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Nitronium Salts in Organic Chemistry

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The review is devoted to the methods of synthesis and properties of nitronium salts. The characteristics of the nitration of various classes of organic compounds by nitronium salts are considered and new aspects of the mechanism of the nitration of aromatic compounds, discovered following the application of nitronium salts, are discussed.
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I. INTRODUCTION

The first solid nitronium salts were synthesised by Hantzsch in 1925. In the 1950's general methods were developed for the synthesis of nitronium salts and these compounds became available as reagents. The introduction of new nitrating agents into chemical practice was very important for the study of nitronium salts. Firstly, nitronium salts have many specific properties and their application greatly expands the synthetic possibilities of the nitration reaction. Secondly, the study of the characteristics of the nitration of aromatic compounds by nitronium salts and the discussion which arose in connection with this problem in the last 10–15 years have played a major role in the further development of our ideas about the nitration mechanism.

There have been few surveys of the literature on nitronium salts—after the review of Olah and Kuhn[1] in 1964, in which data relating to the initial investigation of this class of compound were compiled, no new reviews were published. The literature published up to 1980 is used in the present review.

II. SYNTHESIS AND PROPERTIES OF NITRONIUM SALTS

1. Synthesis of Nitronium Salts

Nitronium salts are ionic compounds containing the NO_2^+ cation and the anions of Lewis oxy-acids or complex acids—ClO_4^-, HSO_4^-, FSO_3^-, SO_4^{2-}, BF_4^-, PF_6^-, etc. The structure of nitronium salts was not established correctly immediately. Hantzsch[2] attributed the structures of nitracidium perchlorate $[H_2NO_3]^+ClO_4^-$ and dinitracidium perchlorate $[H_3NO_3]^{2+}2ClO_4^-$ to the nitronium perchlorate which he obtained for the first time. Later other workers[3,4] reproduced Hantzsch's synthesis and showed that his compounds are simply mixtures of nitronium perchlorate ($NO_2^+ClO_4^-$) and hydronium perchlorate ($H_3O^+ClO_4^-$).

Nitronium perchlorate can be obtained in several ways: by the reaction of nitrogen pentoxide with perchloric acid[3] or of nitrogen oxides with ozone and dry chlorine oxide[5], by the reaction of ClO_2F with nitric acid[6], or by the reaction between nitric acid and chlorine heptoxide[7]. Nowadays the most widely used method involves the synthesis of $NO_2^+ClO_4^-$ from ozone, nitrogen oxides, and chlorine oxide[8–10]. Another chlorine-containing nitronium salt, namely nitronium hexachloroantimonate, has been obtained by the reaction of antimony pentachloride with nitryl chloride in liquid chlorine[11]:

$$NO_2Cl + SbCl_5 \xrightarrow{Cl_2} NO_2^+SbCl_6^-$$

The synthesis and study of the properties of stable nitronium salts based on fluorine-containing Lewis acids have received considerable attention. Several general and specific methods of synthesis of these compounds have been proposed. Woolf and Emeleus[12–14] obtained $NO_2^+BF_4^-$, $NO_2^+PF_6^-$, $NO_2^+AsF_6^-$, $NO_2^+SbF_6^-$, $(NO_2)_2^{2+}SnF_6^{2-}$, $NO_2^+AuF_4^-$, and $NO_2^+FSO_3^-$ by the reaction of nitrogen dioxide with bromine trifluoride and the corresponding oxide (for example, boron oxide) or halide. $NO_2^+VF_6^-$, $NO_2^+NbF_6^-$, and $NO_2^+TaF_6^-$ were synthesised by the same method[15]:

$$NO_2 + B_2O_3 + BrF_3 \rightarrow NO_2^+BF_4^- ,$$
$$NO_2 + PBr_5 + BrF_3 \rightarrow NO_2^+PF_6^- .$$

Aynsley et al.[16] developed a general method of synthesis of nitronium salts by the reaction of nitryl fluoride with metalloids or their fluorides[17,18]:

$$Si + 6NO_2F \rightarrow (NO_2)_2^+SiF_6^- + 4NO_2 ,$$
$$BF_3 + NO_2F \rightarrow NO_2^+BF_4^- .$$

The reactions of oxides (V_2O_5, SO_3, etc.) with an excess of nitryl fluoride also lead to the formation of nitronium salts, for example:

$$SO_3 + NO_2F \rightarrow NO_2^+SO_3F^- .$$

The corresponding nitronium salts has been synthesised by the reaction of nitrogen dioxide with iridium hexafluoride[19].

The above methods of synthesis of nitronium salts are complex and require the use of compounds such as BrF_3 and NO_2F, which are difficult to obtain.

Nitronium salts became readily available reagents for extensive laboratory use only after the studies of Schmeisser and Elisher[20] and also Olah and co-workers[21], who showed that stable fluorine-containing nitronium salts can be obtained by the reaction of nitrogen pentoxide, anhydrous hydrogen fluoride, and a fluorine-containing Lewis acid in nitromethane:

$$N_2O_5 + HF + BF_3 \rightarrow NO_2^+BF_4^- + HNO_3 .$$

The replacement of N_2O_5 by concentrated nitric acids made it possible to simplify still further the synthesis of nitronium tetrafluoroborate[22,23]:

$$HNO_3 + HF + 2BF_3 \rightarrow NO_2^+BF_4^- + BF_3 \cdot H_2O .$$

Other Lewis acids, for example, phosphorus pentafluoride, arsenic pentafluoride, etc., react in the same way[22,24].

When it is necessary to obtain a salt free of an admixture of a nitrosonium salt, it is possible to employ modified methods in which the nitronium cation is generated from alkyl nitrates[25]

or nitryl chloride[26]:

$$RONO_2 + HF + 2BF_3 \rightarrow NO_2^+BF_4^- + ROH \cdot BF_3,$$

$$NO_2Cl + HF + 2BF_3 \rightarrow NO_2^+BF_4^- + HCl \cdot BF_3,$$

The nitronium salt of one of the strongest acids, namely trifluoromethanesulphonic, has been obtained recently[27-29].

Fairly convenient methods of synthesis of various nitronium salts have now been developed. Nitronium tetrafluoroborate, nitronium hexafluorosilicate, nitronium hexafluorophosphate, nitronium hexafluoroantimonate, and nitronium trifluoromethanesulphonate have found most applications as nitrating agents.

2. Physicochemical Properties of Solutions of Nitronium Salts

The solubility of nitronium salts has been inadequately studied. Nitronium tetrafluoroborate (NTFB) and nitronium fluorosulphonate[30] have been most fully investigated (see Table).

The solubilities of nitronium salts at 20 °C.

Solvent	Solubility, wt.%	
	NTFB	nitronium fluorosulphonate
Acetonitrile	3.1	1.6
Nitromethane	1.2	1.0
1,4-Dioxan	1.2	0.3
Methyl ether of ethylene glycol acetate	0.7	—
Methyl acetate	4.1	3.8
Ethyl acetate	0.1	0.1
Trimethyl phosphate	19.9	12.7
Tripropyl phosphate	6.0	5.4
Tributyl phosphate	1.9	1.6

NTFB dissolves only slightly in nitroethane and nitropropanes[1,31]. The rate of dissolution of NTFB is determined by diffusion processes and varies in parallel with its solubility in a number of solvents[30].

Nitronium hexafluoroantimonate, hexafluorophosphate, and hexafluoroarsenate are more soluble in organic solvents than NTFB and 50% solutions of these salts can be obtained for example in nitromethane.

The salts also dissolve readily in nitroethane, nitropropanes, sulpholane, and trifluoroacetic acid[31]. Less than 0.3% of NTFB and ~0.5% of $NO_2^+ClO_4^-$ dissolve in nitromethane at 25 °C.[21,31] The saturated NTFB solution in sulpholane at 25 °C contains 7% of the salt, while that in acetonitrile contains 10% of the salt. The solubility of NTFB in nitroethane and nitropropane is insignificant but there are no quantitative data[1,31].

A solution of NTFB in liquid hydrofluoric acid is a true electrolyte, like a KBF_4 solution[32]. Cryoscopic studies of NTFB solutions in sulpholane[31] showed that, at a concentration of ~ 3 mole %, NTFB exists in the form of ion pairs, of which less than 2% are dissociated into ions. With increase of the NTFB concentration in sulpholane, the conductivity of the salt rises linearly[21,27,31]. Solutions of nitronium trifluoromethanesulphonate[27] and NTFB[21] have very similar specific conductances. Conductimetric measurements on solutions of nitronium salts of monobasic and dibasic acids have shown that the nature of the anion has little influence on the degree of dissociation of the salt[33]. A solution of nitronium perchlorate in nitromethane is less than 6% dissociated[1].

On the basis of cryoscopic[34] and other data, Olah and Kuhn[1] believe that in concentrated solutions nitronium salts exist in the form of conducting ion triplets. On dilution of the solution, the triplets are converted into non-conducting ion pairs. Further dilution of the solution leads to the separation of the ion pairs into simple ions, which are also conducting; this enabled the authors to account for the minimum in the conductivity of nitronium perchlorate solutions in nitromethane with increase of the nitronium salt concentration. A conductivity minimum has also been observed for solutions of a series of uni-uni- and uni-bi-valent solutions of nitronium salts in ethyl acetate[33] and is also due to the existence of ionic associated species. On the other hand, a linear relation has been found[35] between the specific conductance of a solution of nitronium hexafluorophosphate in nitromethane and the concentration, no signs of the formation of ionic associated species being observed up to a nitronium salt concentration of 0.4 M.

The interpretation of the conductimetric data for nitronium salts in aprotic solvents is at present obscure. The problem is complicated by the fact that many physicochemical characteristics of nitronium salts in organic solvents and particularly their stability and electrical conductivity are to a large extent determined by the content of moisture and impurities and also by the nature of the interaction with the solvent employed. However, in the communications published up to 1970[1,21,31,36] no characteristics of the impurity and water contents in the solvents are given, which is the reason for the contradictory nature of the results.

Spectroscopic studies have been particularly important for the elucidation of the structure of nitronium salts. The study of infrared spectra led to the conclusion that nitronium ions have a linear structure in solution[37]. In nitronium perchlorate crystals the linearity of the nitronium ion breaks down[36,38]. Studies of the infrared and Raman spectra of a series of nitronium salts have led to the conclusion[39] that the nitronium ion in NO_2–X compounds is bent and that the amount of ionic character of the NO_2–X bond increases in parallel with the ONO angle in the sequence $NO_2Cl < NO_2F < NO_2^+SO_3F^- < NO_2^+S_2O_6F^- < NO_2^+ClO_4^- = NO_2^+BF_4^-$. These results are extremely interesting but they require additional tests, particularly since some experimental data do not agree with the measurements of other workers[27].

III. NITRATION BY NITRONIUM SALTS

An extremely important stage in the research into nitronium salts involves the choice of solvent. As mentioned above, nitronium salts have a limited solubility and interact with the majority of organic solvents. Solvents such as acetonitrile, acetic and phosphoric acid esters, nitromethane, dioxane, and sulpholane are usually employed for nitration. Nitroderivatives of aromatic hydrocarbons have been synthesised in an excess of the aromatic compound or in ether[21]. However, ethyl ether interacts with NTFB on mixing. Apart from the solvents indicated, aliphatic hydrocarbons, methylene chloride, and acetic anhydride have been used for nitration by nitronium salts. Nitration by NTFB has been carried out[40] in anhydrous acetic acid, but the latter interacts with NTFB at room temperature to form another nitrating agent—acetyl nitrate.

