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Reactions of Acetylene in Superbasic Media

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The results of studies of fundamentally new reactions of acetylene and its substituted derivatives in media of very high basicity are surveyed. They lead to hitherto unknown or relatively inaccessible monomers, reagents, and intermediates: 2-vinyloxybuta-1,3-diene, pyrroles, and *N*-vinylpyrroles, divinyl sulphide, divinyl telluride, 4-methylene-1,3-oxathiolan, di(buta-1,3-dienyl) sulphide, dihydrothiophen, 1-vinyl-2-thiabicyclo[3,2,0]hept-3-ene, etc.
The most important properties of superbasic media consisting of an alkali metal hydroxide and a dipolar aprotic solvent as well as the probable mechanisms of their activating effect on anions and the triple bond are examined. An attempt is made to analyse these reactions in terms of coordination catalysis by alkali metal cations.
The bibliography includes 199 references.

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I. INTRODUCTION

As one of the key types of chemical raw material, acetylene, which was somewhat eclipsed in the 1960's by petrochemical ethylene and propene, is now again attracting the attention of investigators and technologists because of the progressive increase in the cost of petroleum and gas in the work markets[1].

As a result of the development of plasma, laser, and ultrasonic techniques, cheap acetylene will soon be obtainable not only from the petroleum raw material but also from different kinds of coal and combustible shale[2]. Research programmes designed to create a plasma technology for the direct synthesis of acetylene from coal are being developed[3]. Successful studies are being made[4] on the utilisation of liquid acetylene for technological purposes.

The majority of chemical reactions of acetylene are known not to require a supply of energy and are in fact accompanied by its evolution. There are many reasons why acetylene should become in the future the sole raw material for industrial organic synthesis[5]. It has been calculated[6] that acetylene obtained from calcium carbide already constitutes a realistic alternative to the petroleum raw material. On the other hand, a fall in the consumption of ethylene has been noted; for example, in 1978 the ethylene factories in the USA failed to utilise almost half their capacity[7].

A further development of the foundations of the chemistry of acetylene, laid as early as the beginning of this century by Academician A.E.Favorskii, has therefore become an urgent necessity. A new field—the chemistry of acetylene in super basic media—is rapidly developing on the basis of Favorskii's research[8]. In the present review an attempt is made to summarise the main results obtained in this field.

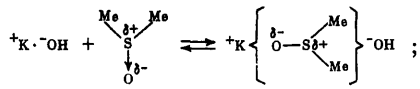
II. THE GENERATION AND CERTAIN CHARACTERISTICS OF SUPERBASIC MEDIA

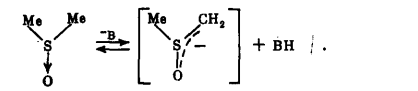
Superbasic media include those consisting of a strong base and a solvent or reagent capable of specific binding of the cation, "baring" the anion[8,9]. Superbasic systems can be obtained on the basis of linear and cyclic glycol ethers, macrocyclic polyethers (crown-ethers), dipolar aprotic solvents such as dimethyl sulphoxide (DMSO), sulpholane, hexamethylphosphoramide (HMP), and phosphine oxides, as well as amides, liquid ammonia, amines, etc. For example, the basicity of sodium methoxide in 95% DMSO is higher by 7 orders of magnitude than in pure methanol[10]:

0.025 M $NaOCH_3$	
Solvent	Acidity function H_
Methanol	12.2
95% DMSO + 5% methanol	19.4

A particularly dramatic increase of basicity occurs at the maximum concentrations of a dipolar aprotic solvent. Thus tetramethylammonium hydroxide in 99.5% aqueous DMSO is more basic by 14 orders of magnitude than in pure water[11].

The superbasicity of the KOH–DMSO system is caused to a first approximation by the separation of the ion pair of the base[12] and by the formation of the highly basic and little solvated dimsyl anion[9] (B^- is a strong base):



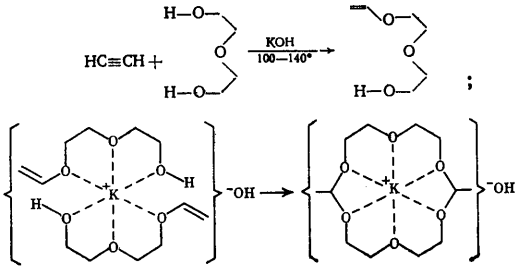


However, this does not exhaust the role of DMSO. In the general case account must be taken of cooperative effects involving changes in factors such as the dielectric constant of the medium, hydrogen bonding, the activity of water, dispersion interactions, and changes in the structure of water and in the degree of ion hydration[11,13,14].

The situation arising under the conditions of interfacial catalysis[15,16], where one of the phases is highly concentrated alkali and hydroxide ions are transferred by bulky organophilic cations incapable of forming a contact ion pair, can also be regarded as superbasic.

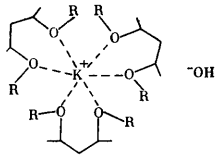
The significant acceleration of the nucleophilic addition to the triple bond in media specifically solvating the cation was first noted in a study of the vinylation of poly(ethylene glycol).[17] As a result of the chelation of the potassium cation

by poly(ethylene glycol) chains, side reactions involving the cleavage and disproportionation of the poly(ethylene oxide) fragments[18,19] and probably also "template" heterocyclisation, leading to macrocyclic crown-like acetals, which, together with linear oligomers, accelerate the process



autocatalytically, are characteristic of reactions of this kind.

The catalytic effects of the side products of the vinylation of monohydric alcohols[20,21]—low-molecular-weight thermopolymers of alkyl vinyl ethers $-[-CH_2-CH(OR)-]_n-$—also capable of chelating the cations, are apparently of the same type:



These studies led to the development and industrial application of a new technology for the vinylation of butanol at atmospheric pressure[20,21] and to the intensification of the processes involving the vinylation of diethylene glycol[22] and ethanolamines[23], which are nowadays carried out on an experimental industrial scale.

