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The Mechanism of the Reaction of C-Nitroso-compounds with Alkenes

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Published data on the study of the chemical aspects of the reaction of C-nitroso-compounds with alkenes have been examined and critically reviewed. The multi-stage nature of the process has been emphasised. The dependence of the mechanisms of the primary stage and subsequent stages of the reaction on the structure of the reagents and the reaction conditions has been discussed. An attempt has been made to explain the contradictory data on the structure of the final reaction products in terms of the variety of possible directions for the transformation of the intermediates. The characteristics of the chemical reaction of C-nitroso-compounds with diene polymers have been examined.
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I. INTRODUCTION

The considerable practical importance acquired in recent years by C-nitroso-compounds, which have found application as rubber modifiers and stabilisers both at the polymer formation stage[1-5] and in its conversion to finished rubber articles,[6-12] has led to increased interest in the study of the chemical aspects of the reaction of an unsaturated hydrocarbon chain with C-nitroso-compounds.

However, in spite of the fact that a fairly large number of published papers have been devoted to the mechanism of the reaction of C-nitroso-compounds with alkenes, this extensive but extremely contradictory experimental material has not been reviewed (apart from a brief review[13] dealing only with the reactions of C-nitroso-arenes and covering the literature up to 1970). In the present work an attempt is made to fill this gap.

Most workers who have studied the reaction of C-nitroso-compounds with monoalkenes point out that it is a multistage process, but there is lack of agreement on its basic parameters: the stoichiometry, the reaction centre in the alkene molecule, the nature of the primary attack on the alkene by the nitroso-compound and the intermediate stages, and the structures of the final products. Thus depending on the structure of the reagents and the conditions of the process, the following nitrogen-containing final reaction products have been isolated and identified: alkenylaryl- or alkenylalkyl-hydroxylamines, nitrones, azoxybenzenes, secondary and primary amines, azomethines, oxazetidines, oxadiazoles, isoxazolines, and oxime ethers.

The following main mechanisms have been proposed for the first stage of the reaction of nitroso-compounds with alkenes: 1) "Diels–Alder pseudo-condensation" ene synthesis with the formation of a tertiary hydroxylamine and prototropic displacement of the double bond; some authors assume intermediate 1,2 cyclo-addition with the formation of an oxazetidine; 2) direct radical allyl condensation with the transfer of an allyl proton to the NO group and the formation of a hydroxylamine derivative; 3) the formation of a 2:1 molecular adduct of the nitroso-compound and the alkene as a substituted oxadiazole; 4) a homolytic process involving direct electron transfer from the C=C bond to the NO bond with the formation of nitroxide radicals; 5) the formation of a charge-transfer complex from the alkene and the nitroso-compound and its decomposition via a radical–ion stage.

The products obtained in the first stage undergo further heterolytic and homolytic transformations to give the final products indicated above.

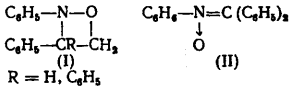
To introduce greater order into the often confused and contradictory published data, the present review is restricted to the study of the reactions of C-nitroso-compounds with alkenes with and without an allyllic hydrogen atom.

The present review examines the reactions of both aromatic and stable aliphatic nitroso-compounds, such as nitrosotrihalogenomethanes and nitroso-t-butane, which although differing in many of their characteristics (spectral,[14] polarographic,[15] etc.), are similar in their chemical properties, in particular in their reactions with alkenes.

II. REACTIONS OF C-NITROSO-COMPOUNDS WITH ALKENES NOT CONTAINING γ-PROTONS

This group of alkenes includes styrene, stilbene, 1,1-diphenylethylene, and their fluorinated analogues, but particular attention has been paid to the reactions of styrene. This interest in styrene is understandable, since aromatic nitroso-compounds are excellent inhibitors of free-radical reactions, and in the study of the processes of radical polymerisation and copolymerisation of styrene, which have found industrial application, it is important to investigate not only the stage involving the termination of the growing polymer chain but also the direct reaction of the inhibitor with the monomer.

In an early paper,[16] the adducts of styrene and 1,1-diphenylethylene with nitrosobenzene were assigned the oxazetidine structure (I).

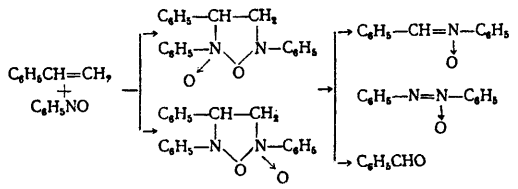


(I) R = H, C_6H_5 (II)

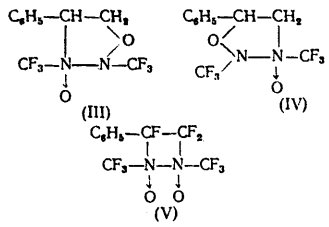
This view was criticised even at the time, however. According to Ref.17, the product of the reaction of nitrosobenzene with 1,1-diphenylethylene has the nitrone structure (II).

Hepfinger[18] considers that the products of the reaction of nitrosobenzene with styrene are unstable isomeric oxadiazole N-oxides, which decompose to give the α,N-diphenylnitrone,

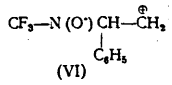
azoxybenzene, and benzaldehyde:



At the same time, one of a cycle of studies of the reaction of trifluoronitrosomethane with alkenes[19] showed that, depending on the reaction temperature, the products may be adducts of this nitroso-compound with styrene and trifluorostyrene in the ratio 2:1 (<−70 °C) and 1:1 (>−70 °C); the 1:1 adduct was assigned the oxazetidine structure (I), and the 2:1 adducts the structures (III) and (IV) for styrene, and (V) for trifluorostyrene:



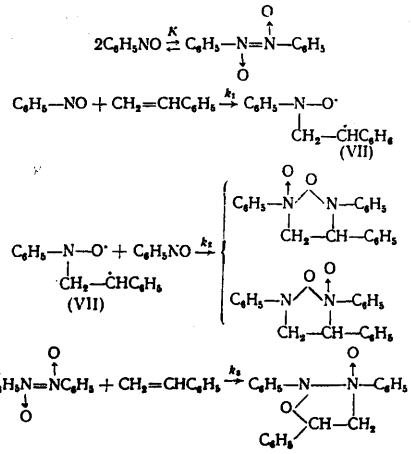
According to Ref.20, the first stage of the process gives a donor–acceptor complex, whose transformations are determined by the structure of the alkene. Paramagnetic intermediate species were detected, and in the case of the reaction of trifluoronitrosomethane with styrene they were assigned the radical–cation structure (VI):



Nitroxide radicals are also formed in the reaction with trifluorostyrene.[21]

The authors cited, however, do not suggest a mechanism which could explain the formation of the cyclic products (III)–(V).

Developing the ideas of Refs.18 and 19, a group of Japanese workers,[22] who studied the reactivity and kinetics of the reaction of nitrosobenzene with styrene, and also the reaction of the corresponding substituted derivatives, proposed the following scheme for the process:



They consider that the data they obtained on the kinetics of the reaction (order of the reaction with respect to nitrosobenzene between 1 and 2; its dependence on the initial concentration of the reagents—an increase with increase in concentration while preserving first order with respect to styrene) confirm the proposed mechanism, since in dilute solutions, the nitroso-compounds, which tend to dimerise,[23] are present chiefly in the monomeric form.

A study of the reactivity of substituted nitrosobenzenes showed that the presence of electron-donor substituents in the *p*-position decreases the reaction rate, whereas the presence of electron-acceptor substituents increases the reaction rate; a linear relationship was obtained between the reaction rate constants for the substituted nitrosobenzenes and the Hammett constants of the substituents for electrophilic reactions $\sigma^{\oplus}$, in good agreement with the view that the double bond in the styrene molecule is nucleophilic.

Among substituted styrenes, α-methylstyrene is much more reactive than β-methylstyrene; this is attributed not only to the more nucleophilic character of the double bond in the α-isomer and the stabilisation of the intermediate biradical (VII) but also to steric hindrance in the β-methylstyrene molecule.

The possible reaction of styrene with various derivatives of nitrosobenzene in the dimeric form has been noted.[24] The reaction is of second order with respect to the nitroso-compound, and paramagnetic species are formed in the reaction.

Thus although different workers have different views on the nature of the reaction of nitroso-derivatives with unsaturated hydrocarbons not containing γ-protons, most believe that cyclic products of the addition of the nitroso-compounds to the double bond are formed. Paramagnetic species are produced in the reaction. Benzylidene-N-phenylnitrone, azoxybenzene, and benzaldehyde have been separated from the decomposition products of the cyclic adducts of nitrosobenzene with styrene.