Nitration by nitronium salts is complicated by the liberation of the corresponding inorganic acids (tetrafluoroboric, hexafluorosilicic, etc.) which can also react in their turn

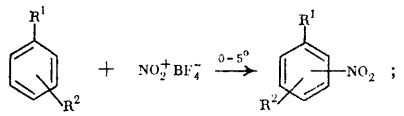
with the solvent, particularly since many of these acids are superacids (for example, trifluoromethanesulphonic acid is 14 times stronger than sulphuric acid[28]).

Some investigators have used solutions of nitronium salts in strong protic acids for nitration—sulphuric[28,40,41], methanesulphonic[40], trifluoromethanesulphonic[28], and fluorosulphonic[41]. However, such nitrating systems differ from the corresponding nitric acid solutions only by the water content and the acidity of the medium and will not be considered in this review.

1. Nitration of Aromatic Hydrocarbons

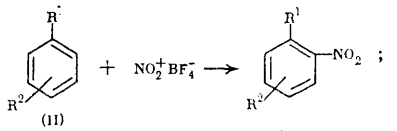
In 1950 it was observed[3] that a solution of nitronium perchlorate in nitromethane nitrates benzene to nitrobenzene almost instantaneously and slowly converts nitrobenzene into dinitrobenzene. However, the low stability of nitronium perchlorate and the risk of the explosion of its mixtures with organic solvents inhibited further investigation of the nitrating activity of this salt.

Olah and Kuhn were the first to carry out extensive studies on nitronium salts as nitrating agents. They showed that not only nitronium perchlorate but also other stable nitronium salts, namely the tetrafluoroborate, hexafluorosilicate, and hexafluoroantimonate, are active nitrating agents[1,21,42]. They investigated NTFB most fully and showed that, in sulpholane[22] or an excess of the substrate[42], $NO_2^+BF_4^-$ nitrates benzene and alkylbenzenes (I) very readily to the corresponding mononitro-derivatives in 80–95% yield:



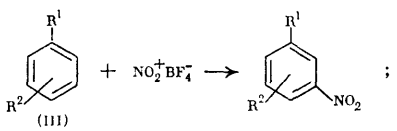
(a) $R^1=H$; $R^2=H$, CH_3, C_2H_5, iso-C_3H_7, n-C_3H_7, n-C_4H_9, iso-C_4H_9, or t-C_4H_9;
(b) $R^1=CH_3$; $R^2=CH_3$(*o*-, *m*-, or *p*-).

Monohalogenobenzenes react under approximately the same conditions, while dihalogenobenzenes are nitrated at a higher temperature (30–50 °C), but the yield is in all cases 80–90%. The nitration of benzene derivatives containing other electron-accepting substituents takes place just as successfully although the reaction is in this case slower and takes place at a higher temperature (up to 40–50 °C, in a few instances 90–100 °C). By nitrating *o*-tolunitrile with NTFB in sulpholane, it proved possible to obtain for the first time 3-dinitro-*o*-tolunitrile in 75% yield[1]. The reactions with other nitrating agents lead to the oxidation of the nitrile group:



(II)

(a) $R^1=Cl$, $R^2=o$-NO_2, *p*-NO_2; (b) $R^1=F$, $R^2=o$-NO_2, *p*-NO_2 ;



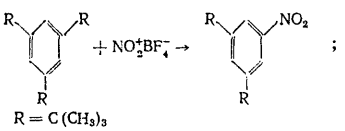
(III)

(a) $R^1=NO_2$, CN, $COOCH_3$, COCl, COF; $R^2=H$; (b) $R^1=CN$, $R^2=o$-NO_2; *m*-NO_2; *p*-NO_2; (c) $R^1=COOC_2H_5$, $R^2=m$-NO_2 .

The readily oxidisable triaryl- and alkyldiaryl-phosphines were nitrated for the first time with NTFB and a series of *meta*-nitro-derivatives of arylphosphines were obtained[43].

The nitration of alkylbenzenes containing the isopropyl or t-butyl group with $NO_2^+BF_4^-$ is accompanied by substitutional nitration with elimination of one of the alkyl groups (*ipso*-substitution)[44]. In the nitration of *p*- and *o*-cumenes the degrees of substitution of the isopropyl group are 9.5 and 41% respectively. In the nitration of 1,4-di-isopropylbenzene one of the isopropyl groups is 56% substituted, while in the nitration of 1,4-di-t-butylbenzene the degree of substitution of the t-butyl group is 20%.

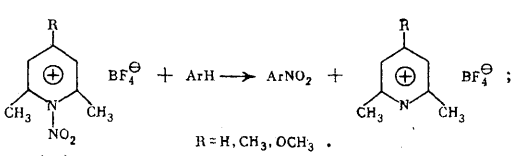
Steric hindrance interferes with the direct nitration of 1,3,5-tri-t-butyl-benzene: on treatment with NTFB, only substitutional nitration takes place with formation of 1,3-di-t-butyl-5-nitrobenzene:



The interaction of polyalkylbenzenes with nitronium salts also leads to different hydroxymethyl derivatives[45,46]. Polynuclear aromatic compounds (biphenyl, naphthalene, and phenanthrene) are nitrated quantitatively by NO_2BF_4,[1] more than 50% of α-nitronaphthalene being obtained from naphthalene and only 9-nitrophenanthrene being formed from phenanthrene.

Comparison of the nitrating capacities of three nitronium salts, namely the tetrafluoroborate, the hexafluorophosphate, and the trifluoromethanesulphonate, with respect to toluene showed that the highest reaction rate or the highest yield of nitrotoluene are obtained when nitronium trifluoromethanesulphonate is used[28]. On the other hand, Olah and Kuhn[47] were unable to detect the influence of the nature of the anion on the yield of *o*-nitrotoluene; they explained the decrease of the content of the *ortho*-isomer from 65 to 55% on passing from sulpholane to nitromethane and toluene by the difference between the degrees of solvation of the ion pairs of the nitrating agent. In the nitration of toluene by nitronium trifluoromethanesulphonate in alkyl halides, the ratio of the *ortho*- and *para*-isomers at temperatures between −60° and −90 °C remains almost constant at 1.63, while at −110 °C it decreases to 1.03. The yield of the *meta*-isomer does not exceed 0.33% under these conditions[47].

Alkylnitropyridinium salts are interesting nitrating agents. The alkyl groups in the 2- and 6-positions of pyridine (VI) prevent the conjugation of the nitro-group with the ring (owing to their non-coplanarity), which leads to a high nitrating capacity of these salts. In contrast to inorganic nitronium salts, pyridinium salts make it possible to carry out nitration readily under homogeneous conditions. Furthermore, the acid formed as a result of the reaction is bound by alkylpyridine, which is very important in the nitration of compounds sensitive to the action of acids[48]:



(IV)

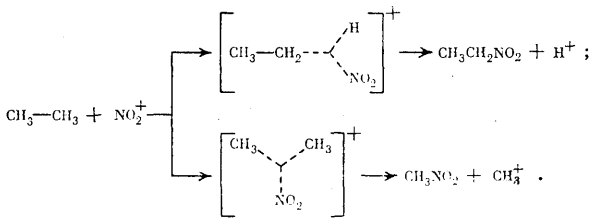
R = H, CH_3, OCH_3 .

The solvent apparently has a considerable influence on the nitrating activity of nitronium salts, but this problem has as yet been little investigated.

2. Nitration at a Saturated Carbon Atom

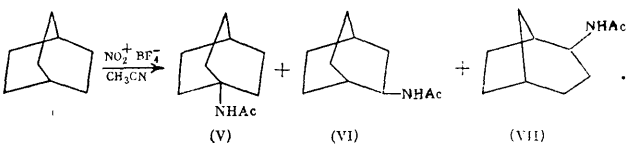
All the nitration reactions of paraffinic and naphthenic hydrocarbons known hitherto take place via a free-radical mechanism involving the $NO_2^{\cdot}$ radical[108]. It has been shown only recently[49] that the nitration of paraffinic hydrocarbons can be achieved with the aid of stable nitronium salts in the methylene chloride–sulpholane system under conditions which virtually rule out the formation of the radicals. Thus the authors obtained nitromethane from methane, albeit with a low yield, nitroethane from ethane, etc. The tertiary C–H bond exhibits the highest reactivity: adamantane is nitrated to 1-nitroadamantane in 10% yield. Nitronium salts can be replaced by the nitro-group and a proton in a methyl group of polyalkylbenzenes[46].

The nitration of paraffinic hydrocarbons is accompanied by nitrolysis with the dissociation of a C–C bond, the process occurring more readily than the nitration at secondary and primary carbon atoms. The nitration of alkanes with the normal structure therefore results in the preferential formation of nitrolysis products. For example, a mixture of 1- and 2-nitrobutanes, nitroethane, and nitromethane has been obtained from n-butane in proportions of 1:1.5:4:5, while a mixture of t-nitrobutane and nitromethane in proportions of 3:1 was obtained from isobutane. According to Olah's hypothesis[50], nitration, like other electrophilic processes (deuterium exchange, alkylation, and acid-catalysed isomerisation), proceeds via the "frontal" attack on a C–H or C–C bond with formation of a triangular transition state and not via the attack by the electrophile on a tetragonal carbon atom:



In the first excited state the linear nitronium cation can be converted into the bent form[51] and can react as an electrophile.

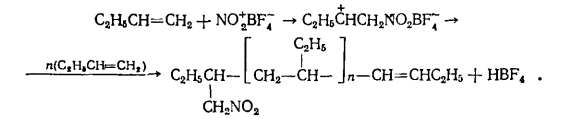
The nitronium cation is also capable of oxidising secondary and particularly tertiary carbon atoms with formation of a carbenium ion[52]. If the reaction takes place in acetonitrile, then the carbocation is converted by the Ritter reaction into the corresponding amide. Thus *N*-(1-adamantyl)acetamide was obtained from adamantane (yield 88%) and *N*-(*exo*-2-norbornyl)acetamide was obtained from norbornane (yield 78%). Bicyclo[2.2.2]octane is converted in 73% yield into the corresponding amides (V)–(VII) in proportions of 65:22:13:



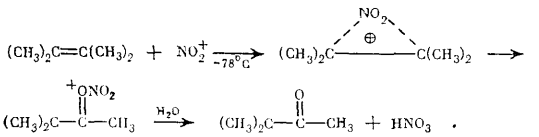
It is striking that the ratio of isomers (VI) and (VII) formed is approximately the same as in the similar isomerisation of the carbocation obtained in the solvolysis of bicyclo[2.2.2]-octyl-2-*p*-bromobenzenesulphonate[53,54], which is also evidence in support of an ionic mechanism of the reaction of polycyclanes with NTFB under consideration. Both *exo*- and *endo*-2-norbornyl bromides react analogously with nitronium salts[55].