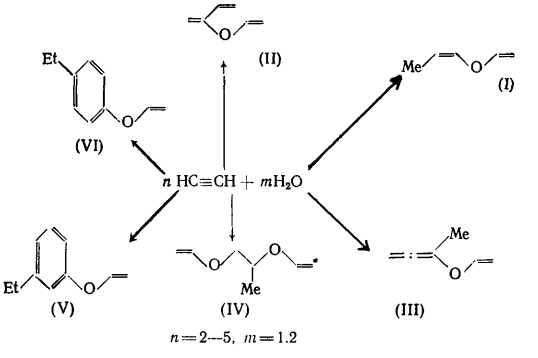
In aprotic dipolar solvents (DMSO, HMP, and methylpyrrolidinone) in the presence of catalytic amounts of alkali, primary alkanethiols add to acetylene even at atmospheric pressure and at a temperature of 10–20 °C, forming vinyl sulphides in 60–90% yield (reaction time 1 h),[24] which corresponds to an increase of the reaction rate by many orders of magnitude. Tertiary and aromatic thiols, which are more difficult to vinylate, react with acetylene much more readily in systems of this kind than under the usual conditions (30–50 °C, 10–15 atm).

Thus in superbasic media in the presence of "bared" anions of strong bases (alkalies, alkoxides, amides, and alkali metals) the nucleophilic addition to the triple bond is very greatly facilitated. However, a much more significant factor is that fundamentally new reactions become possible under these conditions. There exist fundamental thermodynamic grounds for this. Thermodynamic measurements have shown[25] that in aprotic dipolar solvents the free energy of the anions increases sharply and as a result they are converted into supernucleophiles. It is very significant that the activity of weak nucleophiles then increases to a much greater extent than that of strong nucleophiles. For example, on passing from ethanol to DMSO, the relative increment of the Gibbs free energy of the phenoxide anion (a fairly weak nucleophile) is greater by 10 kcal mol^{-1} than for the phenylsulphide anion, which is a stronger nucleophile[25].

III. HYDRATION OLIGOMERISATION OF ACETYLENE

The characteristics of superbasic systems discussed above are responsible for the successful addition to acetylene even of a comparatively weak nucleophile such as the hydroxide ion, the low activity of protons characteristic of such systems inhibiting the prototropic transformation of the intermediate vinyloxide anion into acetaldehyde. However, it has not so far been possible to observe the formation of divinyl ether under these conditions. Instead of this natural pathway, a series of completely unusual reactions have been observed[8,26–31] in the DMSO–KOH system, which proceed under extremely mild conditions (80–120 °C) and which can be combined under the common name "hydration oligomerisation of acetylene" (Scheme 1).

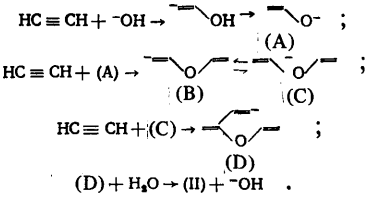
Scheme 1



The simplest oligomer obtained under these conditions is a methylated hydratodimer—1-*cis*-propenyl vinyl ether[26] (DMSO acts as a methylating agent).

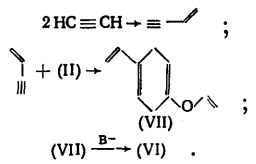
This is followed by the following substance in order of increasing complexity: a hydratotrimer—2-vinyloxybuta-1,3-diene (II) [8,27,29–31] and its allene isomer—3-vinyloxybuta-1,2-diene (III),[30] a methylated dihydratotrimer—1,2-di(vinyloxy)-propane (IV),[28,30] and finally hydratopentamers—*meta*- and *para*-ethyl(vinyloxy)benzenes (V) and (VI).[30] The yields are in general low; however, they depend significantly on the composition and nature of the superbasic catalytic system, particularly on the nature of the cation and the solvent and also on buffer additives such as alkali metal phosphates, which regulate the proton transfer processes. Conditions have been found[27,29,30] under which 2-vinyloxybuta-1,3-diene—one of the most interesting products of the hydration oligomerisation of acetylene—is obtained in a yield greater than 70%. The yields of other hydrato-oligomers can apparently also be increased to a preparatively acceptable level when necessary.

One of the possible ways of forming vinyloxybutadiene involves a multistage "threading" of three acetylene molecules onto the hydroxide ion:



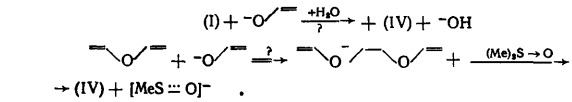
A weak feature of this scheme is the assumption of a prototropic rearrangement of the vinyloxyvinyl β-carbanion (B) to the corresponding α-carbanion (C), which is in all probability less stable owing to the strong repulsion of the charge from the unshared electron pairs of the oxygen atom.

The ethyl(vinyloxy)benzenes (V) and (VI) could be regarded as products of the diene condensation of vinyloxybutadiene (II) and the intermediate vinylacetylene, which is completed by the prototropic rearrangement of the primary vinylcyclohexadiene adduct (VII):

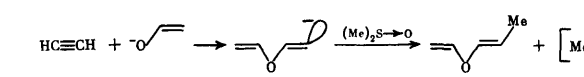


However, ethyl(vinyloxy)benzene could not be obtained by the direct interaction of authentic vinylacetylene and vinyloxybutadiene (II).[29]

It is just as difficult to interpret the formation of 1,2-di(vinyloxy)propane (IV), because it is necessary to assume the highly unlikely nucleophilic addition of the vinyloxide anion to propenyl vinyl ether (I) or to divinyl ether:



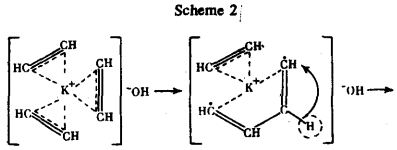
Concluding the enumeration of facts which cannot be acceptably explained within the framework of generally accepted ideas, it is necessary to draw attention also to the configuration of 1-*cis*-propenyl vinyl ether (I). In nucleophilic addition to acetylenes, the intermediate anions usually have the *anti*-configuration, in which the repulsion of the charge and the unshared electron pairs of the heteroatom is a minimum[32]. The formation of the *trans*-isomer rather than the *cis*-isomer of the ether (I) was therefore to be expected:

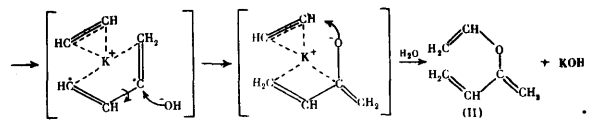


The complete *cis*-stereoselectivity in this case is evidence against simple nucleophilic attack by the vinyloxide anion on the triple bond. Evidently the reactions illustrated in Scheme 1 require other explanations. It was noted above that in superbasic media the anions become supernucleophiles as a result of desolvation and the separation of ion pairs under the influence of strong dipoles (solvent molecules). However, the same factors should also alter the electrophilic activity of the cation. In a system with a markedly reduced activity of water an alkali metal cation, lacking its usual hydration shell and separated by a solvent molecule from its anion, should attempt to compensate for its desolvation by coordinating to some extent to other nucleophiles present in the system, in the given instance acetylene molecules, formally in the same way as in the case of transition metal cations[33]. The coordination leads to the withdrawal of the π-electron density of the acetylene ligands to the cation and the consequent increase of the sensitivity of the triple bonds of the ligands to a nucleophilic attack.