Some authors[25] have studed a series of alkenes without distinguishing between those which contain an allyl hydrogen atom and those which do not, and have examined their reactions with nitroso-compounds from the same viewpoint. The data given below, however, show that the presence or absence of γ-protons in the alkene has a significant influence on the mechanism of the process.

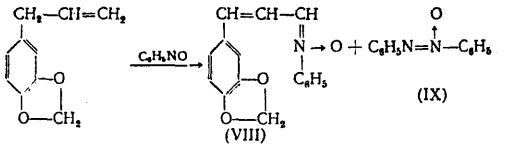
III. THE REACTION OF C-NITROSO-COMPOUNDS WITH ALKENES CONTAINING AN ALLYL HYDROGEN ATOM

Before reviewing studies devoted directly to the mechanism of the reactions of nitroso-compounds with alkenes containing primary, secondary, or tertiary hydrogen atoms in the allyl position, the structure of the final products of this reaction can be considered.

1. Structure of the Final Products

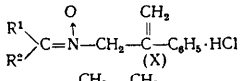
A critical review of published data on the products of the reactions of C-nitroso-compounds with alkenes containing an allyl hydrogen atom is difficult, since on the one hand, workers studying these processes encounter objective difficulties in identifying the final products, because of their tendency to undergo interconversion, and, on the other hand, some authors try to transfer experimental data relating to alkenes and nitroso-compounds with particular structures to other compounds of these classes. In the examination of the experimental material on the structure of the final products, therefore, specific reference will be made to the reagents for which the various regularities have been established.

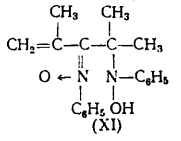
The reaction of C-nitroso-compounds with alkenes (safrole and various others) was first reported in Ref.26; the authors considered that the chief products of the reaction of nitrosobenzene with safrole are the nitrone (VIII) and azoxybenzene (IX).



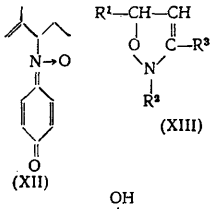
It was later shown[27] that azoxy-derivatives are formed in the reactions of *p*-nitro- and *p*-bromo-substituted nitrosobenzenes with cyclopentene, cyclohexene, propene, isobutylene, but-1-ene, *cis*- and *trans*-but-2-enes, and stilbene, the reaction taking from several seconds to several days, depending on the structure of the starting materials. The complete conversion of the nitrosobenzene into the azoxybenzene requires at least an equimolar quantity of the alkene. An appreciable quantity of azoxybenzene was isolated in the reaction of nitrosobenzene with 2-methylpent-2-ene.[28] The formation of nitrones in the processes studied was not reported.[27,28]

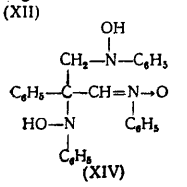
On the other hand, nitrones were identified as products of the reaction of α-methylstyrene and other alkenes containing an allyl hydrogen atom with chloronitrosoadamantane and other α-chloronitroso-compounds, where the nitrones were isolated as the hydrochlorides (X),[29] and also as products of the reaction of nitrosobenzene with tetramethylallene (in this case the bifunctional product (XI) with nitrone and hydroxylamine groups is formed).[30] In the last case, azoxybenzene was also isolated, but only as the product of the high-temperature treatment of compound (XI).





When examining the possible separation of α-alkenylnitrones in the reactions of nitroso-compounds with alkenes, it must be borne in mind[31] that they are stable only when they have a structure capable of undergoing tautomerisation to give more stable forms (for example, the alkenylquinonimine oxide (XII), isomeric with the expected nitrone, is obtained from nitrosophenol and 2-methylpent-2-ene)[31,32] or have a high degree of resonance stability (the nitrone (VIII), isolated in the reaction of nitrosobenzene with safrole).

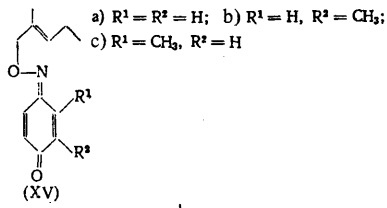




Unstable α-alkenyl-N-arylnitrones may undergo intramolecular cyclisation or react further with the alkene and the unreacted nitroso-compound.[33–38] These reactions naturally also take place with comparatively stable nitrones, but under more severe conditions; for example, the isoxazoline ring (XIII) is formed by intramolecular cyclisation.

The instability of the products of the reactions of nitroso-compounds with alkenes is confirmed by the data of Ref.39. The author cited considers that at low temperatures (−10 °C), nitrosobenzene reacts with α-methylstyrene to form the 3:1 adduct α-[1-phenyl-1,2-di(N-phenylhydroxylamino)ethyl]-N-phenylnitrone (XIV), which subsequently at room temperature loses one N-phenylhydroxylamine fragment to form the cyclic 2:1 adduct, a substituted isoxazoline. Another example is the thermal rearrangement of alkenylquinonimine N-oxides (XII), formed as indicated above by the reactions of nitrosophenols with 2-methylpent-2-ene, to give O-alkenyl quinonimine oxime ethers (XV).[32] This rearrangement, which is analogous to the familiar thermal rearrangement of allylamine oxides into O-alkenylhydroxylamines[40–42] and of nitrones into O-alkenyl oxime ethers,[43,44] takes place only at comparatively high temperatures (100–120 °C) so that oxime ethers were found in appreciable quantities only in the products of the reaction of nitrosocresols with 2-methylpent-2-ene, which requires high temperatures.

The main products isolated[13,31,45] in the reaction of 2-methylpent-2-ene with *p*-nitrosophenol and N,N-dimethyl-*p*-nitrosoaniline are the corresponding *p*-substituted alkenylanilines (XVI).

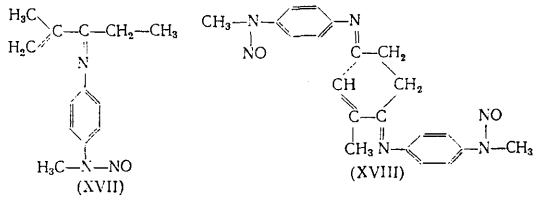


A characteristic feature of the reaction conditions in Ref.31 is a 12-fold excess of the alkene. In this case, in addition to the *p*-substituted N-alkenylanilines, the authors cited isolated a large number of resinous products, which they believed to be condensed nitrone structures. A small quantity of azoxybenzenes, azobenzenes, and primary *p*-substituted anilines, products of side reactions, was also obtained.

The comparative simplicity of the single-stage synthesis of N-alkenyl-*p*-phenylenediamines—a new class of effective antioxidants—by the reaction of N-substituted *p*-nitrosoanilines with alkenes[46] makes this process fully competitive with the industrial method for the production of familiar antioxidants with a similar structure, namely N-alkyl-*p*-phenylenediamines, which are usually obtained by hydrogenating nitroso-compounds followed by reductive alkylation of the anilines with ketones.[47]

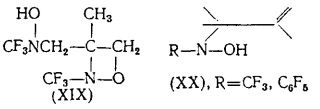
Another possible final structure is indicated in Ref.48, where the products of the reaction of N-methyl-N,4-dinitrosoaniline with alkenes are assigned the anil structure; the reaction with 2-methylpent-2-ene gives the 1:1 adduct (XVII), and the reaction with methylcyclohexane gives the 2:1 adduct (XVIII). The authors of Ref.13 consider, however, that the data given in Ref.48, on the basis of which the functional group in the final products (XVII) and (XVIII) was identified

as the azomethine group, can equally be related to an azomethine oxide (nitrone).



(XVII) (XVIII)

The cyclic products of the reaction of nitroso-compounds with alkenes not containing γ-protons, which are apparently the main final products or intermediate products in the case of allyl alkenes, have been reported to contain not only cyclised nitrones but also oxazetidines[49-51] or compounds containing hydroxylamine and oxazetidine groups.[51] Thus in the opinion of the authors of Ref.51, the 2:1 adduct of trifluoronitrosomethane and isobutylene has the structure (XIX).



(XIX) (XX), R=CF_3, C_6F_5

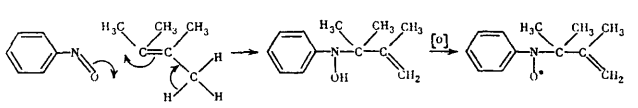
Some authors[25,51,52] consider that the final products of the reactions of alkenes with fluorinated nitroso-compounds are alkenylaryl- or alkenylalkylhydroxylamines (XX). Most workers, however, believe that substituted hydroxylamines are only intermediate compounds, and undergo further transformations, discussed below.