3. Nitration at the Double Bond

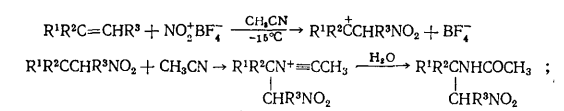
The reactions of nitronium salts with olefins do not take place unambiguously and depend to a large extent on the nature of the alkene and the reaction conditions. When alkenes react with nitronium salts, a reactive nitrocarbenium ion, which can initiate polymerisation, is formed[56]:



The nitrocarbenium ion can be also stabilised as a result of an intramolecular rearrangement to the oxonium ions. The latter reacts with water to form a ketone[57]:

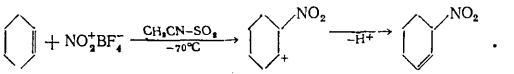


If the nitration of olefins by nitronium salts is carried out in acetonitrile, then the nitrocarbenium ion undergoes the Ritter reaction with the solvent to form nitroacetamides[58]:

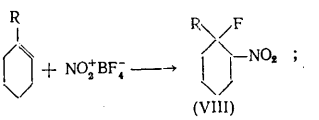


a) $R^1=CH_3$, $R^2=R^3=H$, yield 50%; б) $R^1=R^2=CH_3$, $R^3=H$, yield 23%; в) $R^1=R^3=CH_3$, $R^2=H$, yield 13%.

The mode of the reaction between olefins and nitronium salts depends on the structure of the substrate and the process conditions. For example, cyclohexene reacts with NTFB to form a nitrocarbocation, which is stabilised in the form of 3-nitrocyclohexene (yield 40%)[59,60]:



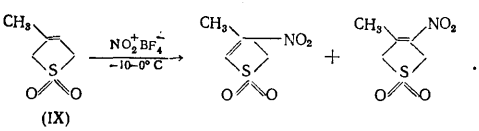
The nitration of 1-substituted cyclohexenes is accompanied by the formation of 2-fluoro-1-nitro-2-R-cyclohexanes (VIII):



(a) R = CH_3, yield 30% [61]; (b) R = Cl, yield 60%.[62]

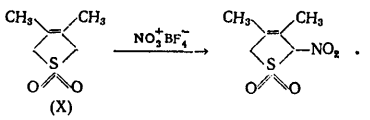
The mechanism of the formation of the fluoro-derivative has not been studied but the stereochemistry of the process has attracted attention—the reaction proceeds via a vicinal-addition mechanism[61].

Alkenes with a reduced electron density, for example 3-methyl-2,5-dihydrothiophen 1,1-dioxide (IX), react with NTFB more or less unambiguously:



The reaction of 3,4-dimethyl-2,5-dihydrothiophen 1,1-dioxide (X), in which the double bond is blocked by the methyl groups, apparently proceeds via an electrophilic substitution

mechanism[63]:



(X)

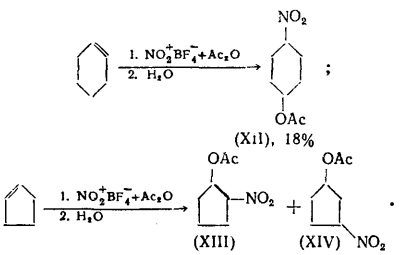
As mentioned above, the reactions of nitronium salts with olefins proceed via the formation of a nitrocarbocation and the decisive factor which determines the success of the reaction is the ease of the stabilisation of nitrocarbocation by its conversion into the final product. One of the methods for such stabilisation involves nitration in acetic anhydride. It has been suggested that the complex $NO_2^+BF_4^-.Ac_2O$ reacts and that 2-acetoxy-1-nitroalkane is obtained in 36–60% yield after the hydrolysis of the reaction mixture with water[64]. The reaction involves mainly *cis*-addition:

$$R^1R^2C{=}CHR^3 + NO_2^+BF_4^- \xrightarrow{Ac_2O,\,H_2O} \underset{(XI)}{AcOCR^1R^2CHR^3NO_2}\ ;$$

a) $R^1{=}CH_3$, $R^2{=}R^3{=}H$; б) $R^1{=}R^2{=}CH_3$ (*cis, trans*), $R^3{=}H$; в) $R^1{=}R^2{=}CH_3$, $R^3{=}H$

4-Acetoxy-4-methyl-2-pentanone was isolated together with the nitroacetate (XIc) after the nitration of isobutene, which indicates the formation of an acylium cation in the reaction mixture.

The nitration of cyclenes is as a rule accompanied by the transfer of the reaction centre and the formation of the β- and γ-nitroacetates (XII)–(XIV) in 18–29% yields[65]:

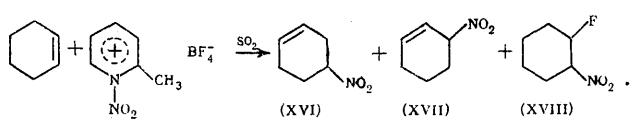


(XII), 18%

(XIII) (XIV)

The high degree of stabilisation of the nitrocarbocation in the nitration of norbornene in acetic anhydride ensures a high (86%) yield of two conformers of 2-acetoxy-7-nitrobicyclo[2.2.1]heptane formed.

Overall, one should say that the nitration of olefins, particularly those containing electron-donating substituents, by nitronium salts is complicated by side reactions and does not always lead to the expected result. In many instances nitration with nitronium tetrafluoroborate takes place with higher yields in the presence of α-picoline[62,66]. In this case the nitrating agent is apparently not the nitronium salt but 1-methyl-*N*-nitropyridinium tetrafluoroborate(XV), which is formed rapidly when NTFB is mixed with α-picoline[48]. The yields of products (XVI)–(XVIII) are respectively 40, 25, and 13%:



(XVI) (XVII) (XVIII)

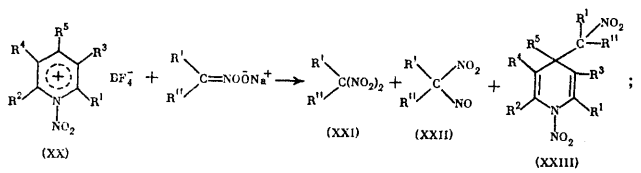
The interaction of nitronium salts with the heteropolar C=N double bond in nitroalkane salts is of great interest. Olsen et al. showed that *gem*-dinitro-compounds are formed in the nitration of 2-nitropropane and nitrocyclohexane salts with NTFB in acetonitrile[67]:

$$\underset{(XIX)}{R^1R^2C{=}NO_2M} + NO_2^+BF_4^- \rightarrow R^1R^2C(NO_2)_2 + MBF_4\ ;$$

(a) M=Li, (b) M=Na, (c) M=K .

The reaction takes place between −35° and −40 °C and its character depends on the nature of the cation. When the lithium salt (XIXa) is used, the yield is 35%, in the presence of the sodium salt (XIXb) it is 25%, while the potassium salt (XIXc) does not react. Apart from the *gem*-dinitro-compounds, the nitration of nitroalkane salts gives rise also to the pseudonitroles $R^1R^2C(NO)NO_2$. In contrast to dinitroalkanes, their yield increases on passing from the lithium to the potassium salts from 5 to 25%.

N-Nitropyridinium tetrafluoroborate salts, which are very mild nitrating agents, can also be used for the nitration of mononitroparaffin salts[68,69]. However, the nitration is in this case complicated by the alkylation of the *N*-nitropyridinium salt of the nitroalkane and the formation of a pseudonitrole (for secondary nitro-compounds):



(XX) (XXI) (XXII) (XXIII)

(a) $R^1{=}R^2{=}R^3{=}R^4{=}R^5{=}H$; (b) $R^1{=}R^2{=}CH_3$, $R^3{=}R^4{=}R^5{=}H$; (c) $R^1{=}R^3{=}R^4{=}R^5{=}H$, $R^3{=}C_2H_5$; (d) $R^1{=}R^2{=}R^3{=}H$, $R^4{=}R^5{=}CH_3$; (e) $R'{=}CH_3$, $R''{=}H$; (f) $R'{=}C_2H_5$; $R''{=}H$; (g) $R'{=}R''{=}CH_3$; (h) R'R''C— cyclohexylidene

The extent of these side reactions depends on the structure of the nitrating agent. *N*-Nitropyridinium tetrafluoroborate (XXa) does not enter into the nitration reaction; only the alkylation product is formed—*N*-nitro-4-nitroalkyl-1,4-dihydropyridine [compounds (XXIII, a and e)–(XXIII, a and g)] in 60–85% yield. The introduction of substituents into the 4- and 2,6-positions of the pyridine ring [compounds (XX, b–c)] promotes the formation of the pseudonitroles (XXII, g and h) (up to 20%) and *gem*-dinitroalkanes (XXI, e–h), whose yield reaches 42%. Primary nitroalkanes react with 3,5-lutidine derivatives (XXd) to form mainly the alkylation products (XXIII, d and e), while secondary nitroalkanes give rise to the *gem*-dinitro-compounds (XXI, g and h) in yields up to 56%. The anion of 1,1-dinitroethane reacts with the salt (XXc) to form only the alkylation product (XXIIIc, $R' = CH_3$, $R'' = NO_2$).

An interesting example of nitration is the reaction of NTFB with the sulphonium dinitro ylide to form a trimethylsulphonium salt[70]:

$$(CH_3)_2\overset{+}{S}{-}\bar{C}(NO_2)_2 + NO_2^+BF_4^- \xrightarrow{CH_3CN} [(CH_3)_2\overset{+}{S}{-}C(NO_2)_3]\,BF_4^-\ .$$

Compounds containing three nitro-groups and an onium cation at the same carbon atom were previously unknown. Such derivatives of trinitromethylselenonium are less stable—all attempts to synthesise such compounds have led to the formation of tetranitromethane. The reaction can be formally regarded as electrophilic substitution at a saturated carbon atom attached to nitro-groups[71]:

$$(C_6H_5)_2\overset{+}{S}e{-}\bar{C}(NO_2)_2 + NO_2^+BF_4^- \xrightarrow{CH_3CN} C(NO_2)_4\ .$$

NTFB reacts with aliphatic, carbocyclic, or aromatic ketoximes in the presence of pyridine to form the corresponding ketones[72].

NTFB reacts just as smoothly with ketone dimethylhydrazones:

$$\begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!C{=}N{-}N(CH_3)_2 \xrightarrow{NO_2^+BF_4^-} \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!C{=}O\ .$$

The reactions take place with high yields and can serve as a preparative method for the regeneration of ketones from their oximes and hydrazones.

4. Nitration at a Nitrogen Atom

The first indication of the possibility of the nitration of amines by nitronium salts was given by Olah and Kuhn[1]. Olsen et al.[67] found that NTFB reacts readily with secondary amines in methylene chloride or acetonitrile to form *N*-nitroamines (XXIV), whose yield is 50–70%:

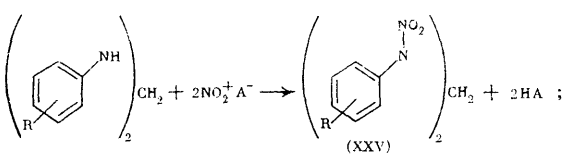
$$2R^2NH + NO_2^+BF_4^- \rightarrow R^2N{-}NO_2 + R^2NH_2 + BF_4^- \ ;$$
(XXIV)

$R^2=(C_4H_9)_2$, $(NCCH_2CH_2^-)_2$, or morpholinyl .