One of the possible mechanisms of such coordination catalysis, involving a partly dehydrated potassium cation in the hydration trimerisation of acetylene, is illustrated in Scheme 2:

Scheme 2





This scheme explains the observed marked dependence of the result of the reaction on the nature of the coordinating cation and predicts the possibility of obtaining benzene (a non-hydrated acetylene trimer) on decrease of the concentration of water in the system. Benzene and toluene (in the DMSO–KOH system) have indeed been detected in the reaction mixtures—in some cases up to 20% and more[34]. The formation of toluene indicates yet again the ability of DMSO to methylate carbanions under these conditions.

The cyclotrimerisation of acetylene is known to take place smoothly only in the presence of transition metal complexes[35]. Methods for the formation of stable adducts of acetylenes with dehydrated alkali metal hydroxides were patented[36,37] several decades ago. It has been stated in a patent[37] that the absorption of acetylene by potassium hydroxide in 1,1-dibutoxyethane increases sharply with increase of temperature, reaching 0.5 mole per mole of KOH at 75–90 °C, which is three times more than at temperatures between −10° and 0 °C. We are therefore dealing with the chemical interaction of acetylene with KOH and not with its simple dissolution. The important role of such complexes, as key intermediates in certain versions of the Favorskii ethynylation[38–41] and vinylation[42] reactions as well as selective hydrogenation[43–45] of acetylenic alcohols and glycols was demonstrated later. In many instances[38–40,45] these complexes were isolated and investigated. Compared with KOH, sodium hydroxide binds acetylene less strongly, while LiOH does not form complexes with acetylene at all according to Tedeschi et al.[45]

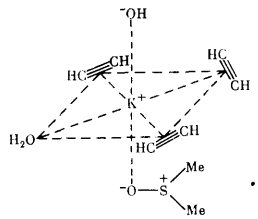
Unfortunately very few experimental data have been published hitherto concerning the nature and structure of the adducts of acetylene and alkali metal hydroxides. It has been reported only that the infrared spectra of complexes of KOH with acetylene[39] and acetylenic alcohols[38] or glycols[38] do not exhibit the usual C≡C and ≡C–H vibrational frequencies, while the O–H stretching vibration band (in the case of alcohols and glycols) is broadened and weakened. On this basis, it was concluded[38,39] that the potassium cation is involved in complex formation reactions with both the π-electrons of the acetylenic linkage and with the oxygen atoms of the hydroxy-groups. In the same study[38–41] evidence is presented showing that the adducts of acetylene with alkali metal hydroxides are chemically fundamentally different from acetylides. According to data obtained by ion-cyclotron resonance and high-pressure mass spectrometry[46], acetonitrile ($CH_3C{\equiv}N$), which is a full electronic analogue of methylacetylene, has a higher chemical affinity for the potassium cation than bases such as ammonia, amines, water, and ethers. Quantum-chemical calculations by the *ab initio* method have shown that this is wholly due to the unexpectedly large contribution of the polarisation of the CH_3CN molecule to the overall energy of its reaction with the cation[47]. Acetylenic compounds should exhibit an equally high affinity for the K^+ cation and an equally marked polarisability under its influence.

Another familiar group of acetylene complexes of alkali metals is derived from acetylides. For example, the oligomerisation of acetylenes under the influence of alkali metals begins with the formation of complexes of acetylides with the initial acetylenes[48–51]. Adducts of phenylacetylides with alkali metals, which are of a radical-ion type and actively initiate the polymerisation of vinyl monomers, have also been isolated recently[52].

According to calculations by the CNDO method[53], preference should be given to an octahedral hydration shell for alkali metal cations with a pronounced electron transfer from oxygen to the metal; the energy gain relative to other possible hydrates then ranges from 24 to 140 kcal mol^{-1}. The charge transfer in such aquo-complexes has been confirmed also by complete theoretical calculations[54]. According to experimental data[55], the sodium cation in the DMSO–dioxan mixture is surrounded by six donor molecules. It is well known that the most stable complexes with potassium cations are formed by crown-ethers containing six oxygen atoms[56].

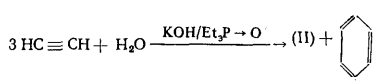
All this justifies the hypothesis that in superbasic catalytic systems a proportion of the usual ligands in the solvation shells of alkali metal cations can be substituted by acetylene molecules, which begin to interact both with one another and with the remaining ligands as a consequence of spatial proximity, polarisation, and partial covalent binding (charge transfer).

The formation of the acetylene hydratotrimers (II)–(IV) can be easily explained by the interaction of ligands, for example, in the following octahedral complex[28]:

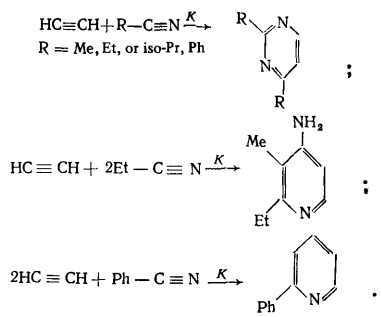


The hydratopentamers (V) and (VI) can be constructed on the same template, provided that two heteroatomic ligands (including DMSO) are replaced by acetylene molecules. Naturally, in real systems there must be a continuous variable spectrum of similar complexes, differing not only in the combinations of the ligands but also in solvation numbers.

