].

Being an acceptor of radicals, tetranitromethane effectively slows down the polymerisation and the cross-linking of polymers initiated by radiation[296,297] or by free radicals[298-303]. The "spin echo method" has shown for methyl methacrylate as example that retardation of polymerisation is favoured by increasing the number of nitro-groups in the polynitroalkane[301]:

$$CH_3NO_2 < CH_3COO(CH_2)_2C(NO_2)_2(CH_2)_2COOCH_3 <$$
$$< CH_3CH(NO_2)_2 < (O_2N)_3C(CH_2)_2COOCH_3 < C(NO_2)_4 .$$

Tetranitromethane inhibits the radical polymerisation of methyl methacrylate in the presence of benzoyl peroxide owing to the formation of relatively inactive free radicals causing chain termination; at the same time it accelerates decomposition of the benzoyl peroxide[304]:

$$(O_2N)_3C-\underset{\underset{OM}{|}}{N}\rightarrow O^{\cdot} + M \longrightarrow (O_2N)_3C-N=O + \sim\sim M-O-M\sim\sim .$$

M - Monomer

As a strong acceptor of electrons, tetranitromethane initiates ionic polymerisation. Thus oxetan is polymerised by a cationic mechanism on the addition of 1,1-diphenylethylene and tetranitromethane[256], which is explained by formation of a nitrocarbonium cation as initiator. Vinylcarbazole is polymerised similarly[305-307] in the presence of methyl methacrylate (1–10%) and tetranitromethane. Donor–acceptor interaction between tetranitromethane and cyclic sulphides[308] promotes ring opening and subsequent polymerisation.

The rules found in the reactions of tetranitromethane with unsaturated compounds are general in character and can be extended to the reactions of these alkenes with trinitromethane derivatives containing other substituents (chloro-, bromo-, and iodo-trinitromethane, trinitroacetonitrile, trinitroacetic ester). Replacing a nitro-group by a different residue changes the direction of addition of the trinitromethanide anion to the carbonium cation and hence the proportions of the reaction products. For example, the tendency of the intermediate trinitromethanide anion to *C*-alkylation is greater with bromo- and iodo-trinitromethane[309-311].

Since the Review was presented for publication several interesting communications have appeared on the chemistry of tetranitromethane. It reacts similarly with mercury and tin aryls[312] and with phenylmagnesium chloride[313]; with aryl derivatives of mercury the products are the corresponding aromatic hydrocarbons (XXIV) and the aryltrinitromethylmercury (XXV). The oxidation involves a stage of one-electron transfer followed by formation of an aryl radical and its interaction with the solvent (RH):

$$ArHgAr + C(NO_2)_4 \rightarrow \begin{bmatrix} Ar^{\cdot}Hg^{+}Ar \\ O_2N^{-}C(NO_2)_3 \end{bmatrix} \rightarrow \underset{\underset{(XXIV)}{ArH}}{Ar^{\cdot}} + \underset{(XXV)}{ArHgC(NO_2)_3} + \dot{N}O_2 \rightarrow N_2O_4 .$$

The detection of $\cdot NO_2$, $\cdot C(NO_2)_3$, and radicals from nucleophiles in the photolysis of tetranitromethane and in its dark reaction with various nucleophilic reagents supports the hypothetical one-electron mechanism in several of its reactions with nucleophiles and provides information on possible modes of breakdown of the tetranitromethane radical-anion in the matrix[314].

The reaction with metallic copper probably also involves a stage of one-electron transfer, with formation of the radical-anion (XXVI), which breaks down into the $\cdot C(NO_2)_3$ and $\cdot NO_2$ radicals[315]:

$$C(NO_2)_4 + Cu^0(Cu^+) \rightarrow \underset{\underset{(XXVI)}{\dot{C}(NO_2)_3\,N\dot{O}_2}}{(O_2N)_3CNO_2^{\cdot-}} + Cu^+(Cu^{2+}) .$$

Discussion has continued on the mechanism of the formation of trinitroethane from iodomethane and tetranitromethane[316]. The mechanism

$$S + C(NO_2)_4 \rightarrow S\cdots NO_2\cdots \underset{(XXVII)}{C(NO_2)_3} \xrightarrow{CH_3I} CH_3C(NO_2)_3 + S + INO_2$$

has been suggested for the process in a polar solvent. In the complex (XXVII) formed by tetranitromethane with the solvent, which was isolated and examined by physicochemical methods, polarisation of a carbon–nitrogen bond facilitates attack by iodomethane and the formation of 1,1,1-trinitroethane.

The formation of 3,3,5-trimethyl-1,1,1,5-tetranitrohexane by the thermolysis of trimethylacetic acid in tetranitromethane is attributed[317] to conversion (which requires further evidence) of the t-butyl radical into isobutene and telomerisation of the latter involving tetranitromethane:

$$2(CH_3)_3\dot{C}H \rightarrow 2\,CH_2=\underset{\underset{CH_3}{|}}{C}-CH_3 \xrightarrow{C(NO_2)_4} (O_2N)_3CCH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CNO_2 .$$

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