In a later study[73] it was shown that the nitration of aromatic amines proceeds differently depending on their basicity. Amines of moderate and low basicity, namely bis(2-cyanoethyl)amine (pK_a = 5.25), bis(2,2-dinitropropyl)amine (pK_a = 3.08), and bis(2,2,2-trinitroethyl)amine (pK_a = 0.05) are nitrated by NTFB to the corresponding *N*-nitroamines in acetonitrile or ethyl acetate in yields of 87–98%. Despite the data of Olsen et al.[67], the nitration of highly basic dialkylamines (pK_a = 8.70–11.25) is accompanied by the partial reduction of $NO_2^+BF_4^-$ to nitrosonium tetrafluoroborate and the formation of nitrosoamines. The content of nitrosoamine in the reaction mixture increases with increase of the reaction temperature. Nitronium hexafluorosilicate proved to be a milder nitrating agent; its application makes it possible to reduce greatly the formation of nitroso-derivatives.

The nitration of aliphatic-aromatic amines also proceeds smoothly and the low acidity of the medium makes it possible virtually to avoid the *N*-nitro-*C*-nitro-rearrangements[73].

Aromatic methylenebisamines, which are unstable in an acid medium, were nitrated for the first time with nitronium salts and *N,N'*-diarylmethylenedinitroamines (XXV) were obtained in a high yield[74]:



(XXV)

$A^-=BF_4^-$, SiF_6^{2-}; R=2-NO_2, 3-NO_2, 4-NO_2, 2,6- and 3,5-$(NO_2)_2$.

The reactions of nitronium salts and nitrogen pentoxide with ammonia have been investigated[24,39,75,76] and it has been shown that nitramide (XXVI) is formed at the temperature of liquid nitrogen:

$$2NH_3 + NO_2^+A^- \rightarrow NH_2NO_2 + NH_4^+A^- \ ;$$
(XXVI)

$A^-=SO_3F^-$, ClO_4^-, BF_4^-, NO_3^- .

The formation of nitramide is determined by the nature of the anion: on passing from nitronium chlorosulphonate to NTFB, the yield increases from 8 to 43%.

On treatment with nitronium salts, primary aliphatic amines are converted into alkyl nitrates (apparently via diazotisation by the nitronium cation), but *N*-2,4,6-tetranitroaniline was obtained in a high yield from the weakly basic picramide[67].

Nitronium salts proved to be particularly useful in the synthesis of *N,N*-dinitroamines which had been previously difficult to obtain. It was shown[77] that the interaction of primary nitroamines with NTFB, nitronium pyrosulphate, fluorosulphonate, fluorosilicate, as well as other nitronium salts leads to the formation of the *N,N*-dinitroamines (XXVII):

$$RN(NO_2)X + NO_2^+A^- \rightarrow RN(NO_2)_2 \ ;$$
(XXVII)

X=H, NH_4, K, Li etc. ; $A=BF_4^-$, $S_2O_7^{2-}$, FSO_3^-, SiF_6^{2-}, ClO_4^-, SbF_6^-, SnF_6^{2-} .

Aliphatic and aromatic amines, including those with other functional groups, readily participate in the reaction. According to the authors' data, best results are obtained in nitration by nitroamine salts in chloroalkanes or acetonitrile. However, the employment of more basic solvents, such as ethers and esters, ensures equally high yields in the nitration of both free nitroamines and their salts[78].

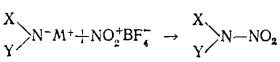
Olsen et al.[67] suggested that NTFB be used in acetonitrile or methylenechloride for the synthesis of the primary nitroamides (XXVIII):

$$RCONH_2 + NO_2^+BF_4^- \rightarrow RCONHNO_2 + HBF_4 \ ;$$
(XXVIII)

$$HBF_4 + KOCOCH_3 \rightarrow KBF_4 + CH_3COOH \ .$$

The nitroamides of benzoic and chloroacetic acids were obtained in satisfactory yields by the method proposed, but the yield of nitroacetamide was only 12%. This can be explained by the fact that the aliphatic nitroamides are hydrolysed in the solvents indicated even in the presence of potassium acetate. Only the use of more basic solvents—ethyl acetate, 1,4-dioxan, or trimethyl phosphate—made it possible to obtain nitroamides of different structure in 40–90% yield[79]. Succinimide is nitrated by NTFB in ethyl acetate in 43% yield[67].

The general method of synthesis of sulphonic acid nitroimides (XXIX) consists in the reaction of NTFB with imide salts[80]:



(XXIX)

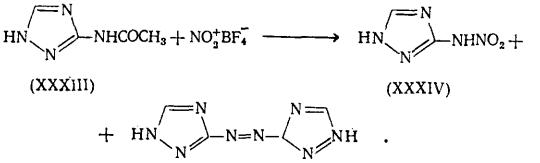
(a) X=*n*-$CH_3C_6H_4SO_2$; Y=COOR; (b) X=Y=CH_3SO_2; $C_6H_5SO_2$

One of the known methods of synthesis of dialkylnitroamines involves the reaction of dialkylamides with nitric acid, which leads to the substitution of the acyl group by the nitro-group (nitrolysis). However, when nitric acid or its mixtures with acetic anhydrides are used, the yield of nitroamines is as a rule low and only the employment of the HNO_3–$(F_3CCO)_2O$ mixture makes it possible to raise it to 90%.[81] For preparative purposes, it is more convenient to nitrate the dialkylamides (XXX) by nitronium salts[82]. The reaction takes place at 20 °C in acetonitrile or esters. The dialkylnitroamines (XXXI) are formed in yields up to 90% and the acyl group is converted into acylium tetrafluoroborate (XXXII):

$$R_2NC(O)R' + NO_2^+BF_4^- \rightarrow R_2N{-}NO_2 + R'CO^+BF_4^- \ ;$$
(XXX) (XXXI) (XXXII)

R=CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, R'=CH_3, C_2H_5, CH_2CN, CH_2Cl, $CHCl_2$, CCl_3 .

The possibility of the nitrolysis of secondary amides with formation of the corresponding primary *N*-nitroamines (XXXIV) [together with 3,3'-azo-1,2,4-triazole (XXXV)] has been demonstrated for an *N*-acyl derivative of 3-amino-1,2,4-triazole (XXXIII)[83]:



(XXXIII) (XXXIV)

(XXXV)

Under the reaction conditions, alkyl-*N*-nitroamines decompose in the presence of the organic acids liberated[84]. Amides containing electron-accepting substituents at the nitrogen

atom also undergo nitrolysis by nitronium salts. Thus *N*-fluoronitroamines (XXXVI) were obtained from *N*-fluoroamides[85]:

$$RNFCOOCH_3 + NO_2^+BF_4^- \rightarrow \underset{\underset{F}{|}}{RNNO_2} \ ;$$

(XXXVI)

R=Alk .

Alkyl-*N*,*N*-dinitroamines (XXXVIII) are formed in high yields from *N*-alkyl-*N*-nitroamides (XXXVII)[84]:

$$\underset{\text{(XXXVII)}}{RN(NO)_2C(O)R'} + NO_2^+BF_4^- \rightarrow \underset{\text{(XXXVIII)}}{RN(NO_2)_2} + R'CO^+BF_4^- \ ;$$

R=CH_3, C_4H_9, R'=CH_3, C_3H_7, CCl_3 .

The reaction of NTFB with *N*-alkylamides has been investigated[67,84] under insufficiently comparable conditions, but nevertheless comparison of the results permits the conclusion that at a low temperature (−30 °C) *N*-butylacetamide and ethyl n-butylcarbamate in acetonitrile are nitrated to the *N*-nitro-derivatives[67], while at higher temperatures (up to +10 °C) nitrolysis takes place with formation of the corresponding carboxylic acid and an alcohol as well as N_2O.[86] The question of the order in which the C–N bond is *N*-nitrated and cleaved in the reactions of *N*-alkylamides with NTFB requires additional study. Aliphatic isocyanates react with NTFB in ethyl acetate or acetonitrile with formation (after hydrolysis) of alkylnitroamines[87]:

$$R(N{=}C{=}O)_n + NO_2^+BF_4^- \xrightarrow{+H_2O} RNHNO_2 + CO_2 + HBF_4 \ ;$$

n=1; R=C_2H_5, C_3H_7, C_4H_9; n=2; R=$(CH_2)_4$, $(CH_2)_6$.

The study of the nitration of a series of *N*,*N*-diacylmethylamines showed that the acetyl group is substituted by the nitro-group and, depending on the conditions and the component ratio, methylnitroacetamide or methyl-*N*,*N*-dinitroamine is formed[88]:

$$CH_3N(COCH_3)_2 + NO_2^+BF_4^- \begin{cases} \rightarrow CH_3N(NO)_2COCH_3 \ ; \\ \rightarrow CH_3N(NO_2)_2 \ . \end{cases}$$

The methanesulphonyl group can also be substituted by the nitro-group. The tosyl or an alkoxycarbonyl group do not enter into this kind of reaction.

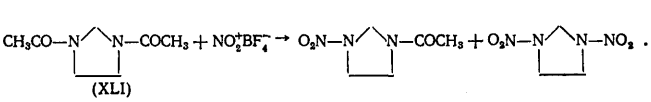
The mode of reaction of NTFB with substituted methylenediamines depends on the nature of the substituents[88,89]. Alkanesulphonyl, arenesulphonyl, or methoxycarbonyl derivatives (XXXIX) undergo nitrolysis at the C–N bond with formation of substituted nitroamines. This reaction pathway is favoured by the formation of the carbonium-immonium ion (XL) stabilised by the mesomeric effect of the amine nitrogen:

$$\underset{\underset{R''}{|}\ \underset{R''}{|}}{R'NCH_2NR'} + NO_2^+BF_4^- \rightarrow \underset{\underset{R''}{|}}{R'N{-}NO_2} + \underset{\underset{R''}{|}}{R'NCH_2^+BF_4^-} \ ;$$

(XXXIX) (XL)

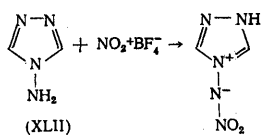
R'=Alk, R''=Alk, $SO_2C_6H_5$, $COOCH_3$.

N,*N*-Diacetylimidazolidine (XLI) undergoes substitutional nitration by nitronium salts to *N*-acetyl-*N'*-nitro- or *N*,*N'*-dinitro-derivatives:



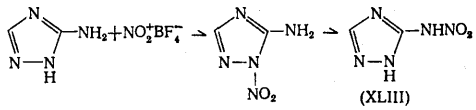
(XLI)

Nitronium salts are convenient nitrating agents for the synthesis of *N*-nitroimides. 4-Amino-1,2,4-triazole (XLII) reacts with NTFB in acetonitrile to form 4-nitroimino-1,2,4-triazole in 65% yield[90]:



(XLII)

1-Aminobenzimidazole is nitrated analogously, 1,1'-azobenzimidazole being formed as a side product. 3-Amino-1,2,4-triazole reacts with NTFB in acetonitrile to form *N*-nitrotriazole, which rearranges to the nitroaminotriazole (XLIII):



(XLIII)

Both nitronium and nitrosonium salts readily react with azodicarboxylate anions in accordance with the following scheme:

$$NO_2^+ + {}^-OOCN{=}NCOO^- \rightarrow N_2O_4 + 2CO_2 + N_2 \ .$$

The reaction of alkyl azodicarboxylates depends on the reactivity of the electrophilic species. NTFB, for example, reacts with ethyl azodicarboxylate, while the weaker electrophile nitrosonium tetrafluoroborate does not react.