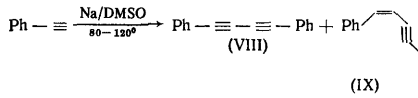
In conclusion of this section, it must be emphasised that DMSO does not constitute the only basis for catalytic systems propagating the reactions under consideration. The superbasic pair KOH–triethylphosphine oxide also catalyses the hydration trimerisation of acetylene. In this case the yield of 2-vinyloxybuta-1,3-diene (II) is 50% and the catalytic reaction mixture contains more than 20% of benzene[34]:



The heterocyclisation of acetylene with nitriles to form pyrimidines and pyridines (1–2% K, 175–200 °C, 13–17 atm, 6–8 h) is known[57]:



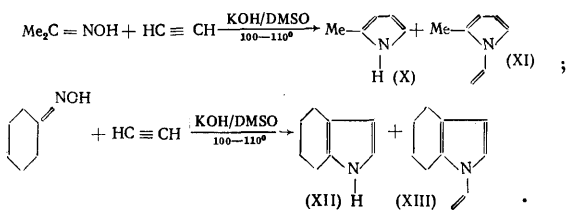
The catalytic system is prepared by the cautious dissolution of metallic potassium in the corresponding nitrile. The yields of 2,4-dialkylpyrimidines and the isomeric 4-aminopyridines are in the range 8–12% (relative to the nitrile which has reacted), but 2,4-diphenylpyrimidine was synthesised in 29–51% yield. The formation of a 2-substituted pyridine was observed only for R = Ph (yield 1.8%). These reactions have now been given a theoretical basis in the light of data[46,47], already quoted, concerning the strong specific interaction of the potassium cation with acetonitrile molecules[46], including their extensive polarisation[47]. The recently discovered[58] dimerisation of phenylacetylene under the influence of a small amount of sodium in DMSO or HMP can also be included in the group of new catalytic reactions under consideration:



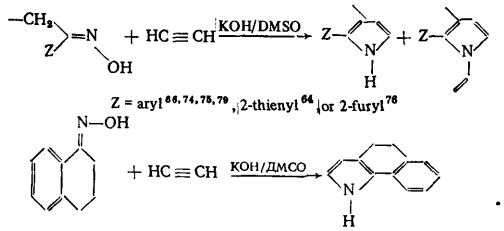
The yield of dimers (VIII) and (IX) reaches 43 and 14% respectively. Other conditions being equal, there is no dimerisation in benzene. Although the oxidative and "additive" dimerisation of acetylenes is well known[59], it has been believed hitherto that these processes can be catalysed only by copper salts.

IV. REACTIONS OF ACETYLENE WITH OXIMES AND AMIDES

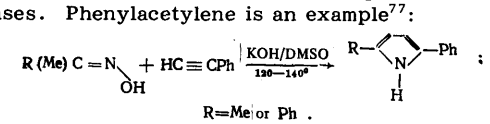
The reaction of acetylene with ketoximes, catalysed specifically by the KOH–DMSO superbasic pair and leading to pyrroles and *N*-vinylpyrroles, was discovered at the beginning of the 1970's.[60,82] For example, 2-methylpyrrole (X) and 2-methyl-1-vinylpyrrole (XI) are formed from acetone oxime[72] while cyclohexanone oxime gives rise to 4,5,6,7-tetrahydroindole (XII) and its 1-vinyl derivative (XIII):[60,67–68,73,78]:



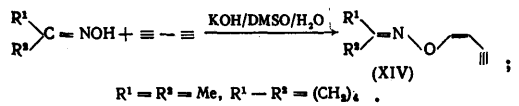
The process proceeds easily and smoothly even at 80–120 °C at atmospheric pressure, being accompanied by a small exothermic effect. The yields of pyrroles are on average 70–80%, reaching 90% and more in certain cases[72,81]. The reaction is of a general type: it involves virtually all ketoximes having at least one CH_2 group in the α-position relative to the oxime functional group, including aromatic[66,74,75,79], heteroaromatic[64,76], and annelated[70] oximes:



Positive results are to be expected when the reaction is extended to certain substituted acetylenes incapable of prototropic isomerisation and stable in the presence of strong bases. Phenylacetylene is an example[77]:



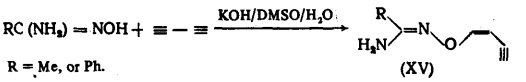
O-Ethynylvinyl derivatives of oximes (XIV) were isolated in 38–41% yield in the reaction with diacetylene instead of the expected 2-ethynylpyrroles[83]:



(XIV)

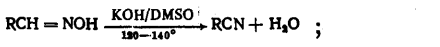
$R^1 = R^2 = Me$, $R^1 - R^2 = (CH_2)_4$.

Under the same conditions, amidoximes react similarly with diacetylene, forming *O*-ethynylvinyl derivatives (XV) in 21–25% yield[84]:



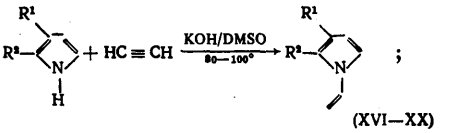
R = Me, or Ph. (XV)

In contrast to ketoximes, aldoximes do not give rise to pyrroles on interaction with acetylene in the KOH–DMSO system, since they are dehydrated to the nitriles[85–87] (yield 65–92%):



R = Me, C_7H_{15}, or Ph .

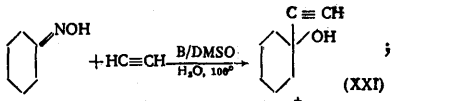
A secondary result of the study of the reactions of ketoximes with acetylene was the development of an effective method for the vinylation of pyrroles at atmospheric pressure[88,89], which is evidently suitable also for the vinylation of other NH-heterocycles. The formation of *N*-vinyl derivatives (XVI)–(XX) in the presence of the KOH–DMSO superbasic pair proceeds under mild conditions (80–100 °C) in 75–95% yield:



(XVI–XX)

$R^1 = Me$, $R^2 = Et$ (XVI); $R^1 = Pr$, $R^2 = Bu$ (XVII);
$R^1 - R^2 = (CH_2)_4$ (XVIII); $R^1 = H$, $R^2 = Ph$ (XIX);
$R^1 = H$, $R^2 = MeOC_6H_4$ (XX) .

In aqueous DMSO the synthesis of pyrroles from ketoximes and acetylene is accompanied by the formation of α-acetylenic alcohols[90]. For the ratio H_2O : DMSO = 1 : 2 (by volume) and at 100 °C, the yield of 1-ethynyl-1-cyclohexanol (XXI) is 47%:[76]



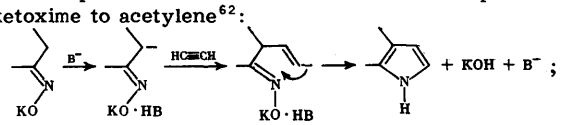
(XXI)

B = NaOH, KOH, RbOH, or $[(Bu)_4\overset{+}{N}]\overline{O}H$.