Analysis of published data on the structure of the final products of the reactions of nitroso-compounds with alkenes containing allyl hydrogen leads to the following conclusions: 1) in a large excess of the alkene, the reaction apparently takes place mainly to give the secondary amine and the nitrone or its transformation products; 2) in the absence of an excess of the alkene, appreciable quantities of azoxy-derivatives are found in the reaction products; 3) for perfluorinated nitroso-compounds, the formation of compounds with hydroxylamine or oxazetidine groups as final products is possible.

2. Mechanism of the Primary Stage of the Reaction

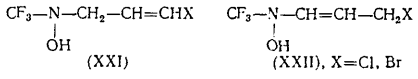
Most workers who have studied the reactions of C-nitroso-compounds with alkenes containing γ-protons consider that the initial stage is the ene addition of the nitroso-compound to give an unsaturated hydroxylamine. However, since these hydroxylamines are unstable and can be isolated and identified only in rare cases, there are other ideas regarding the primary stage.

The possibility of an ene reaction between a nitroso-compound and an alkene containing hydrogen on the α-methylene carbon atom was first reported in 1965.[53] Data were soon published[28] on the formation of a stable alkenyl aryl nitroxide radical, obtained by oxidising an extremely reactive alkenylarylhydroxylamine—an adduct of nitrosobenzene or some of its *o*-, *m*-, and *p*-derivatives with tetramethylethylene, chosen as an alkene whose symmetry makes it possible to obtain a resolved triplet in the EPR spectrum of the reaction product. The intermediate unstable alkenylarylhydroxylamine could not be isolated, and its formation was proved indirectly.



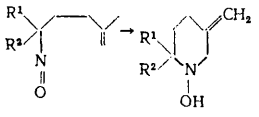
The possibility of ene synthesis with subsequent oxidation of the alkenylhydroxylamine to a nitroxide radical was confirmed in Ref.25, where the ene adduct of pentafluoronitrobenzene and tetramethylethylene was isolated in quantitative yield. Trifluoronitrosobenzene reacts similarly with an alkene. Many other authors also regard ene synthesis as the initial stage of the reactions of nitroso-compounds with alkenes.[20,46,52,54,55] The study of the reactivity of alkenes with different structures in the ene reaction is of considerable interest. The reactivity of butenes towards trifluoronitrosomethane decreases in the following order:[55] *cis*-CH_3–CH=CH–CH_3 > *trans*-CH_3–CH=CH–CH_3 > $(CH_3)_2C=CH_2$ > CH_3–CH_2–CH=CH_2, which is apparently determined by the nucleophilic character of the double bond in the alkene molecule and by steric factors. The presence of electron-acceptor substituents on the allyl carbon atom decreases the reaction rate considerably. A similar conclusion was reached[56] in a study of the kinetics of the reactions of alkenes with different structures with N,N-dimethyl-*p*-nitrosoaniline, which established that the highest rate in this reaction is shown by alkenes with the isostructure, containing an internal double bond on the tertiary carbon atom. A study of the kinetics of the reaction showed that it is formally of first order with respect to both reagents in a large excess of one of them.

To prove that a reaction is an ene reaction, it is important to establish the exact position of the hydroxylamine group in the chain or, if this is impossible because of the ease of oxidation of the hydroxylamine, to establish the position of the resulting nitroxide radical from the hyperfine structure of the EPR spectrum. Thus the presence or absence of hydrogen on the α-carbon atom (relative to the nitroxide group) has a significant influence on the EPR spectrum. Contradictory data are also obtained with this approach, however. Thus the product of the reaction of allyl halides with trifluoronitrosomethane according to some authors[55] is the one adduct (XXI) and according to others[20] the isomeric product (XXII).



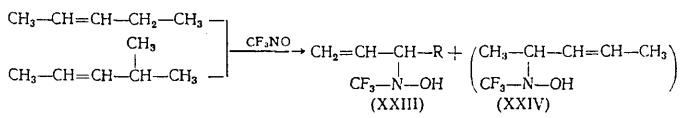
(XXI) (XXII), X=Cl, Br

Nevertheless, many authors give irrefutable data which indicate that the ene adduct is formed, that is that the nitrogen of the nitroso-group is added to the carbon of the double bond with the simultaneous transfer of the allyl hydrogen to the oxygen of the nitroso-group and prototropic displacement of the double bond. One interesting proof is the formation of a cyclic hydroxylamine by an intramolecular ene reaction in nitrosoalkenes:[57]



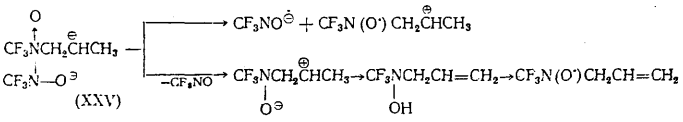
The nitroso-group adds on to the α- or β-unsaturated carbon atom, depending on the nature of the allyl hydrogen atom. The primary and secondary γ-protons are approximately equally readily transferred to the oxygen atom of the nitroso-group,[55] and the proton of the methine group is much more difficult to remove. Thus pent-2-ene reacts with trifluoronitrosomethane to give a mixture of isomers (XXIII) and (XXIV) as a result of the transfer of a hydrogen atom from the CH_3 and CH_2 groups respectively, whereas with 4-methylpent-2-ene, where there is a choice between CH and CH_3 groups, only compound

(XXIII), with R = iso-C_3H_7, is formed.



For alkenes with the iso-structure, the position at which the nitroso-group is added depends not only on the nature of the allyl hydrogen but also on the electronegativity of the carbon of the double bond. Thus an analysis of the EPR and NMR spectra[58] established that nitrosobenzene reacts with 2-methylpent-2-ene to give an ene adduct at the =CH— fragment of the alkene molecule.

Different views of the mechanism of formation of the ene adducts of nitroso-compounds with alkenes, in particular of the structure of the intermediates, have been put forward. In Ref.20 it is stated that the reaction of a nitroso-compound with an alkene gives initially a 2:1 donor–acceptor complex,[25] in which the alkene is generally the donor, and the nitroso-compound the acceptor. An exception is provided by acrylates or vinyl compounds with strong electron-acceptor substituents, where at increased temperatures the unsaturated compound may act as the electron acceptor, and the nitroso-compound as the electron donor. The decomposition of this complex to give 1:1 adducts, for example for the reaction of trifluoronitrosomethane with propene, takes place according to the scheme:



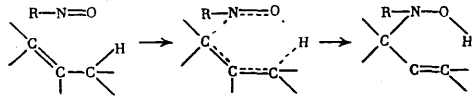
The author cited bases his idea of a single redox mechanism for this process on the reactivity of alkenes with different structures, which is consistent with the values of the ionisation potentials, characterising the donor properties of the alkene,[59] and also with the tendency of the alkenes to form charge-transfer complexes with other acceptors,[60] and the reactivity of alkenes in reactions with electrophilic reagents.[61]

According to another opinion,[50] the reaction involves the formation of a four-membered oxazetidine ring, which subsequently breaks down to give the hydroxylamine derivative.

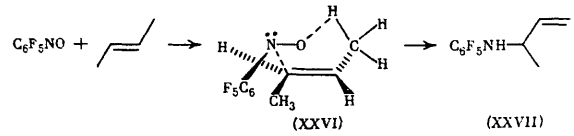
These ideas have been criticised,[55] however, and as proof of the absence of the zwitterion intermediate (the bipolar ion (XXV) in Ref.20), the reaction with β-pinene, which is not accompanied by rearrangement, is considered.

The heterolytic, and not homolytic, character of the first stage of the reaction of a nitroso-compound with an alkene is confirmed by the addition to the alkene carbon, and not to the carbon which was initially the allyl carbon.

In Ref.25 it is considered that the intermediate state of the ene reaction is a six-membered internal associate, and this reaction is regarded as a familiar "synchronous transfer" reaction.

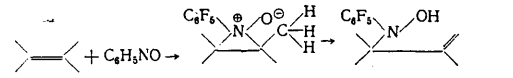


According to these ideas, the formation of the secondary amine (XXVII) as the product of the reaction of pentafluoronitrosobenzene and *trans*-but-2-ene is explained by the role of the steric factors in the intermediate state (XXVI) of the ene reaction.[25]



The recent increased interest in ene reactions with different enophiles such as oxygen,[62–64] triazolinediones,[65,66] and compounds with S=N bonds,[67] however, has led to a re-examination of the idea of a six-membered intermediate state.

Thus a study of the isotope effects produced by the deuteriation of tetramethylethylene led to the conclusion that its reaction with pentafluoronitrosobenzene takes place in two stages,[52] and that the first stage of the process, which is the limiting stage, gives a three-membered cyclic compound, an aziridine oxide, which subsequently undergoes rapid splitting of the C–H and C–N bonds to give the ene product:



The transformations of the ene product, including the formation of nitroxide radicals, will be examined below. It has been suggested, however, that nitroxide radicals in the reactions of nitroso-compounds with alkenes are not necessarily formed by the oxidation of an intermediate alkenylhydroxylamine, particularly since paramagnetic species have also been obtained in the reactions of nitroso-compounds with unsaturated compounds not containing allyl hydrogen, that is in cases where the formation of an ene adduct is impossible. These species have been observed in reactions with styrene,[22] trifluorostyrene,[21] vinyl acetate, and derivatives of acrylic acid (these paramagnetic species were assigned the corresponding radical–cation and radical–anion structures[20]).