The reaction of NTFB with lithium azide in acetonitrile results in the formation of covalent nitronium azide, which is converted into nitrous oxide above −10 °C[91]:

$$NO_2^+BF_4^- + LiN_3 \rightarrow LiBF_4 + NO_2N_3 \xrightarrow{\Delta} 2N_2O \ .$$

5. Nitration of Heterocyclic Compounds

The possibility of the nitration of heterocyclic compounds by nitronium salts was initially demonstrated in relation to pyridine[1,92,93]:

$$C_5H_5N + NO_2^+BF_4^- \rightarrow [C_5H_5NNO_2]^+BF_4^- \ .$$

In the presence of an excess of pyridine, the resulting salt is converted into derivatives of glutaconic aldehyde[92]:

$$[C_5H_5NNO_2]^+BF_4^- \xrightarrow{C_5H_5N} \left[C_5H_5^+NCH{=}CH{-}CH{=}CHCHN(NO_2)\right]BF_4^- \rightarrow$$

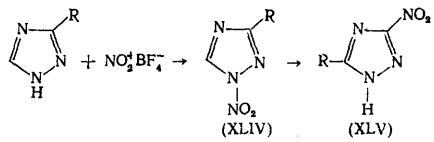
$$\xrightarrow{H_2O} [C_5H_5NCH{=}CHCH{=}CHCHO]^+BF_4^- \ .$$

N-Nitropyridinium salts are fairly stable and the N–C migration of the nitro-group is not observed even on heating. On the other hand, alkylnitropyridinium salts are "mild" nitrating agents (see Section III, subsection 1, subsection 3, and subsection 6).

Olah and Kuhn reported that thiophen[1] forms nitrothiophen in 91% yield on nitration with NO_2BF_4, while the nitration of furan results in a 14% yield of nitrofuran. 3-Nitro-6-phenyl-2-pyridone has been obtained in 40% yield by the nitration of 6-phenyl-2-pyridone with NTFB[94].

C-Nitroazoles are known to be difficult to synthesise by direct nitration with nitric acid. The use of NTFB in acetonitrile made it possible to obtain a series of 3-substituted 1,2,4-triazoles. The reaction proceeds via a stage involving

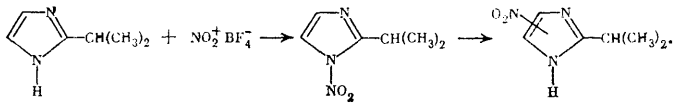
the formation of the *N*-nitro-derivative (XLIV), which isomerises to the *C*-nitro-compound (XLV)[95]:



(XLIV) (XLV)

R=H, CH_3, Cl, Br

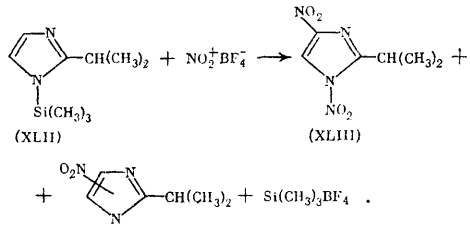
2-Isopropylimidazole (XLVI) is apparently nitrated analogously[96]:



(XLVI)

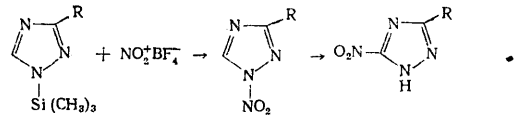
The yield of *C*-nitrotriazoles is as a rule low as a consequence of the dinitration of the *N*-nitro-compounds under the influence of fluoroboric acid formed on nitration.

A very interesting modification of this method, which rules out the formation of acid, has been proposed, namely one involving the nitration of trimethylsilyl derivatives. It has been shown for 2-isopropyl-1-trimethylsilylimidazole (XLVII) that this method makes it possible to obtain compounds which could not be synthesised previously, for example, 2-isopropyl-1,4-dinitroimidazole (XLVIII)[96]:



(XLII) (XLIII)

The nitration of *N*-trimethylsilyl-1,2,4-triazoles (XLIX) makes it possible to obtain *N*-nitrotriazoles, which can be used to synthesise *C*-nitro-derivatives in yields up to 90%[95]:

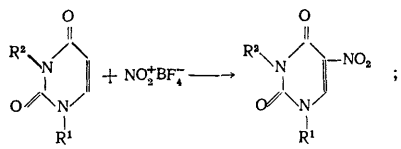


(XLIX)

R=H, CH_3, Cl, Br

Despite the additional labour involved in the synthesis of the trimethylsilyl derivatives, this method is most convenient for the preparation of 3(5)-nitro-1,2,4-triazoles.

Uracil and its 1-methyl and 1,3-dimethyl derivatives are nitrated to 5-nitro-derivatives (L) in high yields by NTFB in sulpholane:



(L)

R^1, R^2=H or CH_3 .

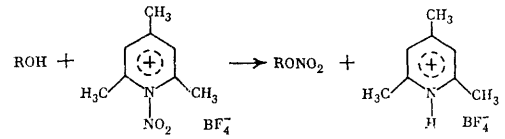
The attempts to nitrate a pyrimidine nucleoside (a 2'-deoxyglycoside) by NTFB as a rule leads to the degradation of the molecule or the formation of 5-nitrouracil, but the corresponding nucleotide (nucleoside 5'-monophosphate) is nitrated in the 5-position in the pyrimidine ring[97].

6. Nitration of Alcohols and Ethers

Aliphatic alcohols are readily nitrated by NTFB to the corresponding nitrates in 70–90% yields[98]:

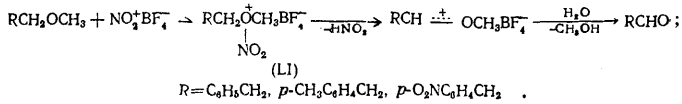
$$ROH + NO_2BF_4 \rightarrow RONO_2 + HBF_4 \ ;$$
$$R = Alk,\ HalCH_2CH_2,\ CF_3CH_2 \ .$$

The use of *N*-nitrocollidinium tetrafluoroborate in acetonitrile instead of a nitronium salt makes it possible to nitrate alcohols under milder, readily controlled conditions:



Aliphatic and carbocyclic alcohols enter into the reaction, the yield of nitrates being almost quantitative even in the nitration of the readily oxidisable diols and glycerol. It has been shown for benzyl alcohol that the reaction is fairly selective and permits nitration at the oxygen atom without involving the benzene ring[99].

Nitronium salts also react with the oxygen of the ether linkage. The nitroxonium ion (LI) formed in the reaction is readily converted, in high yields, into the corresponding aldehyde or ketone[100]:

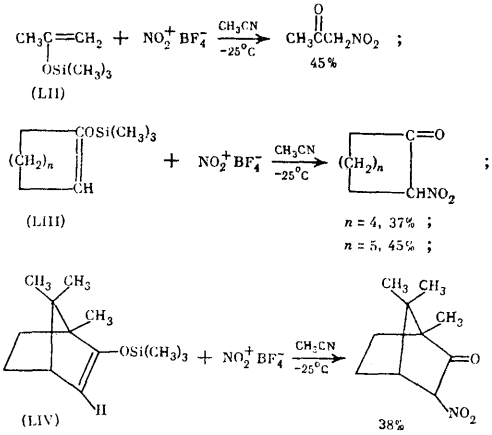


(LI)

R=$C_6H_5CH_2$, *p*-$CH_3C_6H_4CH_2$, *p*-$O_2NC_6H_4CH_2$.

The methyl ethers of cyclohexanol and cyclopentanol are converted into the methyl esters of the corresponding ω-hydroxyiminocarboxylic acids.

The nitration with nitronium salts of derivatives of the enolic vinyloxysilanes (LII)–(LLIV), leading to α-nitroketones which are usually difficult to obtain, is of special interest[101]:



(LII) (LIII) (LIV)

The reaction apparently proceeds via the formation of a substituted vinyl nitrate, which is comparatively stable in aprotic media and rearranges to an α-nitroketone.

7. Reactions of Nitronium Salts with Organoelemental and Complex Compounds

Diphenyl sulphide reacts with NTFB or $NO_2^+PF_6^-$ at −78 °C with formation of diphenyl sulphoxide. Dialkyl(aryl) selenides, triaryl(acyl)phosphines, triarylarsines, and triarylstibines undergo analogous reactions[102]. ^{13}C, ^{15}N, and ^{31}P NMR studies have shown that the reaction proceeds via the formation of the corresponding nitro-onium salts (LV), which are irreversibly converted into the nitrato-onium salts (LVI) and further into the corresponding oxides:

$$R{-}S{-}R' + NO_2^+ \rightleftarrows \underset{(LV)}{\left[\begin{array}{c} NO_2 \\ | \\ R{-}S{-}R' \end{array}\right]^+} \rightarrow \underset{(LVI)}{\left[\begin{array}{c} ONO \\ | \\ R{-}S{-}R' \end{array}\right]^+} \rightleftarrows \begin{array}{c} O \\ \uparrow \\ R{-}S{-}R' \end{array} + NO^+ .$$

This is the first reliably demonstrated instance of the isomerisation of a nitro-derivative to the *O*-nitrite. Similar reactions have also been postulated for $C{-}NO_2$ carbonium ions (see Section III, subsection 3).

Organotin compounds, for example, trimethylstannylacetylenes (LVII), undergo substitutional nitration by nitronium salts with formation of nitroacetylenes[103]:

$$\underset{(LVII)}{R_3SnC{\equiv}CR'} + NO_2^+BF_4^- \xrightarrow[-20^\circ]{} R'C{\equiv}CNO_2 + R_3SnBF_4 .$$

An analogous reaction of a derivative of another Group IV element (silicon) is described in subsection 5.

Ferrocenyl(triphenylphosphine)gold reacts with NTFB to form a complex mixture of products: ferrocene, biferrocenyl, [ferrocenyl(triphenylphosphine)gold]triphenylphosphinegold tetrafluoroborate[104]. The reaction of dichlorodicymantrenylstannane with NTFB is accompanied by the reduction of the latter[103] and proceeds via the mechanism

$$[C_5H_4Mn(CO_3)]_2SnCl_2 \xrightarrow[-2CO_2]{2NO_2^+BF_4^-} \{[C_5H_4Mn(CO)_2NO]_2SnCl_2\}^{2+}(BF_4^-)_2 .$$

Nitroso-complexes are also formed on interaction of platinum group transition metals with NTFB[105,106]:

$$Ir(CO)Cl[P(C_6H_5)_3] + NO_2^+BF_4^- \rightarrow Ir(CO)(NO)Cl(BF_4)[P(C_6H_5)_3]_2 ;$$
$$RhCl[P(C_6H_5)_3]_3 + NO_2^+BF_4^- \rightarrow RhCl(NO_2)[P(C_6H_5)_3]_3^+BF_4^- .$$

The reduction of nitronium salts to NO^+ is also observed in the reaction of NTFB with nitrogen-containing iron(II) and cobalt(II) complexes[105].