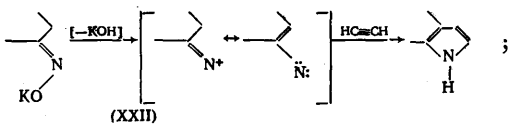
This reaction also proceeds in dioxan and dioxan–DMSO mixtures[90].

The mechanism of the formation of pyrroles from ketoximes and acetylene is not as yet entirely clear. The key stage of the reaction could be one of the following:

(a) nucleophilic addition of the carbanionic component of the ketoxime to acetylene[62]:

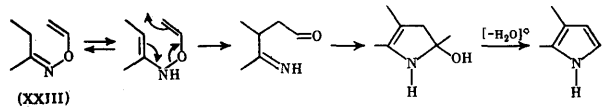


(b) 1,3-dehydration of the ketoxime and the addition of the 1,3-dipole (XXII) (or the corresponding vinylnitrene) to the triple bond[62,65,87]:



(XXII)

(c) sigmatropic rearrangement of the intermediate *O*-vinyloximes (XXIII):[90]

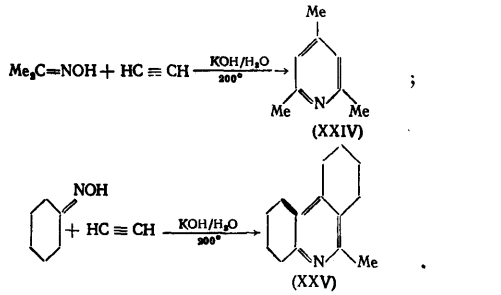


(XXIII)

So far there is no reason to reject only the last mechanism: the *O*-vinyloximes isolated in a low yield on thermolysis in the absence of acetylene do not give rise to pyrroles[92]. Furthermore, as mentioned above, the reaction involving phenylacetylene results in the formation of 5-phenylpyrroles, while the rearrangement of the intermediate (XXIII) should have resulted in the introduction of the phenyl group in the 4-position in the pyrrole ring (nucleophiles add to the terminal carbon atom of phenylacetylene)[32].

The systematic development of this new field, which has arisen at the boundary between the chemistries of acetylene and pyrrole, is being continued[93–106]. The data accumulated show convincingly that the reaction under consideration constitutes at present one of the simplest and most effective methods of synthesising pyrrole systems.

It is of interest that in an aqueous medium without DMSO the base-catalysed interaction of acetylene with ketoximes proceeds quite differently: instead of pyrroles, pyridines are formed[87,107]. For example, symmetrical collidine (XXIV) is obtained from acetoxime, and 9-methyloctahydrophenanthridine (XXV) is formed from cyclohexanone oxime:

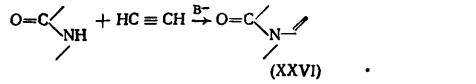


(XXIV)

(XXV)

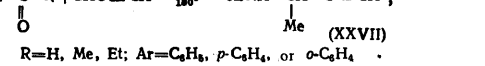
The yield of pyridines is 20–30%, but so far no attempt has been made to optimise this new and extremely promising reaction.

The vinylation of carboxylic acid amides with acetylene in the presence of bases leads to *N*-vinylamides (XXVI):[108–110]



(XXVI)

However, if the catalyst of this reaction is obtained by dissolving metallic potassium in a mixture of an anilide and tetrahydrofuran (THF) or dioxan, then 3-arylamino-1-butynes (XXVII) are formed from these reagents in yields up to 47% together with *N*-vinyl derivatives (XXVI).[111,112] Like the potassium derivatives of anilides obtained via alkoxides, the analogous sodium system does not catalyse the reaction:



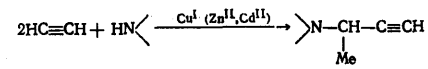
(XXVII)

R=H, Me, Et; Ar=C_6H_5, *p*-C_6H_4, or *o*-C_6H_4 .

The structure of the aminobutyne fragment is independent of the substituent R, which means that the acid component of the anilide is split off, being replaced by the acetylene dimer.

The optimisation of the reaction[113] by mathematical design made it possible to suppress vinylation almost completely, maintaining the yield of acetylenic amines (XXVII) at the level of 35%. It was established that the formation of the

catalyst involves the reductive cleavage of the anilide, one of the products being potassium arylamide (ArNHK), which belongs to the class of superbases[114–118]. It was believed that the familiar reaction of acetylene with secondary amines, resembling to some extent the reaction considered here and leading to the same aminobutynes, proceeds only in the presence of transition metal salts[119]:



However, recently† an analogous reaction between acetylene and aniline was achieved also in the presence of potassium anilide:

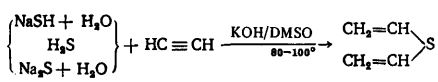
$$PhNH_2 + 2HC\equiv CH \xrightarrow{PhNHK} PhNHCH(Me)C\equiv CH$$

The yield of 3-phenylaminobut-1-yne was ~24%, while the degree of conversion of aniline was 21% (160 °C, 12 atm C_2H_2, 2 h, dioxan). The reaction proceeds with approximately the same yield (25%) albeit with a higher degree of conversion of aniline (41%) when it is catalysed by the specially prepared copper acetylide (20–60 °C, 14 atm C_2H_2 + 3 atm N_2, ethanol–acetic acid)[120].

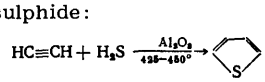
Thus a certain parallelism in the type of activation of acetylene by alkali metal cations under superbasic conditions and metal complexes is again revealed.