Thus a study[68] of radical processes in a nitroso-compound–alkene system (for the reactions of nitrosobenzene and *p*-chloronitrosobenzene with oct-1-ene, cyclohexene, butadiene, and cycloheptatriene) leaves open the question of the mechanism of the first stage of the process. The following reaction scheme is given:

$$ArNO + CH_2{=}CHR \rightarrow ArN(O^{\cdot})CH_2{-}\dot{C}HR \quad (1)$$

$$2ArN(O^{\cdot})CH_2{-}\dot{C}HR \rightarrow [ArN(O^{\cdot})CH_2{-}CH(R){-}]_2 \quad (2)$$

$$ArNO + ArN(O^{\cdot})CH_2{-}CH{-}\dot{C}HR_2' \rightarrow ArN(O^{\cdot})CH_2CH{=}CR_2' + ArNHO^{\cdot} \quad (3)$$

$$ArNO + ArN(O^{\cdot})CH_2{-}\dot{C}HR \rightarrow ArN(O^{\cdot})CH{=}CHR + ArNHO^{\cdot} \quad (4)$$

$$ArNO + ArN(O^{\cdot})CH_2{-}\dot{C}HR \rightarrow ArN(O^{\cdot})CH_2CH(R){-}N(O^{\cdot})Ar \quad (5)$$

The biradical formed according to Eqn.(1) reacts rapidly according to Eqns.(2)–(5) to give other radicals which are then transformed more slowly by disproportionation, recombination, or reaction with the starting materials to give nitrones, hydroxylamines, azoxybenzenes, etc.

The approach in Ref.68 to the determination of the mechanism of the primary stage of the reactions of nitroso-compounds with alkenes appears too cautious; the nitroxide radicals are most probably formed by the oxidation of the intermediate alkenylhydroxylamine by the nitroso-compound. Data confirming this view are given below.

3. The Mechanism of the Subsequent Stages of the Reactions of C-Nitroso-compounds with Alkenes

The examination of the mechanism of the subsequent stages of the reactions of nitroso-compounds with alkenes should essentially be concerned with the reactions of disubstituted

hydroxylamines with nitroxide radicals, that is the intermediates whose formation (at least one of them) is postulated by most authors.

a) Reactions of disubstituted hydroxylamines

The chemistry of alkylarylhydroxylamines and alkenylarylhydroxylamines has been little studied; most data relate to their decomposition and oxidation.

The chief products of the thermal decomposition of these compounds are a nitrone and a secondary amine,[69,70] formed by the disproportionation of two moles of the disubstituted hydroxylamine. It has been confirmed[13] that the decomposition is of second order with respect to the hydroxylamine, and that the decomposition rate depends on the nature of the substituent; electron-donor substituents increase the reaction rate. A study of the thermal decomposition of *p*-substituted N-phenylhydroxylamines showed that the reaction products are nitrones and azoxy-arenes.[13] Another possible direction of transformation of substituted hydroxylamines when heated is dehydration to give an azomethine.[48]

However, the most important reaction of alkenylarylhydroxylamines as intermediate products of the reaction of nitroso-compounds with alkenes is undoubtedly their oxidation by oxygen in the reaction mixture or, if it is not present, by the unreacted nitroso-compound.

The mechanism of this reaction can be considered. Thermodynamic studies have shown[71,72] that stable radicals X$^{\cdot}$ may be produced by the removal of only mobile hydrogen by the reaction:

$$RN{=}O + XH \rightarrow RNHO^{\cdot} + X^{\cdot} \qquad (6)$$

The low dissociation energy of the OH bond in alkenylaryl- and alkenylalkylhydroxylamines[73] facilitates this reaction. Reaction (6), which involves molecular homolysis by the rupture of a simple bond under the influence of the reagent, in the opinion of the authors of Ref.72 corresponds more closely to the experimental data than two other reactions which may give radicals, namely the reaction of two π-systems to give biradicals, and donor–acceptor electron exchange to give two radicals or a radical–ion.[74] Under certain conditions, the last type of homolysis is probably involved in the reactions of nitroso-compounds with unsaturated compounds not containing γ-protons.

Direct proof of the formation of nitroxide radicals in the reactions of nitroso-compounds with hydroxylamines has been given.[75]

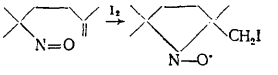
Evidence of a reaction of type (6) between a nitroso-compound and an N-substituted hydroxylamine is also provided by recent data on the formation of nitroxide radicals in the reactions of nitroso-compounds with other compounds containing active hydrogen: carbonyl compounds capable of enolisation, thiols, and phenols,[54] thiophenols,[76], imines in the enamine tautomeric form,[77] diketones,[78] etc.

At the same time, the importance of the photolysis of nitroso-compounds in the production of nitroxide radicals in a reacting system has been emphasised:[72] the light source may be natural light or ordinary artificial laboratory illumination.

$$RN{=}O \xrightarrow{h\nu} R^{\cdot} + NO^{\cdot}$$
$$R^{\cdot} + RNO \rightarrow R_2NO^{\cdot}$$

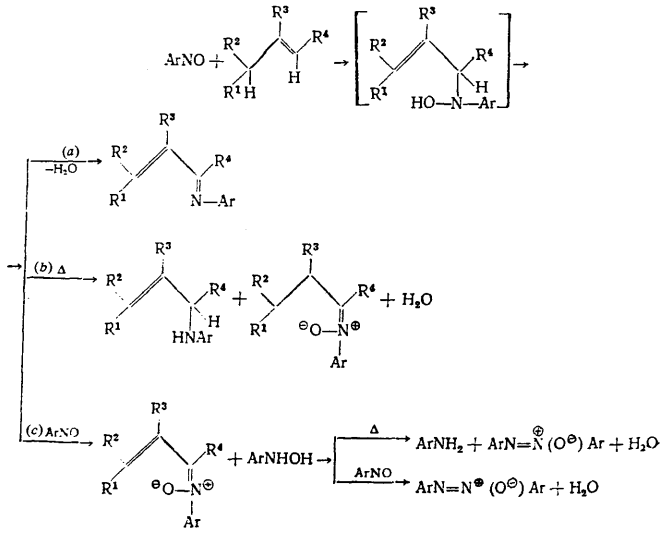
Nevertheless, most authors attribute the formation of nitroxide radicals in the reactions of C-nitroso-compounds with alkenes to the oxidation of an intermediate hydroxylamine,[20,25,28,55,57,58] the oxidant usually being the nitroso-compound itself (when the reaction is carried out in an inert medium), although if the aim is to obtain the nitroxide it is possible to introduce oxidising agents specially, for example silver oxide[79] or iodine.[80]

The last paper is of particular interest, since it proposes a general method for synthesising cyclic nitroxides by the action of iodine on δ, ε-unsaturated nitroso-compounds.



There are very few published data on the final oxidation products of disubstituted hydroxylamines. The final products of the oxidation of N-benzyl-N-phenylhydroxylamine by different *p*-substituted nitrosobenzenes are the α,N-diphenylnitrone and *p*-substituted azoxybenzenes.[13] When the aromatic nitroso-compound contains strong electron-donor substituents, an appreciable quantity of derivatives of primary amines is found in the reaction mixture, in addition to azoxybenzenes.

From their experimental data and an analysis of published data, the following scheme was proposed for the reactions of nitroso-compounds with alkenes containing an allyl hydrogen atom:[13]



According to this scheme, the first stage of the reaction is an ene reaction, leading to the formation of an alkenylarylhydroxylamine, which subsequently undergoes transformations characteristic of disubstituted hydroxylamines: oxidation (*c*), thermal decomposition (*b*), and dehydration (*a*) to give the nitrone, azoxybenzene, amines, and an azomethine.

An undoubted advantage of the proposed scheme is that the authors tried to use known reactions to explain the transformation of N-substituted hydroxylamines into products which in the opinion of many workers are the final products of the reactions of nitroso-compounds with alkenes containing an allylic hydrogen atom.

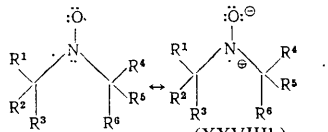
At the same time, the scheme has a serious shortcoming, in that it ignores the fact that nitroxide radicals are formed in the reactions of nitroso-compounds with alkenes, and the relationship between the structures of the radicals and the final products.