IV. THE MECHANISM OF THE NITRATION OF AROMATIC COMPOUNDS

The range of studies devoted to the kinetics and mechanism of nitration by nitronium salts is fairly wide. They are all devoted to the nitration of aromatic hydrocarbons, but the absolute rates of reaction have been measured only for deactivated substrates containing nitro-groups in the aromatic ring, such as nitrobenzene[32,40,41], nitrotoluenes, 1,3-dinitrobenzene, and 2,4- and 2,6-dinitrotoluenes[41]. In these studies the nitration by nitronium salts was carried out mainly in acids (sulphuric, hydrofluoric, and methanesulphonic) and it was shown that nitration by nitronium salts in such media takes place analogously to nitration by nitric acid. The nitrating activity of nitronium salts solutions in acetonitrile[40] and nitromethane[41] is much higher than that of nitric acid.

Measurement of the absolute rates of nitration of benzene and alkylbenzenes by nitronium salts proved to be impossible even by the stopped flow method, because a sufficiently rapid way of arresting the reaction could not be found[107]. All the experiments on the nitration of benzene and alkylbenzenes were therefore carried out by the competitive method developed by Ingold[108,109].

Processes involving nitration by nitronium salts and nitric acid solutions differ most markedly as regards the rate of nitration of benzene and toluene. The ratio of the rates of nitration of toluene (K_t) and benzene (K_b) by nitric acid solutions is 25.[108,110] In competitive nitration by nitronium salts, the ratio $K_t/K_b = 1.67$ was obtained, approaching unity with increase of temperature from 25° to 55 °C (K_t/K_b = 1.13).[111] The relative rate depends also on the nature of the anion in the nitronium salt and on the solvent[47]. In the nitration of 4-methoxy-2,6-dimethyl-*N*-nitropyridinium tetrafluoroborate, $K_t/K_b = 44.5$.[48]

The sharp decrease of the sensitivity with respect to the nature of the substrate in nitration by nitronium salts (decrease of substrate selectivity) is apparently due to the increase of reactivity and the associated decrease of the directing influence of the substituent, i.e. the ratio of the *ortho*- and *para*-isomers formed in the nitration of toluene should approach the statistical value (2:1). This situation is observed, for example, in free-radical nitration by nitrogen dioxide, where a low substrate selectivity ($K_t/K_b = 2.6$) is accompanied, as was to be expected, by a decrease of the positional selectivity (37.2% of the *ortho*-isomer, 38.1% of the *meta*-isomer, and 24.7% of the *para*-isomer)[107].

The fundamentally novel feature of Olah's data for nitration by a nitronium salt was that, with a sharp decrease of substrate selectivity, the authors obtained almost the same ratio of the isomers as in nitration by nitric acid. These two results—decrease of substrate selectivity with retention of positional selectivity—were very difficult to reconcile.

Nowadays it has come to be believed that electrophilic substitution in aromatic compounds (including nitration by nitric acid solutions) proceeds via stages involving the formation of π- and σ-complexes[108,110,112,113]. Initially the π_1-complex is converted into the σ-complex, which is then converted into the π_2-complex and finally into the reaction product. The rate-limiting stage of the process is the formation of the σ-complex, which is particularly indicated by the correlation between the basicity of arenes (which determines the stability of the σ-complexes) and the rates of the electrophilic substitution reactions[110,113,114,115]. The energy profile of the reaction is presented in Fig. 1.

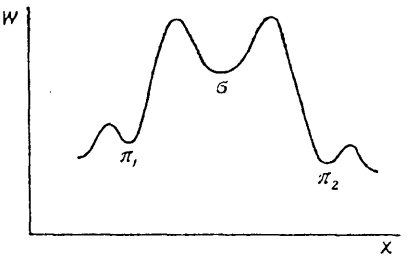


Figure 1. The energy profile of the electrophilic substitution reaction; W = energy; χ = reaction coordinate.

Olah observed that the rates of nitration by nitronium salts are better correlated with the stability of the π-complex[1,41,116,117], which led him and his co-workers to suggest that, in nitration by nitronium salts, the rate-determining stage is the formation of the π-complex and not the σ-complex (Fig. 2). This concept is extremely unusual for the theory of aromatic substitution.

Olah also believes that, in contrast to nitration by nitric acid solutions in which the π-complex arises on interaction with the electron system of the ring as a whole, nitronium salts form a directional π-complex where the nitronium cation is oriented towards the carbon atom with the maximum electron density. In the transformation of the π-complex into the internal σ-complex there is therefore no great energy expenditure and preferential *ortho–para* direction is achieved. The substrate selectivity in the nitration reaction is low, since the π-electron density in aromatic compounds depends little on the number of alkyl groups[112].

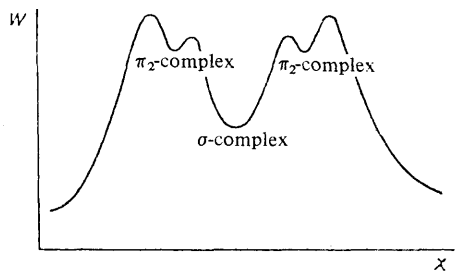


Figure 2. The energy profile of the reaction involving nitration by nitronium salts: $ArH + NO_2^+ \rightarrow ArNO_2 + H^+$; π_1-complex = $ArH...NO_2^+$; π_2-complex = $H^+...ArNO_2$; σ-complex = $ArHNO_2^+$.

Olah's interpretation of the experimental data has been criticised by a number of investigators[34,108,110,118–120]. Sikiguchi et al.[119] questioned the reliability of the ratios K_t/K_b obtained. They observed that in the competitive nitration of the benzene–toluene pair the ratio K_t/K_b depends on the dielectric constant ε of the solvent and changes from 2.15–2.31 for CCl_4 (ε = 2.23) to 16.3–19.7 for CH_3NO_2 (ε = 35), i.e. from a quantity close to that obtained by Olah to the usual values for nitric acid solutions. However, their study[119] nevertheless does not account for the low substrate selectivity in nitration by NTFB (also in nitromethane). Furthermore, their results[119] might have been influenced by the heterogeneity of the system, since nitric acid is very sparingly soluble in CCl_4 and aliphatic hydrocarbons.

Ritchie and Win[121] found that competitive nitration by NTFB in sulpholane caused different relative rates for binary (toluene–benzene) and quaternary (benzene–toluene–chlorobenzene–fluorobenzene) mixtures. They suggested that the nitration by nitronium salts is not fully kinetically controlled and that this might have been the cause of the "anomalous" results obtained by Olah and co-workers.

Doubts about the justification of the application of the competitive method to the study of the relative reactivities have been expressed by Tolgyesi[122], who showed, in relation to the nitration of the toluene–benzene pair by NTFB in sulpholane, that the ratio K_t/K_b increases with increase of the efficiency of mixing and the concentration of the hydrocarbons in solution and also with decrease of the NTFB concentration. Under certain conditions, the ratio K_t/K_b reaches 25–30, i.e. values corresponding to the reactivity in nitration by nitric acid solutions. However, it was shown later[107] that these results are due to the interaction of NTFB with the impurities present in the solvent.

In the nitration of durene (1,2,4,5-tetramethylbenzene) by solutions of nitronium hexafluorophosphate in nitromethane the yield of dinitrodurene was 8–10 times higher than that of mononitrodurene. On the other hand, under conditions of a more effective mixing of the reactants, mononitrodurene predominates[34]. These facts show that the reaction in essence occurs as soon as the components are mixed and that mass transfer processes therefore determine the reaction rate and the composition of the products. The nitration of pentamethylbenzene proceeds at a rate which is so high that the process is limited solely by the rate of mixing of the components[118,123]. The role of the mixing of the components has been confirmed by the nitration of bibenzyl in sulpholane. The main product of this reaction is the symmetrical dinitrobibenzyl even when there is a deficiency of the nitronium salt[124–126]. Thus the reactivity of NO_2^+ in nitronium salts is so high that the role of mass transfer increases sharply in the nitration process and to a greater extent the higher the reactivity of the substrate. Studies of the kinetics of the heterogeneous nitration of a number of substrates by NTFB using the "rotating disc" method[127] showed that, whereas the nitration of benzene takes place in the kinetic region, toluene is nitrated in the mixed region and the kinetics of the nitration of the still more reactive xylene and mesitylene are determined solely by diffusion processes. As was to be expected, the mass transfer conditions influence the substrate selectivity but not the positional selectivity[120,128,129].

Thus, in nitration by nitronium salts the concentration of the more reactive reactant at the site of mixing of the reactants diminishes so rapidly that the reactant cannot be supplied sufficiently rapidly by diffusion and the second reactant therefore reacts faster than would correspond to the ratio of the reactant concentrations, i.e. it is seemingly more reactive. This type of macroscopic diffusion effect can be eliminated in principle by rapid mixing and by employing a very low concentration of the more reactive substrate[110,122,126]. Furthermore, a second diffusion effect may appear in the system—a microscopic effect, whose essential feature is that the rate-determining process in the reaction becomes the collision of the reactants and not the formation of the reactive σ-complex. It has been shown[110,126,130–133] that the rate of nitration of alkylbenzenes by nitric acid in various media is limited by the number of encounters of the nitronium cation with the aromatic hydrocarbon, i.e. there is a limit to the reactivity of the substrate above which the introduction of activating substituents into the ring no longer increases the reaction rate. It is striking that, under conditions close to those corresponding to the maximum reaction rate, low substrate selectivities are obtained. The authors believe that, also in the case of very rapid nitration of alkylbenzenes by nitronium salts, the reaction rate is likewise limited by the rate of encounters with the substrate and this is why low substrate selectivities are obtained. Diffusion effects have been observed also in chlorination and bromination as well as nitration[134].

In later investigations[41,116,117] Olah admitted that the kinetics of the nitration of benzene and alkylbenzenes are determined by the encounter rate. Nevertheless he continues to believe that the mechanisms of the nitration of highly reactive compounds (benzene and alkylbenzenes) and deactivated substrates such as nitrobenzene and nitro- and dinitrotoluenes are different. An "early" transition state resembling an aromatic compound (a π-complex) is formed for highly reactive compounds. A low substrate selectivity (from 27 to 1) and a high (in the range 1–2) ratio of the *ortho*- and *para*-isomers are then usually observed. Relatively unreactive compounds (nitrobenzene, *o*- and *p*-nitrotoluenes, 2,4- and 2,6-dinitrotoluenes, etc.) give rise to

"late" transition states resembling a σ-complex. A high substrate selectivity is characteristic of such compounds (for example, the ratio of the rates of nitration of nitrotoluenes and nitrobenzene K_{nt}/K_{nb} is 100–500 and more for a low ratio of the *ortho*- and *para*-isomers (0.3–0.8).

According to Dewar[135,136] the "early" transition state retains aromatic properties to a considerable degree and is in many respects similar to an unperturbed aromatic system: the bond with the electrophile is still weak. The reaction with a strong electrophile is highly exothermic and one may therefore expect a relative stability of the intermediate and an appreciable difference between the latter and the transition state, which should be similar to the reactants in this instance according to Hammond's postulate[137]; the higher the reactivity of the electrophile, the smaller the influence of the substrate structure.

Schofield and co-workers reject Olah's concept of the "early" and "late" transition states[126,138] and, as already mentioned, explain the low substrate selectivity by the fact that the rate of nitration is limited by the diffusional process involving the formation of the "encounter complex" $ArH.NO_2^+$. The aromatic molecule as a whole and not just one carbon atom of the latter is involved in the formation of such a complex[126,130,138].