V. OLIGOMERISATION OF ACETYLENE WITH PARTICIPATION OF SULPHUR-CONTAINING NUCLEOPHILES

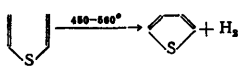
The reactions of acetylene with sulphur-containing nucleophiles are no less varied and unexpected in superbasic media. The simplest of these nucleophiles, the sulphide ion generated from hydrogen sulphide in the presence of an excess of alkali or from alkali metal sulphides in DMSO, adds under very mild conditions (at a temperature of only 80° to 100 °C) and almost quantitatively (under optimum conditions) to two acetylene molecules, forming divinyl sulphide[121–125]:



This at first sight simple and evident reaction has its history. At the beginning of the century the high-temperature catalytic addition of hydrogen sulphide to acetylene was investigated by Chichibadin[126,127], but he obtained thiophen instead of divinyl sulphide:

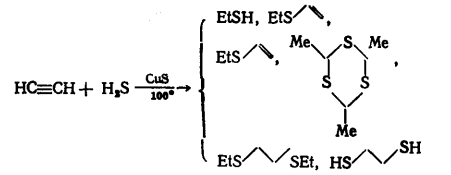


Subsequently investigators frequently returned to this synthesis using as catalysts metal sulphides[128–130], nickel and cobalt on alumina[131], and an aluminolanthanochromium catalyst[132], but the formation of divinyl sulphide was never mentioned. It has been shown recently that at high temperatures divinyl sulphide is thermodynamically unstable and is dehydrocyclised to thiophen[133]:

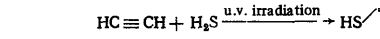


† See B.A.Trofimov, S.F.Malysheva, and E.P.Vyalykh, Zhur.Org.Khim., **15**, 880 (1979).

Towards the end of the 1930's, Reppe again attempted to synthesise divinyl sulphide from acetylene and hydrogen sulphide. He obtained a complex mixture of organosulphur products[134,135], but divinyl sulphide was not present among them:



When a mixture of acetylene and hydrogen sulphide in the liquid phase (−78 °C) or in the gas phase (20 °C) is irradiated with ultraviolet light, ethylenethiol is formed in 33% yield[136]:

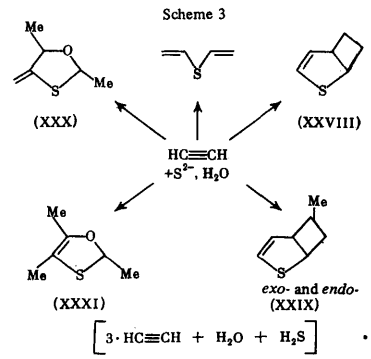


The homologues of acetylene react similarly, the yield of propenethiols (from methylacetylene) amounting to 87%.[136]

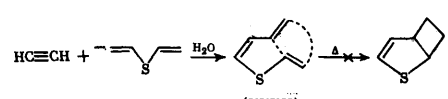
Thus neither high-temperature nor photochemical initiation nor heterogeneous catalysis permit the direct synthesis of divinyl sulphide from acetylene and hydrogen sulphide. This monomer has been obtained by multistage reactions via mustard gas[137–142], di(2-bromoethyl)sulphide[143–145], or thiodiglycol[146–148]. Until recently, it was therefore only of strictly theoretical interest. The reaction of acetylene with the sulphide ion in a superbasic medium made divinyl sulphide a very readily available and cheap product, which can now be manufactured industrially on any scale.

As in the case of the hydroxide ion, the addition of sulphide anions to acetylene in superbasic media is accompanied by unusual heterocyclo-oligomerisation reactions (Scheme 3). Thus the reaction in the NaOH–DMSO–H_2O system yields, together with divinyl sulphide, a new bridged heterocycle—2-thiabicyclo[3,2,0]hept-3-ene (XXVIII) and its *exo*- and *endo*-6-methyl derivatives (XXIX),[149–151] which are in essence thiylated trimers, as well as 2,5-dimethyl-4-methylene-1,3-oxathiolan (XXX) and its endocyclic isomer 2,4,5,-trimethyl-1,3-oxathiol (XXXI),[152–155] made up of three acetylene molecules, a hydrogen sulphide molecule, and a water molecule:

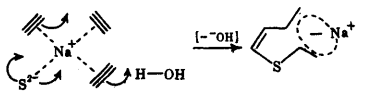
Scheme 3



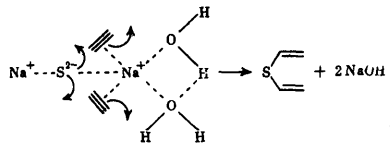
Evidently template cyclisation again takes place under these conditions. The dark [2 + 2]-cyclisation of the probable intermediate 1-vinylthiobuta-1,3-diene (XXXII) is prohibited by orbital symmetry rules:



However, in the electric field of the coordinated cation, where the π-symmetry of the ligands is violated, the prohibition of cyclisation is removed:



One cannot rule out the possibility that the divinyl sulphide molecule (which in this context can be regarded as a sulphur-containing acetylene dimer) is also produced by a single-stage process in the initial matrix:



One of the roles of DMSO under these conditions may involve the partial dehydration of the Na^+ cation as a result of the formation of stable complexes of the type $Me_2SO.2H_2O$ [156,157] as well as hydrogen bonds between H_2O and DMSO molecules, which are stronger than in the self-associated water species[158].

The second order of the reaction with respect to phenylacetylene in the synthesis of di(2-phenylvinyl)sulphide (XXXIII) from phenylacetylene and hydrated sodium sulphide in DMSO, HMP, and triethylphosphine oxide may be regarded as the kinetic confirmation of the reality of the "template effect":[159]

$$PhC\equiv CH + Na_2S\cdot 9H_2O \xrightarrow{80\text{–}100^\circ} Ph\diagup\!\!\diagdown S\diagup\!\!\diagdown Ph \quad (XXXIII)$$

Such formal kinetics are characteristic of many metal complex reactions of acetylene via a coordination mechanism[160]. The activation parameters—the unusually low energy barrier ($\Delta H^{\neq} \cong 7$ kcal mol^{-1}) accompanied by an enormous decrease of entropy ($\Delta S^{\neq} \cong -50$ e.u.)—are consistent with this mechanism; thus the transition state of the reaction does indeed have a highly ordered structure and the dissociation and formation of bonds are to a large extent synchronised. When the reaction was followed by ^1H NMR over a wide range of conversions (up to 70%), the splitting of the signals due to the olefin protons, which might have been caused by the formation of an intermediate 2-phenylvinyl sulphide anion in the case of a multistage addition of the sulphide ion to two phenylacetylene molecules, was not observed[159].