Since there are no published data on this relationship, those reactions of nitroxide radicals which can apparently take place during the formation of the products of the reactions of nitroso-compounds with alkenes will be considered.

b) Reactions of nitroxide radicals

The chemistry of nitroxide radicals is a widely studied field, to which a large contribution has been made by Soviet scientists.[81–83] The thermodynamic stability of nitroxide radicals

is determined by the degree of delocalisation of the unpaired electron between oxygen and nitrogen (XXVIIIa, b); for dialkyl nitroxides the delocalisation energy is ~30 kcal mole^{-1}.



(XXVIIIa) (XXVIIIb)

In general, the stability of the free radicals correlates well with the dissociation energy of the bonds broken on radical formation.

Thus reactions such as the oxidation of hydroxylamines having a low energy of removal of the hydrogen of the hydroxyl group[73] or the "spin capture" of carbon-centred radicals by spin traps such as nitroso-compounds and nitrones[84] lead to the rapid formation of nitroxide radicals.

An important condition for the stability of disubstituted nitroxide radicals is the absence of hydrogen atoms on the α-carbon atom.[85] At the same time, monosubstituted nitroxides and dialkyl or alkyl aryl nitroxides containing methyl, methylene, or methine groups in the α-position, that is the radicals most frequently formed in the reactions of nitroso-compounds with alkenes, are generally insufficiently stable, and undergo recombination and disproportionation, and also react with reagents or intermediates in the reaction system.

The chemical properties, in particular the ability to undergo recombination and disproportionation, of mono- and disubstituted nitroxides can be considered separately.

Monoaryl and monoalkyl nitroxides. The oxidation of N-phenyl-hydroxylamine by nitrosobenzene to give the phenyl nitroxide radical was first reported in Ref.86; the study of this reaction in different media shows that it gives azoxybenzene; the intermediate is a radical–anion in the presence of a strong base, and a nitroxide radical in the absence of a strong base.

A study of the kinetics of the decomposition of methyl, isopropyl, t-butyl, and phenyl nitroxides in solution[71] established that both reversible disporportionation to hydroxylamino- and nitroso-derivatives, and slower recombination to give an azoxy-compound, take place. For the phenyl derivative, the equilibrium constants and rates of the following reactions were calculated:

$$2C_6H_5NHO^{\cdot} \overset{K}{\rightleftharpoons} C_6H_5NHOH + C_6H_5NO \qquad (7)$$

$$2C_6H_5NHO^{\cdot} \xrightarrow{k_{azo}} C_6H_5N{=}NC_6H_5 + H_2O \qquad (8)$$

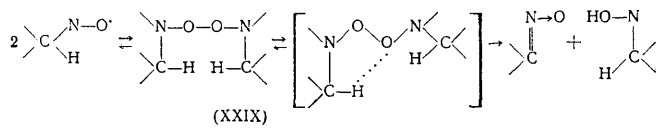
$$\downarrow O$$

The authors assume, however, that direct condensation of nitrosobenzene and N-phenylhydroxylamine to give azoxybenzene may take place.

At the same time, a study of the catalysis of this reaction using Fe^{2+} and Fe^{3+} salts[87] showed that the formation of azoxybenzene undoubtedly involves the dimerisation (recombination) of the nitroxide radical, that is according to Eqn.(8).

Important results were obtained in a study of the dependence of the stability of nitroxide radicals on the concentration in the solution. The rate of the decomposition of these radicals increases with decrease in their concentration.[71,86]

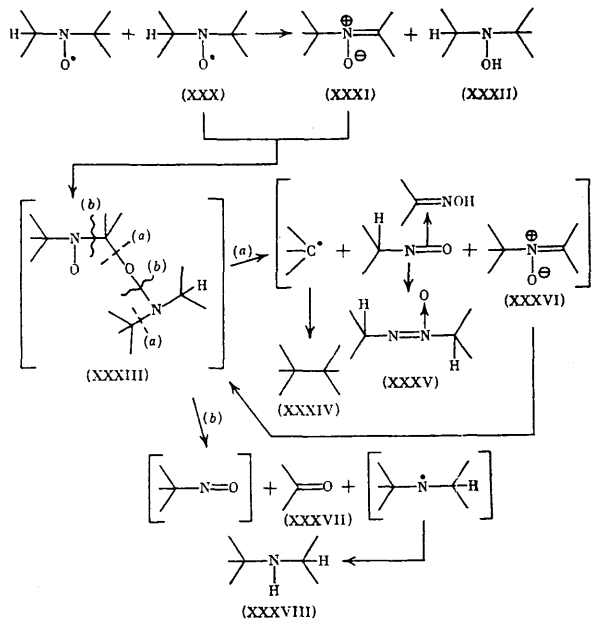
Disubstituted nitroxide radicals. The most stable radicals are di-t-alkyl nitroxides. In contrast to this, nitroxides having at least one hydrogen atom on the α-carbon atom usually disproportionate to hydroxylamines and nitrones. According to Refs.88 and 89, the mechanism of this reaction involves the dimerisation of the nitroxide and the subsequent slow decomposition of the diamagnetic dimer:



(XXIX)

The participation of the α-hydrogen atom in the limiting stage of the process was proved by replacing it with deuterium. The reaction shows a strong isotopic effect ($k_H/k_D \cong 9$).[93] At the same time, the structure of the dimer (XXIX) is not considered to have been proved,[90,91] since a thermochemical examination of the process[88,91] indicates that the formation of the O–O bond is endothermic, with an energy expenditure of 28 kcal mole^{-1}. The formation of at least three types of dimer with O–N, O–C, and N–N bonds has been reported.[92]

In a study of the decomposition of t-butyl isopropyl nitroxide radicals, doubt was cast[93] on the mechanism involving dimerisation, and the following scheme was given for the process:

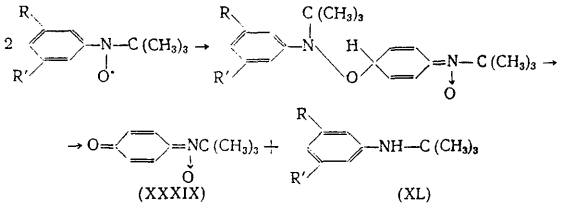


(XXX) (XXXI) (XXXII) (XXXIII) (XXXIV) (XXXV) (XXXVI) (XXXVII) (XXXVIII)

According to this scheme, the disproportionation of the nitroxide radicals (XXX) gives a hydroxylamine (XXXII) and a nitrone (XXXI), which being an excellent spin trap reacts with the original nitroxide radical to give an unstable secondary radical (XXXIII); decomposition of the latter gives products such as the alkane (XXXIV), the dimer of the nitroso-compound (XXXV), the oxime (XXXVI), the ketone (XXXVII), and the secondary amine (XXXVIII). Under certain conditions, the nitrone may be formed not by the disproportionation of the nitroxide but by its oxidation by an oxidant present in the system; this takes place in the formation of dibenzyl nitroxide from dibenzylhydroxylamine.[94]

Aryl t-alkyl nitroxides are much less stable than di-t-alkyl nitroxides. At first sight this fact is difficult to explain, since in the aryl derivatives the phenyl ring provides an additional region for delocalisation of the unpaired electron, and this should have led to an increase in the stability of the radical. The reason for this phenomenon is the dimerisation of the aryl t-alkyl nitroxides by the formation of a bond between the oxygen atom of the nitroxide and the *para*- or

ortho-positions of the benzene ring with subsequent decomposition of the dimer to the *p*-benzoquinone-N-t-alkylimine (XXXIX) and N-t-alkylaniline (XL).[95-100]



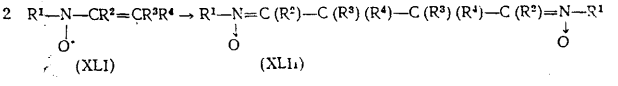
(XXXIX) (XL)

The formation of the dimer is inhibited by the presence of substituents in the *ortho*-position, which prevents the delocalisation of the electron density of the nitroxide group and hence decreases the spin density in the aromatic ring.[98] Bulky substituents in the *para*- or *meta*-positions also stabilise the radical as a result of the production of steric hindrance for radical attack.[95,98,100]

The influence of the structure of substituents on the stability of nitroxide radicals is effectively illustrated not only by their decomposition but also by their ability to recombine with hydrocarbon radicals. Thus aromatic nitroxides react with triphenylmethyl,[101] whereas nitroxides with aliphatic substituents do not react with it.[102]

Vinyl nitroxide radicals represent another important type of paramagnetic species for the chemistry of homolytic processes taking place in the reactions of nitroso-compounds with alkenes. These radicals may be formed either according to the scheme proposed in Ref.68 or by the oxidation of nitrones containing a hydrogen atom in the β-position, which in the opinion of many authors are among the main products of the reactions of nitroso-compounds with alkenes. As might have been expected, vinyl nitroxides are further stabilised by the delocalisation of the unpaired electron by conjugation with the vinyl group. At the same time they are fairly reactive.[103]

The recombination of vinyl nitoxide radicals (XLI) to give nitrones (XLII) takes place by the formation of a C–C bond in the β-position.