Stock[139] adheres to analogous views, believing that there are at present no data permitting the interpretation of Schofield's "encounter complex" as an oriented π-complex. He suggests the following mechanism of the nitration of aromatic compounds:

$$HNO_3 + H^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} H_2O + NO_2^+ \ ;$$

$$NO_2^+ + ArH \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} ArHNO_2^+ \ ;$$

encounter complex

$$ArHNO_2^+ \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} + \text{(H, NO}_2\text{)} +$$

$$+ \text{(H, NO}_2\text{)} + B \xrightarrow{K_4} \text{(NO}_2\text{)} + BH^+ \ ;$$

B = base.

However, it has been noted[126] that the concept of the "encounter complex" which Schofield took from the diffusion theory, resembles somewhat Olah's concept of the "oriented π-complex". This became particularly apparent in a study[138] in which it was claimed that an intermediate preceding the σ-complex must be included in the nitration mechanism. The formation of such an intermediate, i.e. of the "encounter complex" is the rate-determining diffusion stage and the rearrangement of the complex to the σ-complex determines the composition of the products.

In his latest studies Olah[140,141] also assumes that the formation of the σ-complex is preceded by two stages:

$$RC_6H_5 + NO_2^+ \overset{\text{stage 1}}{\rightleftharpoons} [RC_6H_5NO_2]^+ \overset{\text{stage 2}}{\rightleftharpoons} \underset{\text{(LVIII)}}{RC_6^+H_4\text{(H, NO}_2\text{)}} \overset{\text{stage 3}}{\xrightarrow{-H^+}} RC_6H_4NO_2 \ .$$

Stage *1* determines the overall rate of reaction and is responsible for the substrate selectivity, while stage *2* is responsible for the positional selectivity, i.e. the proportions of the isomers in nitration. The author explains by the presence of these two stages the high positional selectivity accompanied by a very low substrate selectivity in the nitration of highly reactive aromatic hydrocarbons by nitronium salts. The nature of the intermediate (LVIII) has been elucidated and Olah believes that this can be a π-complex, Schofield's "encounter complex", or even a radical pair of NO_2 and ArH^+, whose existence has been postulated for aromatic hydrocarbons with a high electron density[144]. The closeness of Olah's and Schofield's views is evident.

The question of the position of the transition state on the reaction coordinate, i.e. the determination of the stage responsible for the formation of a π- or σ-complex in nitration by nitronium salts, is more complex. The differences between Olah and Schofield as regards this question arise apparently from the different interpretations of the Hammett equation and Hammond's postulate. Johnson and Schofield[143,144] believe that it is quite inadmissible to employ the reaction constant as a characteristic of the selectivity–reactivity relation derived from Hammond's postulate. The large variations in selectivity found by Olah are a consequence of the inaccuracy of the competitive method for high reaction rates. Johnson[144] notes that the principle of selectivity implies the validity of the isokinetic relation, but the proportionality between the enthalpy and free energy by no means always holds. In many instances Hammonds postulate is invalid, i.e. one cannot regard as valid the hypothesis that the reaction constant ρ always reflects exactly the character of the transition state. The author believes that Hammond's postulate is insufficiently justified for electrophilic substitution reactions and that the conclusions usually associated with the values of ρ determined from the Hammett equation are exactly the opposite of those which follow from Hammond's postulate. If an attempt is made to determine the nature of the transition state for a given reaction with the aid of the Hammett equation on the basis of the different reaction rates in the presence of different substituents, then it follows from Hammond's postulate that the character of the transition state itself varies with the rate of the process.

Evidently a more detailed description of the conflict in the interpretation of the Hammett equation and Hammond's postulate is outside the framework of the present review.

New conclusions and the controversy concerning the nitration reaction and other electrophilic aromatic substitution reactions, whose mechanism appeared to be rigorously proved and understood after the publication of Ingold's book[108], have shown that studies in this field must be continued and that the treatment and interpretation of experimental data must be particularly thorough with allowance for diffusion processes.

REFERENCES

1. G.A.Olah and S.J.Kuhn, "Friedel–Crafts and Related Reactions", Vol.3 (Edited by G.A.Olah), Interscience, New York, 1964, Chapter 43.
2. A.Hantzsch, Ber., 1925, 58, 958.
3. D.R.Goddard, E.D.Hughes, and C.K.Ingold, J.Chem.Soc., 1950, 2559.
4. D.R.Goddard, E.D.Hughes, and C.K.Ingold, Nature, 1946, **158**, 480.
5. W.E.Gordon and J.W.T.Spinks, Canad.J.Res., 1940, **18B**, 358.
6. M.Schmeisser and W.Fink, Angew.Chem., 1957, **69**, 780.
7. C.W.Schoenfelder and M.S.Cohen, US P.3244474 (1964); Chem.Abs., 1966, **64**, 17096.
8. E.A.Fiskin and H.W.Wilson, US P.3842162 (1973).
9. R.A.Brown and D.S.Fetterman, US P.3186790 (1965); Chem.Abs., 1965, **63**, 3931.
10. J.Lakritz and J.R.Lowett, US P.3558456 (1971); Chem.Abs., 1971, **74**, 77933.
11. F.Seel, J.Norgadi, and R.Rosse, Z.anorg.Chem., 1952, **269**, 197.
12. A.A.Woolf and H.J.Emeleus, J.Chem.Soc., 1950, 1050.
13. A.A.Woolf and H.J.Emeleus, J.Chem.Soc., 1950, 1053.

14. A.A.Woolf and H.J.Emeleus, Chem.Ind., 1953, 868.
15. H.C.Clark and H.J.Emeleus, J.Chem.Soc., 1958, 190.
16. E.E.Aynsley, G.Hetherington, and P.L.Robinson, J.Chem.Soc., 1954, 1119.
17. J.P.Gechman and P.R.Ogle, Inorg.Chem., 1963, **2**(3), 1012.
18. J.H.Holloway and H.Selig, Inorg.Nuclear Chem., 1968, **30**(2), 473.
19. P.L.Robinson and G.L.Westland, J.Chem.Soc., 1956, 4481.
20. M.Schmeisser and E.Elisher, Z.Naturforsch., 1952, **7b**, 583.
21. G.A.Olah, S.J.Kuhn, and A.Mlinko, J.Chem.Soc., 1956, 4257.
22. S.J.Kuhn and G.A.Olah, J.Amer.Chem.Soc., 1961, **83**, 4564.
23. G.A.Olah and S.J.Kuhn, Org.Syn., 1967, **47**, 56.
24. P.Vast, Rev.Chim.Miner., 1970, **7**(4), 757.
25. S.J.Kuhn, Canad.J.Chem., 1962, **40**, 1660.
26. S.J.Kuhn, Canad.J.Chem., 1967, **45**, 3207.
27. L.M.Yagupol'skii, I.I.Maletina, and V.V.Orda, Zhur.Org.Khim., 1974, **10**, 2226.
28. C.L.Coon, W.G.Blucher, and M.E.Hill, J.Org. Chem., 1973, **38**, 4243.
29. S.K.Yarbo, R.E.Noftle, and W.B.Fox, J.Fluor. Chem., 1975, **6**, 187.
30. Yu.V.Guk, E.K.Legostaeva, B.A.Lebedev, and B.V.Gidaspov, Zhur.Prikl.Khim., 1978, **51**, 2602.
31. G.A.Olah and S.J.Kuhn, J.Chem.Soc., 1961, **83**, 4564.
32. M.I.Kilpatrick, M.Kilpatrick, and J.G.Jones, J.Phys. Chem., 1965, **69**, 2248.
33. S.S.Odokienko and Yu.A.Fedorov, Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) of the USSR Academy of Sciences, No.3466-75, 1975.
34. G.A.Olah, S.J.Kuhn, S.H.Flood, and J.C.Evans, J.Amer.Chem.Soc., 1962, **84**, 3687.
35. S.B.Hanna, E.Hunziker, T.Saito, and H.Zollinger, Helv.Chim.Acta, 1969, **52**, 1537.
36. J.C.Schumacher, in "Perkhloraty: Svoistva, Proizvodstvo i Primenenie" (Perchlorates: Properties, Manufacture, and Applications), GKhI, Moscow, 1963, p.77.
37. D.Cook, S.J.Kuhn, and G.A.Olah, J.Chem.Phys., 1960, **33**, 1669.
38. M.D.Marshall and L.L.Lewis, in "Sovremennaya Khimiya Raketnykh Topliv" (Modern Chemistry of Rocket Fuels), Atomizdat, Moscow, 1972, p.87.
39. H.Barbes and P.Vast, Rev.Chim.miner., 1971, **8**, 851.
40. L.L.Cigecio and R.A.Marcus, J.Amer.Chem.Soc., 1962, **84**, 1838.
41. G.A.Olah and H.C.Lin, J.Amer.Chem.Soc., 1974, **96**, 349.
42. G.A.Olah and S.J.Kuhn, Chem.Ind., 1956, 98.
43. G.P.Schiemenz and K.Röhlk, Chem.Ber., 1971, **104**, 1219.
44. G.A.Olah and S.J.Kuhn, J.Amer.Chem.Soc., 1964, **86**, 1067.
45. A.N.Detsina, V.I.Mamatyuk, and V.A.Koptyug, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 263.
46. E.Hunziker, J.R.Penton, and H.Zollinger, Helv. Chim.Acta, 1971, **54**, 2043.
47. G.A.Olah and S.J.Kuhn, J.Amer.Chem.Soc., 1962, **84**, 3684.
48. G.A.Cupas and B.L.Pearson, J.Amer.Chem.Soc., 1968, **90**, 4742.
49. G.A.Olah and H.C.Lin, J.Amer.Chem.Soc., 1971, **93**, 1259.
50. G.A.Olah, in "Chemical Reactivity and Reaction Paths" (Edited by G.Klopman) (Translated into Russian), Izd.Mir, Moscow, 1977, p.262.
51. L.Burnelle, P.Beaudowin, and L.J.Schaad, J.Phys.Chem., 1967, **71**, 2240.
52. R.D.Bach, J.W.Holubka, R.C.Badger, and S.Y.Rajan, J.Amer.Chem.Soc., 1979, **101**, 4416.
53. H.M.Walborsky, M.E.Baum, and A.A.Yossef, J.Amer.Chem.Soc., 1961, **83**, 988.
54. H.L.Goering and M.F.Sloan, J.Amer.Chem.Soc., 1961, **83**, 1397.
55. R.D.Bach, J.W.Holubka, and T.H.Taaffee, J.Org.Chem., 1979, **44**, 35.
56. G.A.Olah, H.W.Quinn, and S.J.Kuhn, J.Amer. Chem.Soc., 1960, **82**, 426.
57. G.A.Olah, P.Schilling, P.W.Westerman, and H.C.Lin, J.Amer.Chem.Soc., 1974, **96**, 3581.
58. M.L.Scheinbaum and M.Dines, J.Org.Chem., 1971, **36**, 3641.
59. V.A.Smit, A.V.Semenovskii, V.F.Kucherov, M.Z.Krimer, O.V.Lyubinskaya, and T.N.Chernova, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 1681.
60. W.A.Smit, A.V.Semenovsky, V.F.Kucherov, T.H.Chernova, M.Z.Krimer, and O.V.Lubinskaya, Tetrahedron Letters, 1971, 3107.
61. I.G.Mursakulov, M.M.Guseinov, V.A.Smit, A.G.Talybov, and N.S.Zefirov, Zhur.Org.Khim., 1977, **13**, 1121.
62. I.G.Mursakulov, A.G.Talybov, M.M.Guseinov, and V.A.Smit, Zhur.Org.Khim., 1979, **15**, 95.
63. E.M.Speranskii, V.M.Berestovitskaya, V.V.Perekalin, and V.A.Gukkel' [possibly Tiukkel], "XXVI Gertsenovskie Chteniya. Khimiya. Nauchnye Doklady" (The XXVIth Gertsen Lectures. Chemistry. Scientific Reports), Leningrad, 1973, No.2, p.79.
64. S.G.Zlotin, M.M.Krayushkin, V.V.Sevostyanova, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2362.
65. S.G.Zlotin, M.M.Krayushkin, V.V.Sevostyanova, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2286.
66. A.G.Talybov and I.G.Mursakulov, Azerb.Khim. Zhur., 1978, No.3, 64.
67. R.E.Olsen, D.W.Fish, and E.E.Hamel, in "Sovremennaya Khimiya Raketnykh Topliv" (Modern Chemistry of Rocket Fuels), Atomizdat, Moscow, 1972, p.55 [Adv.Chem.Ser., 1965, **54**, 48].
68. A.A.Onishchenko, T.V.Shernikova, O.A.Luk'yanov, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser. Khim., 1975, 2342.
69. A.A.Onishchenko, T.V.Shernikova, O.A.Luk'yanov, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser. Khim., 1976, 2530.
70. S.A.Shevelev, V.V.Semenov, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2530.
71. S.A.Shevelev, V.V.Semenov, and A.A.Fainzil'berg, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1091.
72. G.A.Olah and T.L.Ho, Synthesis, 1976, 610.
73. M.A.Ilyushin, E.L.Golod, and B.V.Gidaspov, Zhur.Org.Khim., 1977, **13**, 11.
74. M.A.Ilyushin, Yu.V.Guk, E.L.Golod, G.M.Frolova, and B.V.Gidaspov, Zhur.Org.Khim., 1979, **15**, 103.
75. P.Vast and J.Heubel, Compt.rend., 1967, **864c**, 1697.
76. P.Vast and J.Heubel, Compt.rend., 1965, **260**, 5799.
77. B.P.1126591 (1968); US P.3428667 (1969); Chem.Abs., 1969, **70**, 67584.