Yet another property is characteristic of superbasic catalytic systems, which distinguishes them from typical metal complex catalysts, namely the outcome of the reaction frequently depends fundamentally on the nature of the components of these systems. Thus, when DMSO is replaced by HMP, it is possible to select conditions for the reaction of acetylene with hydrogen sulphide[161] such that its only product is ethanethiol:

$$HC\equiv CH + H_2S \xrightarrow[90^\circ]{KOH/HMP} \begin{cases} \diagup\!\!\diagdown S\diagup\!\!\diagdown \\ EtSH \end{cases}$$

This synthesis is of fundamental importance, because it illustrates strikingly the ability of certain superbasic systems to stimulate oxidation-reduction processes of the type

$$\diagup\!\!\diagdown S^- + H_2S \xrightarrow{KOH/HMP} EtS^- + S$$

In a superbasic system involving DMSO or HMP the cyclic octamer of elemental sulphur is readily cleaved already at 80 °C, forming as a result of reaction with acetylene the same product as the sulphide ion; the main product is divinyl sulphide[29,162,163], which can be obtained in 75–80% yield by this reaction:

$$HC\equiv CH + S_8 \xrightarrow{KOH/DMSO/H_2O} \diagup\!\!\diagdown S\diagup\!\!\diagdown$$

The elemental sulphur–alkali metal hydroxide–DMSO system was later proposed[163] as a new reagent for the synthesis of organosulphur compounds from organic halides. Analogous direct oxidation-reduction vinylation reactions proved to be possible also for elemental selenium[27,29,31] and tellurium[29,164–166]. The latter reacts more effectively in HMP. The yield of divinyl derivatives (XXXIV) and (XXXV) is greater than 50%:

$$HC\equiv CH + Se_\alpha \xrightarrow[95\text{–}120^\circ]{KOH/DMSO/H_2O} \diagup\!\!\diagdown Se\diagup\!\!\diagdown \quad (XXXIV)$$

$$HC\equiv CH + Te \xrightarrow[110\text{–}120^\circ]{KOH/HMP/H_2O} \diagup\!\!\diagdown Te\diagup\!\!\diagdown \quad (XXXV)$$

The direct synthesis of divinyl selenide (XXXIV) and divinyl telluride (XXXV) from the elements and acetylene leads to interesting prospects for the development of the chemistry of unsaturated organoselenium and organotellurium compounds.

The reactions with alkali metal polysulphides, which also proceed with the cleavage of the polysulphide chain and the formation of divinyl sulphide in 70–92% yield[167], are closely related to the above group of oxidation-reduction processes:

$$HC\equiv CH + Na_2S_n \xrightarrow[100^\circ]{KOH/DMSO/H_2O} \diagup\!\!\diagdown S\diagup\!\!\diagdown \quad (n = 2-4)$$

In the reaction with organic disulphides acetylene is readily inserted in the S–S bond, forming *cis*-1,2-di(organylthio)-ethylenes (XXXVI) in 60–80% yield:[168–170]

$$HC\equiv CH + \underset{R=Alk \text{ or } Ph}{R\diagup S\diagdown S\diagup R} \xrightarrow[130^\circ]{t\text{-}BuOK/DMSO} R\diagup S\diagdown\diagup S\diagdown R \quad (XXXVI)$$

If favourable conditions are created at the same time for the transfer of a proton (for example, by adding H_2O to the system), alkyl vinyl sulphides are also formed[171–174] in a yield which can be raised to 80%:[172]

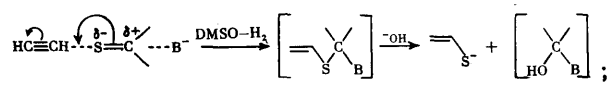
$$HC\equiv CH + Alk\diagup S\diagdown Alk \xrightarrow{KOH/H_2O} \diagup\!\!\diagdown S\diagup\!\!\diagdown Alk$$

The ease of cleavage of the S–S bond under these conditions hinders the synthesis of divinyl polysulphides. However, they are probably nevertheless formed as intermediates, as shown by the formation of 1,2-di(vinylthio)ethylene (XXXVII) from acetylene and sodium disulphide[155,167,175]:

$$HC\equiv CH + Na_2S_2 \xrightarrow[80^\circ]{KOH/DMSO/H_2O} \diagup\!\!\diagdown S\diagup\!\!\diagdown S\diagup\!\!\diagdown$$

$$\left[\diagup\!\!\diagdown S\diagup\!\!\diagdown S\diagup\!\!\diagdown\right] + HC\equiv CH \quad (XXXVII)$$

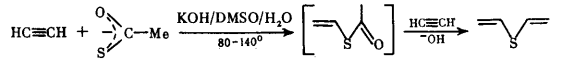
Unusual reactions of acetylene with thione systems—carbon disulphide[177,178], thiourea[176,179,180], dithiocarbamate[176,181–184] and phosphorothioate[185] esters and salts, and even sodium thiosulphate[176]—take place readily in a superbasic medium[176]. As a result of its high polarisability, the thione fragment behaves under these conditions as a powerful uncharged nucleophile. Ultimately the series of successive (or synchronous) addition and substitution steps usually leads to divinyl sulphide (yield 70–80%):



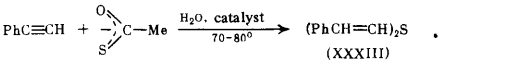
$B = {}^-OH, {}^-SNa$

$$HC\equiv CH + \diagup\!\!\diagdown S^- \xrightarrow{H_2O} \diagup\!\!\diagdown S\diagup\!\!\diagdown$$

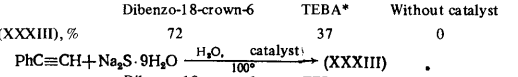
Under superbasic conditions, extremely weak nucleophiles such as the thioacetate anion, add readily to the triple bond[182,184,186], although previously they were believed to be incapable of this:



The yield of divinyl sulphide by this reaction is 60%.[186] The same reaction with phenylacetylene served as one of the examples used to demonstrate for the first time that interfacial catalysis by crown-ethers and tetraorganylammonium salts can be used successfully to accelerate nucleophilic addition to the triple bond[187]:



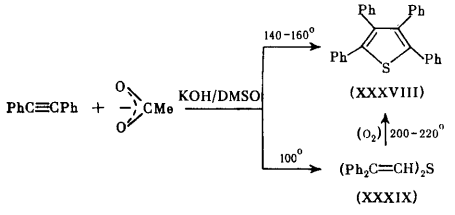
Catalyst	Dibenzo-18-crown-6	TEBA*	Without catalyst
yield of (XXXIII), %	72	37	0



Catalyst	Dibenzo-18-crown-6	TEBA	Without catalyst
Yield of (XXXIII), %	40	22	9

*Triethylbenzylammonium chloride.