(XLI) (XLII)

Nitroso-compounds, nitrones, dienes, etc. also add on to the β-position of the vinyl group. The length of the chain is increased, with the formation of substituted nitroxide radicals.[103] These data illustrated a familiar fact in the chemistry of nitroxide radicals: the dependence of their stability and reactivity on their structure is determined by a combination of thermodynamic and kinetic factors, that is the degree of delocalisation of the unpaired electron and the steric hindrance at the atoms with a high spin density.

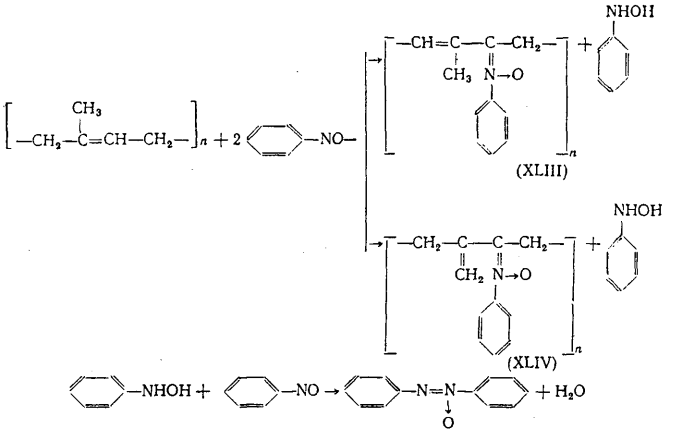
Thus analysis of published data on the reactions of nitroxide radicals shows that the compounds detected in the products of their recombination, disproportionation, oxidation, etc. include many of those compounds (azoxybenzenes, hydroxylamines, nitrones, secondary amines) which are regarded as the main products of the reactions of nitroso-compounds with alkenes. This confirms that these products may be formed in the reactions of C-nitroso-compounds with alkenes via nitroxide radicals as intermediates.

At the same time, the indefinite nature of conclusions about the structure of the reaction products is apparently due to the wide range of possible directions for the reactions of nitroxide radicals, characteristic of all homolytic processes, the results of which depend on the structure of the starting materials and on the reaction conditions. These reactions generally have a low selectivity and often give mixtures of products.

IV. CHARACTERISTIC FEATURES OF THE REACTION OF NITROSO-COMPOUNDS WITH DIENE POLYMERS

The study of the reaction of nitroso-compounds with diene polymers to determine the reaction mechanism is difficult, because of the difficulty of isolating and identifying the functional fragments; on the other hand, however, this study extends the possibility of estimating the changes in the dimensions of the molecules taking place in the course of the reaction.

The reaction of nitroso-compounds with natural *cis*-1,4-polyisoprene was first studied in Ref.26, and in more detail in Ref.104, where a reaction scheme was proposed, based on the reaction of three moles of the nitroso-compound with one monomer unit, leading to the formation of two isomeric conjugated nitrones and azoxybenzene.



(XLIII)

(XLIV)

The authors cited, however, could not decide between the adduct structures (XLIII) and (XLIV).

In a development of these ideas, it was concluded[105] that the nitrone of "iso-rubber"† (the terminology of the authors cited) can be obtained in pure form only by carrying out the reaction without heating, in a nitrogen atmosphere.

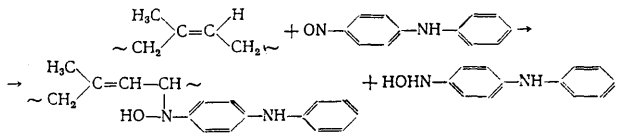
This scheme was adopted by various workers as a possible mechanism of structure formation in saturated rubbers with C-nitroso derivatives[106] and of the modification of polyisoprene by N-substituted *p*-nitrosoanilines.[107]

Alternative structures suggested for the functional fragment formed in the reaction of polyisoprene with N-methyl-N,4-dinitrosoaniline are the anil structure,[48] and in the reaction with *p*-nitrosodiphenylamine the secondary amine[6,108] and hydroxylamine[109] structures; in the last case the reaction product is not the ene adduct but the product of the addition of the nitroso-group to the allyl carbon (XLV).

The authors of Ref.48 describe the mechanism of the process as ene synthesis with subsequent dehydration of the intermediate alkenylarylhydroxylamine and the formation of a Schiff base, whereas in Ref.109 the mechanism of the process is described as molecular homolysis with the removal of allyl hydrogen and the subsequent recombination of the radicals

†The term iso-rubber refers to *cis*-1,4-polyisoprene with isomeric location of the double bonds in the 1,5- and 1,4-positions.

to give diphenylaminohydroxylamine in the free state or combined with the polymer chain.

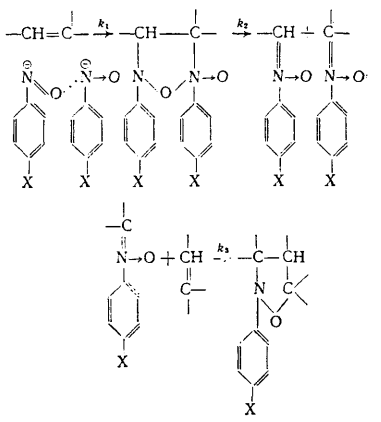


The main characteristic of the reaction of a nitroso-compound with a polydiene is the degradation of the polymer chain. In the case of the reaction with low-molecular-weight alkenes, only the authors of Refs.18 and 26, who describe the reaction of styrene with nitrosobenzene, note the possibility of rupture of the hydrocarbon chain, whereas for the diene polymer the effect of degradation is marked.

However, although in Ref.109 it is suggested that the nitroso-compound initiates the thermo-oxidative degradation of the polymer at a high temperature (143 °C), it has been shown[100-112] that rupture of the polymer chain takes place as a result of the chemical reaction of the polydiene with the nitroso-compound, and that there is a good correlation between the nitroso-compound : polyene molar ratio and the molecular mass of the degradation product.[110-113] Conditions have been found for the synthesis of oligoisoprenes over a wide range of molecular masses.[114,115]

Comparison of the number-average molecular masses of the original and reacted polyisoprene with the number of functional groups combined with the rubber shows that an average of about two molecules of the nitroso-compound is added on for every rupture of the macromolecule.[113] A more detailed analysis of the molecular structure of the oligoisoprenes formed[116] showed that the maximum of the distribution of the oligomer with respect to functionality corresponds to 2, and the molar concentration of bifunctional molecules reaches 40. At the same time, an appreciable quantity of mono-, tri-, tetra-, and pentafunctional molecules, and a small quantity of molecules of higher functionality, were detected in the oligomer.

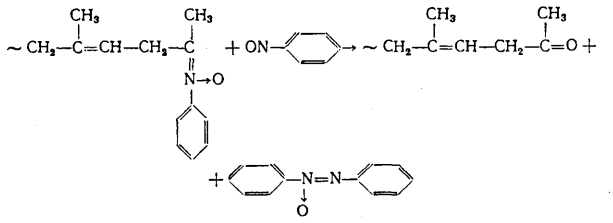
These experimental data, together with the results of a study of the kinetics of the reaction (first order with respect to the nitroso-compound in an excess of the polymer)[113] and an analysis of the structure of the final products[117] led to the proposal of the following scheme for the degradation and subsequent branching of the polymer molecules:



X = N(C_2H_5)$_2$, NHC_6H_5

According to this scheme, the final reaction products are nitrones or the products of their transformation.[113,117]

At the same time, Japanese workers isolated,[110] in addition to degradation products which were also identified as polymeric nitrones, side products: an aldehyde (or ketone) and azoxybenzene.



In contrast to the reaction in solution, the reaction of *cis*-1,4-polyisoprene with *p*-nitrosodiphenylamine in the mass at high temperatures is often accompanied by the formation of a cross-linked rubber. According to Ref.109, structure formation takes place by the recombination of the hydrocarbon polymeric radicals produced in this reaction. A specific feature of the chemical modification of diene polymers by so-called small additives is that the process is carried out in a large excess of one of the reagents (the polymer), so that some of the reactions which are observed in the reaction of equimolar quantities of the nitroso-compound and the alkene or in an excess of the nitroso-compound cannot be observed in this case.