78. B.A.Lebedev, M.A.Ilyushin, S.A.Andreev, and B.V.Gidaspov, Zhur.Org.Khim., 1978, **14**, 2055.
79. S.A.Andreev, B.A.Lebedev, and I.V.Tselinskii, Zhur.Org.Khim., 1978, **14**, 2513.
80. O.A.Luk'yanov, I.K.Kozlova, and V.A.Tartakovskii, "Tezisy VI Vsesoyuznogo Soveshchaniya po Khimii Nitrosoedinenii" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry of Nitro-compounds), Moscow, 1977, p.68.
81. J.H.Robson, J.Amer.Chem.Soc., 1955, **77**, 107.
82. S.A.Andreev, L.A.Novik, B.A.Lebedev, I.V.Tselinskii, and B.V.Gidaspov, Zhur.Org.Khim., 1978, **14**, 240.
83. M.S.Pevzner, T.N.Kulibabina, N.A.Povarova, and L.V.Kilina, Khim.Geterotsikl.Soed., 1979, 1132.
84. S.A.Andreev, B.A.Lebedev, G.I.Koldobskii, I.V.Tselinskii, and B.V.Gidaspov, Zhur.Org.Khim., 1978, **14**, 907.
85. V.Grakauskas, US P.3300181 (1968); Chem.Abs., 1968, **69**, 35406.
86. S.A.Andreev, B.A.Lebedev, and I.V.Tselinskii, Zhur.Org.Khim., 1978, **14**, 909.
87. L.V.Cherednichenko, B.A.Lebedev, and B.V.Gidaspov, Zhur.Org.Khim., 1978, **14**, 735.
88. O.A.Luk'yanov, T.G.Mel'nikova, N.M.Seregina, and V.A.Tartakovskii, "Tezisy VI Vsesoyuznogo Soveshchaniya po Khimii Nitrosoedinenii" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry of Nitro-Compounds), Moscow, 1977, p.33.
89. O.A.Luk'yanov, N.M.Seregina, and V.A.Tartakovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 225.
90. A.R.Katritzky and J.W.Mitchell, J.Chem.Soc., Perkin Trans.(I), 1973, 2624.
91. M.P.Doyle, J.A.L.Whitefleet, D.J.Debruyn, and W.Wierenge, J.Amer.Chem.Soc., 1977, **99**, 494.
92. G.A.Olah, J.A.Olah, and N.A.Overchuk, J.Org. Chem., 1966, **30**, 3373.
93. J.Jones, Tetrahedron Letters, 1964, 2177.
94. N.P.Shusherina and G.I.Likhomanova, Khim. Geterotsikl.Soed., 1972, 1374.
95. M.S.Pevzner, T.N.Kulibabina, S.L.Ioffe, I.A.Maslina, B.V.Gidaspov, and V.A.Tartakovskii, Khim.Geterotsikl.Soed., 1979, 550.
96. R.S.Glass, J.F.Blount, and D.Batler, Canad.J. Chem., 1972, **50**, 3472.
97. G.F.Huang and P.F.Torrenu, J.Org.Chem., 1977, **42**, 3821.
98. G.A.Olah, L.Noszko, S.J.Kuhn, and M.Szelke, Chem.Ber., 1956, **89**, 2374.
99. G.A.Olah, S.C.Narang, R.L.Pearson, and C.A.Cupas, Synthesis, 1978, 452.
100. T.L.Ho and G.A.Olah, J.Org.Chem., 1977, **42**, 3097.
101. I.I.Shvarts, V.N.Yakovenko, M.M.Krayushkin, S.S.Novikov, and V.V.Sevost'yanov, Izv.Akad. Nauk SSSR, Ser.Khim., 1976, 1674.
102. G.A.Olah, B.G.B.Gupta, and S.C.Narang, J.Amer. Chem.Soc., 1979, **101**, 5317.
103. A.N.Nesmeyanov, T.I.Tolstaya, and V.V.Korol'kov, Dokl.Akad.Nauk SSSR, 1978, **241**, 1103.
104. E.G.Perevalova, D.A.Lemenovskii, T.V.Bakova, E.I.Smyslova, K.I.Grindberg, and A.N.Nesmeyanov, Dokl.Akad.Nauk SSSR, 1972, **206**, 883.
105. H.N.Rabinowitz, K.D.Karlin and S.J.Lippard, J.Amer.Chem.Soc., 1977, **99**, 1420.
106. J.Reed, J.Inorg.Nuclear Chem., 1976, **38**, 2239.
107. G.A.Olah and N.A.Overchuk, Canad.J.Chem., 1965, **43**, 3279.
108. C.K.Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1973.
109. C.K.Ingold and F.R.Shaw, J.Chem.Soc., 1927, 2918.
110. J.G.Hoggett, R.B.Moodie, J.R.Penton, and K.Schofield, "Nitration and Aromatic Reactivity", Cambridge University Press, Cambridge, 1971.
111. G.A.Olah, S.J.Kuhn, and S.H.Flood, J.Amer. Chem.Soc., 1961, **83**. 4571.
112. E.Berliner, in "Sovremennye Problemy Fizicheskoi Organicheskoi Khimii" (Modern Problems in Physical Organic Chemistry), Izd.Mir, Moscow, 1967, p.444.
113. J.H.Ridd, in "Studies of Chemical Structure and Reactivity", London, 1966, Chapter 7.
114. P.Rys, P.Skrabal, and H.Zollinger, Angew.Chem., Int.Ed.Engl., 1972, **11**, 874.
115. K.L.Nelson and H.C.Brown, in "The Chemistry of Petroleum Hydrocarbons", Reinhold Publ.Corp., New York, 1955, **3**, p.465.
116. G.A.Olah and H.C.Lin, J.Amer.Chem.Soc., 1974, **96**, 2892.
117. G.A.Olah, Acc.Chem.Res., 1971, **4**, 240.
118. E.Hunziker, J.R.Penton, and H.Zollinger, Helv.Chim.Acta, 1971, **54**, 2043.
119. S.Sikiguchi, A.Hirose, S.Kato, and K.Matsai, Bull.Chem.Soc.Japan, 1973, **46**, 646.
120. F.Pfister, P.Rys, and H.Zollinger, Helv.Chim.Acta, 1975, **58**, 2093.
121. C.D.Ritchie and H.Win, J.Org.Chem., 1964, **29**, 3093.
122. W.S.Tolgyesi, Canad.J.Chem., 1965, **43**, 243.
123. H.Zollinger, Tetrahedron Letters, 1965, 1739.
124. P.F.Christy, J.H.Ridd, and N.D.Stears, J.Chem.Soc.(B), 1970, 797.
125. J.H.Ridd and A.Gastaminza, J.Chem.Soc., Perkin Trans., II, 1972, 813.
126. J.H.Ridd, Acc.Chem.Res., 1971, **4**, 248.
127. Yu.V.Guk, E.L.Golod, and B.V.Gidaspov, Zhur.Org.Khim., 1977, **13**, 17.
128. F.Nabholz and P.Rys, Helv.Chim.Acta, 1977, **60**, 2937.
129. P.Rys, Helv.Chim.Acta, 1975, **58**, 2074.
130. R.G.Coombes, R.B.Moodie, and K.Schofield, J.Chem.Soc.(B), 1968, 800.
131. J.G.Hoggett, R.B.Moodie, and K.Schofield, J.Chem.Soc.(B), 1969, 1.
132. J.G.Hoggett and R.B.Moodie, Chem.Comm., 1969, 605.
133. S.R.Hartshorn, R.B.Moodie, and K.Schofield, J.Chem.Soc.(B), 1971, 2447.
134. S.Y.Caille and J.P.Corriu, Chem.Comm., 1967, 1251.
135. M.J.S.Dewar, T.Mole, and E.W.T.Warford, J.Chem.Soc., 1956, 3581.
136. M.J.S.Dewar and T.Mole, J.Chem.Soc., 1957, 342.
137. G.S.Hammond, J.Amer.Chem.Soc., 1955, **77**, 334.
138. R.B.Moodie, K.Schofield, and J.B.Weston, Chem. Comm., 1974, 382.
139. L.M.Stock, in "Progress in Physical Organic Chemistry", Vol.12 (Edited by R.W.Taft), Interscience, 1976, p.21.
140. G.A.Olah, H.C.Lin, J.A.Olah, and S.C.Narang, Proc.Nat.Acad.Sci.USA, 1978, **75**, 545.
141. G.A.Olah, H.C.Lin, J.A.Olah, and S.C.Narang, Proc.Nat.Acad.Sci.USA, 1978, **75**, 1045.

142. C.L.Perrin, J.Amer.Chem.Soc., 1977, **99**, 5516.
143. C.D.Johnson and K.Schofield, J.Amer.Chem.Soc., 1973, **95**, 1270.
144. C.D.Johnson, "The Hammett Equation" (Translated into Russian), Izd.Mir, Moscow, 1977.

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