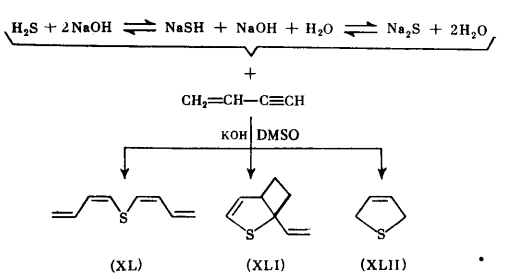
Depending on the conditions, either tetraphenylthiophen (XXXVIII) or di(2,2-diphenylvinyl) sulphide (XXXIX) can be obtained by the reaction of the thioacetate anion and diphenylacetylene[190]:



The "geminal" structure of the sulphide (XXXIX) is a result of an unexpected rearrangement with transfer of the phenyl group. The thermo-oxidative cyclisation of this sulphide to tetraphenylthiophen involves the reverse 1,2-migration of the phenyl groups[190]. A similar 1,2-migration is observed on heating the sulphide (XXXIX) with alkali in DMSO, which results in the reformation of diphenylacetylene[180,190].

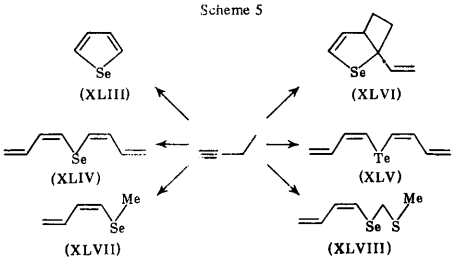
In conclusion of this section, it must be specially emphasised that almost all the reactions considered here are fairly general and are characteristic not only of acetylene itself but also of substituted acetylenes. For example, vinylacetylene reacts with sulphide anions in a superbasic medium to form di(buta-1,3-dienyl) sulphide (XL) [191] in a yield exceeding 90% (Scheme 4). By altering the conditions, it is possible to induce heterocyclisation reactions leading either to 1-vinyl-2-thiabicyclo[3,2,0]hept-3-ene (XLI) [192] or to dihydrothiophen (XLII),[193,194], which has been hitherto difficult to synthesise. The latter can be obtained in a virtually quantitative yield.

Scheme 4

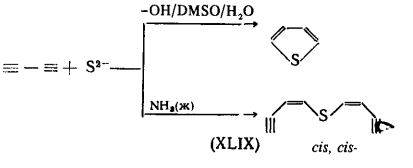


Direct single-stage syntheses (Scheme 5) of selenophen (XLIII), di(buta-1,3-dienyl) selenide (XLIV),[195] di(buta-1,3-dienyl) telluride (XLV),[195] 1-vinyl-2-selenabicyclo[3,2,0]-hept-3-ene (XLVI), as well as buta-1,3-dienyl methyl selenide (XLVII) [196] and buta-1,3-dienyl methylthiomethyl selenide (XLVIII), formed with participation of DMSO, have been achieved on the basis of vinylacetylene and the corresponding elements in superbasic media. The syntheses based on vinylacetylene and elemental selenium or tellurium in the KOH–HMP–H_2O and KOH–DMSO–H_2O systems at 100–120 °C are illustrated in Scheme 5 below:

Scheme 5



Sulphide anions react with diacetylene in superbasic media to give a quantitative yield of thiophen[197] or *cis,cis*-di(but-1-en-3-ynyl) sulphide (XLIX) in 89% yield[198]:



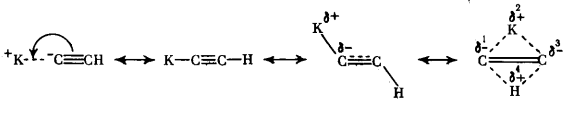
The last reaction has been achieved in liquid ammonia, which is also an effective superbasic medium, since it exhibits a high dielectric constant and an unsurpassed ability to solvate alkali metals, while its autoprotolysis constant is negligible.

VI. CONCLUSION

In conclusion one must say that, in order to avoid making the schemes and discussions unduly cumbersome, we excluded the ionisation of acetylene and the dissociation of acetylides:

$$HC\equiv CH + KOH \rightleftarrows {}^{+}K^{-}C\equiv CH + H_2O;$$
$${}^{+}K^{-}C\equiv CH \rightleftarrows K^{+} + {}^{-}C\equiv CH .$$

It would be a mistake to underestimate the influence of these reactions, particularly when one is dealing with superbasic media. Ideed, in the acetylide ion pair the triple bond, subjected to the influence of the charge and the electron cloud of the cationised alkali metal atom, should be very highly polarised and loosened:



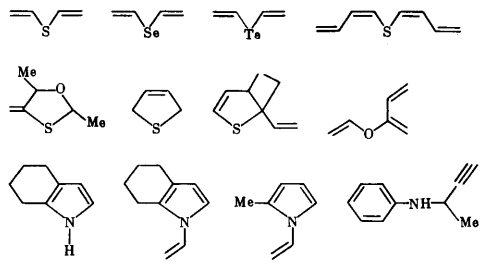
The extensive rehybridisation and stretching of the C≡C bond under the influence of the alkali metal attached to it directly is indicated particularly by the considerable decrease of the stretching vibration frequencies ν(C≡C) and ν(≡C–H) in the spectra of acetylides compared with alkylacetylenes[199]:

Acetylenic compound	$\nu_{C\equiv C}$, cm^{-1}	$\nu_{\equiv C-H}$, cm^{-1}
$CH_3C\equiv CH$	2121	3320
$LiC\equiv CH$	1990	3245
$NaC\equiv CH$		3216
$KC\equiv CH$		3224

One cannot rule out the possibility that the formation of acetylides makes a decisive contribution to the activation of acetylene by superbasic media. It may be that acetylene undergoes complex formation and is involved in key inner-sphere transformations precisely in the form of a polarised anion.

The review can be aptly concluded by listing the structures of the most readily available monomers, intermediates, and synthons (Scheme 6), which can now be readily obtained from acetylene in superbasic media and to which it is desirable to draw the attention of synthetic chemists, specialists in polymer chemistry, pharmacologists, biologists, and technologists.

Scheme 6



Thus a new stratum of fundamental and applied developments has arisen in acetylene chemistry. The possibilities of superbasic catalytic systems are by no means exhausted. The next development should be the creation of a rigorous quantitative theory, which would permit the specific employment of the above systems in practice as well as in further research.

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