Even with allowance for this characteristic feature, however, and also for the specific features of the transformations in the polymer chains, it must be said that the schemes given for the reactions of nitroso-compounds with diene polymers are oversimplified, and do not take critical account of the extensive experimental material accumulated in the study of the mechanism of the reaction of a nitroso-compound with low-molecular-weight alkenes, so that they require, at the least, serious refinement.

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Progress in fundamental and applied studies of the use of C-nitroso-compounds as paramagnetic inhibitors, spin traps, stabilisers and modifiers of rubber and plastics, and promoters of the reaction of rubber with technical carbon has stimulated interest in the investigation of the mechanism of the reactions of nitroso-compounds with alkenes. For this reaction, as for other processes involving the formation of extremely reactive intermediates, the possible directions of the reaction and the structures of the final products depend on the nature of the substituents in the reagents and on the reaction conditions. In this respect, each new study carried out on individual representatives of both classes of compound extends the picture of the reaction as a whole.

Many general features of the reactions with alkenes with and without an allyl hydrogen atom have now been established, however. These general characteristics apparently include the heterolytic character of the first stage of the addition, attack by the nitroso-compound on the carbon atom of the double bond, the formation of paramagnetic species in one of the subsequent stages, etc.

The achievements in the application of C-nitroso-compounds have increased interest in their reactivity and the mechanism of their reactions with alkenes; the data obtained have in turn led to new ideas for the practical utilisation of this reaction.

Thus the experimentally observed rupture of the hydrocarbon chain in the reaction of a polymeric alkene with a nitroso-compound has made it possible to synthesise for the

first time an oligoisoprene with the *cis*-structure with functional polar groups, that is a material which has not yet been prepared by polymerisation methods. The paramagnetic species in the reaction system under certain conditions can be used to initiate the radical grafting of unsaturated polar compounds to an unsaturated hydrocarbon substrate.

There is no doubt that this extremely important reaction in organic chemistry will continue to attract the attention of research workers for a long time.

REFERENCES

1. I.M.Belgorodskii, L.M.Kogan, V.A.Krol', V.P.Smirnov, and N.F.Kovalev, Rubber World, 1978, 36.
2. L.M.Kogan, V.P.Smirnov, N.F.Kovalev, and V.A.Krol', Kauchuk i Rezina, 1978(9), 5.
3. L.M.Kogan, V.A.Kro', A.S.Estrin, O.I.Belgorodskaya, N.B.Monastyrskaya, V.P.Smirnov, B.M.Bolkhovets, N.F.Kovalev, I.M.Belgorodskii, et al., USSR P.587138, 1976; 1978(1), 70.
4. L.M.Kogan et al., USSR P.594126, 1976; 1978(7), 103.
5. L.M.Kogan et al., US P.4115636, 1978; 1979(11–56), 63.
6. M.E.Cain, G.T.Knight, P.M.Lewis, and B.Saville, J.Rubber, 1968, 150(11), 10.
7. P.Hamed and L.A.Walker, Rubber World, 1970(4), 51.
8. S.M.Kavun, T.B.Fedorova, A.S.Lykin, and M.N.Maleev, Kauchuk i Rezina, 1972(9), 44.
9. D.B.Boguslavskii, E.G.Guslistaya, and Kh.N.Borodushkina, Kauchuk i Rezina, 1972(4), 13.
10. E.Ya.Devirts, L.S.Zherebkova, and A.S.Novikov, Kauchuk i Rezina, 1967(3), 14.
11. M.Hirouki, J.Soc.Rubber Ind.(Japan), 1972, 41, 81.
12. M.E.Cain and B.Saville, B.P.1185896, 1970; 22C903.
13. G.T.Knight and B.Pepper, Tetrahedron, 1971, 27, 6201.
14. C.N.R.Rao and K.R.Bhaskar, in H.Feuer (Editor), "Chemistry of the Nitro and Nitroso Groups" (Translated into Russian), Izd.Mir, Moscow, 1972, p.102.
15. V.A.Ginsburg, V.V.Smolyanitskaya, A.N.Medvedev, V.S.Faermark, and A.P.Topilov, Zhur.Obshch. Khim., 1971, 41, 2284.
16. C.K.Ingold and S.D.Weaver, J.Chem.Soc., 1924, 125, 1456.
17. G.N.Burkhardt, A.Lapworth, and J.Walkden, J.Chem. Soc., 1925, 127, 2458.
18. N.F.Hepfinger and C.E.Griffin, Tetrahedron Letters, 1963, 1361.
19. V.A.Ginsburg, L.L.Martynova, S.S.Dubov, B.I.Tetel'baum, and A.Ya.Yakubovich, Zhur. Obshch.Khim., 1965, 35, 851.
20. V.A.Ginsburg, A.N.Medvedev, L.L.Martynova, P.O.Gitel', and G.E.Nikolaenko, Zhur.Org.Khim., 1972, 8, 486.
21. V.A.Ginsburg, A.N.Medvedev, S.S.Dubov, P.O.Gitel', V.V.Smolyanitskaya, and G.E.Nikolaenko, Zhur.Obshch.Khim., 1969, 39, 282.
22. A.Yoneda, M.Tanaka, and N.Murata, Kogyo Kagaku Zasshi, 1970, 73(10), 123.
23. V.V.Keussler and W.Luettke, Z.Electrochem., 1959, 63, 614.
24. L.Sumegi, F.Tudos, and I.Kende, Acta Chim.Acad. Sci.Hung., 1971, 68(1–2), 75.
25. R.A.Abramovitch, S.R.Challand, and Y.Yamada, J.Org.Chem., 1975, 40, 1541.
26. L.Alessandri, A.Angeli, and R.Pegna, Atti acad. Lincei, 1910, 19, 650.
27. J.Hamer and A.Macaluso, Tetrahedron Letters, 1963, 381.
28. A.B.Sullivan, J.Org.Chem., 1966, 31, 2811.
29. C.Schenk and T.J.De Boer, Tetrahedron, 1979, 35, 147.
30. R.K.Howe, J.Org.Chem., 1968, 35, 2848.
31. G.T.Knight and B.Pepper, Chem.Communs. 1971, 1507.
32. B.Pepper and M.Porter, Chem.Communs., 1974, 130.
33. J.Hamer and A.Macaluso, Chem.Rev., 1964, 64, 473.
34. G.R.Delpierre and M.Lamchen, Quart.Rev., 1965, 19, 329.
35. R.Huisgen, H.Seidl, and I.Bruening, Chem.Ber., 1969, 102, 1102.
36. N.A.Le Bel, M.E.Post, and J.J.Whang, J.Chem. Soc., 1964, 86, 3759.
37. N.A.Le Bel, G.M.J.Slusarczak, and L.A.Spurlock, J.Chem.Soc., 1962, 84, 4361.
38. R.Huisgen, Angew.Chem., 1963, 75, 742.
39. N.P.Kolak, Dis.Abstr.Int., 1972, 6921.
40. J.Meisenheimer, Ber., 1919, 52, 1661.
41. J.P.Lorand, R.W.Grant, P.A.Samuel, E.O'Connell, and J.Zaro, Tetrahedron Letters, 1969, 4087.
42. A.R.Lepley, P.M.Cook, and G.F.Willard, J.Amer. Chem.Soc., 1970, 92, 1101.
43. M.Martynoff, Ann.Chem., 1937, 7, 424.
44. D.G.Morris, Chem.Communs., 1971, 221.
45. C.S.L.Baker, D.Barnard, and M.Porter, Rub.Chem. and Techn., 1970, 43, 501.
46. M.E.Cain, G.T.Knight, and P.M.Lewis, Chem.and Ind., 1970, 126.
47. I.P.Maslova (Editor), "Khimicheskie Dobavki k Polimeram" (Chemical Additives in Polymers), Izd. Khimiya, Moscow, 1981, p.24.
48. L.S.Zherebkova, A.S.Shashkov, T.N.Dyumaeva, E.Ya.Devirts, and F.A.Galil-ogly, Vysokomol.Soed., 1969, 11A, 227.
49. D.A.Barr, R.N.Haszeldine, and C.J.Willis, J.Chem. Soc., 1961, 1351.
50. I.L.Knunyants, B.L.Dyatkin, and A.A.Gevorkyan, Izv.Akad.Nauk SSSR, Ser.Khim., 1966, 1377.
51. V.A.Ginsburg, A.N.Medvedev, M.F.Lebedeva, and L.L.Martynova, Zhur.Org.Khim., 1974, 10, 1416.
52. C.A.Seymour and F.D.Greene, J.Org.Chem., 1982, 47, 5226.
53. R.E.Banks, M.G.Barlow, and R.N.Haszeldine, J.Chem.Soc., 1965, 4714.
54. W.A.Waters, J.Chem.Soc., Perkin Trans.II, 1979, 1078.
55. M.G.Barlow, R.N.Haszeldine, and K.W.Murray, J.Chem.Soc.Perkin Trans.I, 1980, 1960.
56. E.N.Petropavlovskaya, L.M.Kogan, N.B.Monastyrskaya, and V.A.Krol', Zhur.Obshch. Khim., 1984, 54, 1645.
57. W.B.Motherwell and J.S.Roberts, Chem.Communs., 1972, 329.
58. E.L.Zhuzhgov, N.V.Strunina, V.F.Komarov, S.F.Zorik, and D.Yu.Tsvetkov, Kinetika i Kataliz, 1972, 13, 1405.

59. V.I.Vedeneev, L.V.Gurvich, V.A.Kondrat'ev, and E.L.Frankevich, in collected papers "Potentsialy Ionizatsii i Srodstvo k Elektronu" (Ionisation Potentials and Electron Affinity), Izd.Nauka, Moscow, 1962.
60. K.Tsuji, I.Imanishi, K.Hayashi, and S.Okamura, J.Polym.Sci., 1965, **58**, 449.
61. C.K.Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Izd.Inostr. Lit., Moscow, 1959.
62. M.B.Grdina, M.Orfanopoulos, and L.M.Stephenson, J.Amer.Chem.Soc., 1979, **101**, 3111.
63. L.M.Stephenson, M.B.Grdina, and M.Orfanopoulos, Acc.Chem.Res., 1980, **13**, 419.
64. A.A.Frimer, P.D.Bartlett, A.F.Boschung, and J.G.Jewett, J.Amer.Chem.Soc., 1974, **99**, 7977.
65. C.A.Seymour and F.D.Greene, J.Amer.Chem.Soc., 1980, **102**, 6884.
66. K.-W.Leong and G.B.Butler, J.Macromol.Sci.Chem., 1980, **14A**, 287.
67. H.Muensterer, G.Kresze, M.W.Brechbiel, and H.Kwart, J.Org.Chem., 1982, **47**, 2677.
68. D.Mulvey and W.A.Waters, J.Chem.Soc., 1978, 1059.
69. G.Renner, Z.Anal.Chem., 1963, **193**, 92.
70. G.E.Utzinger and F.A.Regenass, Helv.Chim.Acta, 1954, **37**, 1892
71. D.F.Bowman, J.L.Brokenshire, T.Gillan, and K.U.Ingold, J.Amer.Chem.Soc., 1971, **93**, 6551.
72. C.Chatgilialoglu, J.Amer.Chem.Soc., 1981, **103**, 4833.
73. L.R.Mahoney, G.D.Mendenhall, and K.U.Ingold, J.Amer.Chem.Soc., 1973, **95**, 8611.
74. W.A.Pryor, J.H.Coco, W.H.Daly, and K.N.Houk, J.Amer.Chem.Soc., 1974, **96**, 5591.
75. T.A.J.W.Wajer, A.Mackor, and T.J.De Boer, Tetrahedron, 1969, **25**, 175.
76. G.C.Yang and A.Joshi, J.Phys.Chem., 1980, **84**, 228.
77. R.W.Layer, Tetrahedron Letters, 1970, 4413.
78. B.L.Booth, D.J.Edge, and R.N.Haszeldine, J.Chem. Soc., Perkin Trans.II, 1977, 7.
79. R.E.Banks, R.N.Haszeldine, and P.J.Miller, Tetrahedron Letters, 1970, 4417.
80. W.B.Motherwell and J.S.Roberts, Chem.Communs., 1972, 328.
81. E.G.Rozantsev, "Svobodnye Iminoksil'nye Radikaly" (Iminoxy Free Radicals), Izd.Khimiya, Moscow, 1970.
82. A.L.Buchachenko and A.M.Vasserman, "Stabil'nye Radikaly" (Stable Radicals), Izd.Khimiya, Moscow, 1973.
83. E.G.Rozantsev and V.D.Sholle, "Organicheskaya Khimiya Svobodnykh Radikalov" (The Organic Chemistry of Free Radicals), Izd.Khimiya, Moscow, 1979.
84. P.Schmid and K.U.Ingold, J.Amer.Chem.Soc., 1978, **100**, 2493.
85. J.F.W.Keana, Chem.Rev., 1978, **78**, 37.
86. G.A.Russell, E.J.Geels, F.J.Smentowski, K.Chang, J.Reynolds, and G.Kaupp, J.Amer.Chem.Soc., 1967, **89**, 3821.
87. D.Mulvey and W.A.Waters, J.Chem.Soc., Perkin Trans.II, 1977, 1868.
88. D.F.Bowman, T.Gillan, and K.U.Ingold, J.Amer. Chem.Soc., 1971, **93**, 6555.
89. G.D.Mendenhall, D.Griller, and K.U.Ingold, Chem. Brit., 1974, **10**, 248.
90. J.Martinie-Hombrouck and A.Rassat, Tetrahedron, 1974, **30**, 433.
91. G.D.Mendenhall and K.U.Ingold, J.Amer.Chem. Soc., 1973, **95**, 6390.
92. J.L.Brokenshire, J.R.Roberts, and K.U.Ingold, J.Amer.Chem.Soc., 1972, **94**, 7040.
93. R.Briere and A.Rassat, 1976, **32**, 2891.
94. P.A.S.Smith and S.E.Gloyer, J.Org.Chem., 1975, **40**, 2508.
95. A.Calder and A.R.Forrester, J.Chem.Soc., 1969, 1459.
96. A.R.Forrester and R.H.Thomson, Nature, 1964, **203**, 74.
97. A.R.Forrester, J.M.Hay and R.H.Thomson, "Organic Chemistry of Stable Free Radicals", Acad. Press, London–New York, 1967, p.405
98. A.R.Forrester and S.P.Hepburn, J.Chem.Soc., 1970, 1277.
99. A.Calder, A.R.Forrester, and G.McConnachie, J.Chem.Soc., Perkin Trans.I, 1974, 2198.
100. A.R.Forrester and S.P.Hepburn, J.Chem.Soc., Perkin Trans.I, 1974, 2203.
101. J.Kenyon and S.Sugden, J.Chem.Soc., 1932, 170.
102. V.A.Golubev, R.I.Zhdanov, V.M.Gida, and E.G.Rozantsev, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 2815.
103. A.G.Aurich, Canad.J.Chem., 1982, **60**, 1414.
104. G.Bruni and E.Geiger, Rub.Chem.and Techn., 1928, **1**, 177.
105. R.Pummerer and W.Guendel, Rub.Chem.and Techn., 1929, **2**, 375.
106. R.Rehner and P.J.Flory, Rub.Chem.and Techn., 1946, **19**, 900.
107. T.R.Gendler, D.B.Boguslavskii, G.M.Levit, and V.A.Sapronov, Kauchuk i Rezina, 1972(1), 11.
108. M.E.Cain, K.F.Gazeley, I.R.Gelling, and P.M.Lewis, Rub.Chem.and Techn., 1972, **45**, 204.
109. S.M.Kavun, T.V.Fedorova, G.I.Akin'shina, Z.N.Tarasova, and I.V.Khodzhaeva, Vysokomol. Soed., 1973, **15A**, 2378.
110. A.Yoneda, M.Tanaka, and N.Murata, Kogyo Kagaku Zasshi, 1971, **74**, 1701.
111. L.M.Kogan, V.A.Krol', N.B.Monastyrskaya, L.M.Davydov, and O.I.Belgorodskaya, Vysokomol. Soed., 1976, **18A**, 1076.
112. L.M.Kogan, V.A.Krol', N.B.Monastyrskaya, and V.S.Fikhtengol'ts, "Tezisy Kratkikh Soobshchenii Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii" (Summaries of Short Papers Presented at the International Symposium on Macromolecular Chemistry), Vol.4, Tashkent, 1978, p.53.
113. L.M.Kogan, V.A.Krol', N.B.Monastyrskaya, and V.S.Fikhtengol'ts, Kauchuk i Rezina, 1979(10), 6.
114. N.B.Monastyrskaya, Candidate's Thesis, All Union Scientific Research Institute for Synthetic Rubber, Leningrad, 1978.
115. L.M.Kogan and V.A.Krol', Zhur.Vses, Khim.Obshch. im.D.I.Mendeleeva, 1981, **26**, 272.
116. V.I.Valuev, L.M.Kogan, T.A.Lemesheva, and N.B.Monastyrskaya, Kauchuk i Rezina, 1983(3), 3.
117. V.S.Fikhtengol'ts, L.M.Kogan, V.A.Krol', and N.B.Monastyrskaya, "Promyshlennost' SK. Nauchn-tekhnicheskii Sbornik" (The Synthetic Rubber Industry. Collected Scientific and Technical Papers), No.4, Izd.TsNIITEINEFTEKhIM, Moscow, 1979, p.6.

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