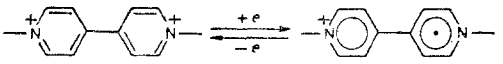
HETEROCYCLIC CATION RADICALS (REVIEW)

A. S. Morkovnik and
O. Yu. Okhlobystin

UDC 541.515:547.718:543.422.27

The modern state of the chemistry of heterocyclic cation radicals is examined. Methods for the preparation (generation) of these particles, as well as their stabilities and the factors that determine them, are described. The mechanisms of the reactions of heterocyclic cation radicals with nucleophiles and specific examples of such reactions are discussed. Special attention is directed to the role of cation radicals as intermediate particles in dehydrogenation, nitration, and radical substitution reactions and in processes involving the cleavage of C–C bonds and dehydrodimerization in the heterocyclic series. The cation radicals of some natural heterocyclic compounds and their possible role in the functioning of biochemical systems are also examined.

The one-electron oxidation of heterocyclic compounds, like the reduction of their dications, leads to the corresponding cation radicals (CR), the chemistry of which is currently a rapidly developing and promising area of chemical science. This research area originated with the studies of Michaelis and co-workers [1, 2], who first described the reduction of bis(pyridinium) salts to "viologenic" cation radicals:



A new chapter in the chemistry of cation radicals was begun after the discovery of EPR spectroscopy, when oxidative methods for the generation of cation radicals underwent extensive development. However, the nature of the radical particles that develop under the influence of oxidizing agents on aromatic and heteroaromatic compounds remained unclear right from the start [3-7].

For a number of objective reasons the chemistry of heterocyclic cation radicals is in general the most developed branch of the chemistry of cation radicals. It is becoming increasingly apparent that the formation of cation radicals is one of the most important characteristics in the chemical behavior of many heterocyclic compounds that frequently predetermines the mechanisms of their reactions.

The cation radicals of chlorophyll play a decisive role in photosynthesis processes [8, 9]; the cation radicals of other natural heterocyclic substrates are evidently the usual intermediates in a large number of biochemical redox reactions.

The aim of the present paper, which does not pretend to exhaustively encompass the experimental data, was to outline the general state of this research area and to contemplate the most promising trends in its development.

Stabilities and General Properties

The stabilities of heterocyclic cation radicals vary over extremely wide limits as a function of the nature of the starting heterocycle and the substituents in it, the properties of the medium, and the experimental conditions. Whereas virtually nothing was heretofore known regarding the cation radicals of some of the simplest unsubstituted heterocycles (furan, thiophene, pyrrole, etc.), the cation radicals of many other heterocyclic compounds have been isolated preparatively in the form of ion-radical salts. This pertains to the cation radicals of phenothiazines [10-13], phenoxazines [11, 13], phenoxathiin [14, 15], dibenzodioxin [16],

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1011-1029, August, 1980. Original article submitted December 18, 1979.

0009-3122/80/1608-0777$07.50

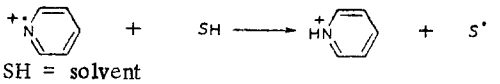
thianthrene [7, 17, 18], 5,10-disubstituted 5,10-dihydrophenazine [13, 19], and derivatives of 4,4'-bis(pyranylidene) [20, 21], 3,3'-dicarbazolyl [22], 1,4-bis(p-bromophenyl)-1,4-dihydrotetrazine [23], cyclazine [24], 9,9'-bis(9-azabicyclo[3.3.1]nonane) [25], and some metalloporphyrins [26, 27].

The most usual situation is the intermediate case in which the formation and destruction of cation radicals are reliably recorded by some physical method (EPR, electronic absorption spectra, and voltammetry); however, the stabilities of cation radicals are not high enough to make attempts to isolate them expediently.

The stabilities of cation radicals are limited by their high reactivities, which are associated with the presence of an unpaired electron, the considerable positive charge on the carbon atoms, and facile deprotonation and fragmentation processes. Upon the whole, the stabilities of cation radicals, like the stabilities of free radicals, generally increase as the delocalization of the unpaired electron and the steric shielding of the reaction centers, where the spin density is maximal, increases. In contrast to unsubstituted substrates, tetraphenylthiophene [28] and polyphenylpyrroles [29] give relatively stable cation radicals. The cation radicals of carbazole and its N-substituted derivatives dimerize rapidly [22, 30, 31]; however, the presence of strongly shielding tert-butyl groups in 1,3,6,8-tetra-tert-butylcarbazole makes its cation radicals completely stable [32]. Other things being equal, the stabilities of cation radicals are promoted by the absence of "acidic" hydrogen atoms, which hinders or makes impossible deprotonation leading to a neutral free radical:

$$RH^{+\cdot} \rightleftharpoons R^{\cdot} + H^{+}$$

The lower the degree of delocalization of the unpaired electron, the greater the extent to which the cation radicals display the properties of active free radicals. Thus, the cation radicals of pyridine can simply be regarded as particles that are formed after the removal of one of the electrons of the unshared pair [33-37]; as before, the remaining electron interacts weakly with the aromatic sextet of the ring and for this reason is localized rigidly on the nitrogen atom. Cation radicals of this type, like active radicals, readily detach hydrogen atoms from the solvent and are thereby converted to pyridinium cations:



The cation radicals of quinuclidine behave similarly [38].

The cation radicals are, of course, unstable in the presence of reducing agents that are capable of one-electron transfer; this pathway for their destruction is the reverse of the principal pathway for their formation:

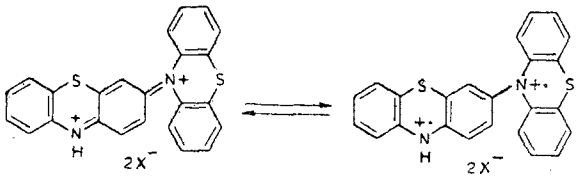
$$RH^{+\cdot} + e \longrightarrow RH$$

There is no direct correspondence between the stability of the cation radicals and the ease of their formation, which is estimated from the half-wave potentials of the anode oxidation of the neutral compounds. However, there is a tendency for an increase in the stability of the cation radicals as the half-wave potential for the oxidation of the heterocyclic compound associated with them increases.

The various heterocyclic cation radicals display a tendency for reversible conversion to diamagnetic dimers in solutions; this was established by a study of the dependence of the electronic absorption spectra of solutions of cation-radical salts on the temperature [26, 39-43].

A remarkable property of some heterocyclic dications is the presence of low-lying triplet levels, as a consequence of which they display EPR spectra that are characteristic for triplet compounds. The dication of 2,3,7,8-tetramethoxythianthrene [44] and I, the triplet state of which can be represented simply as a bis(cation radical) [45-47], are compounds of this type: (formula, top, following page).

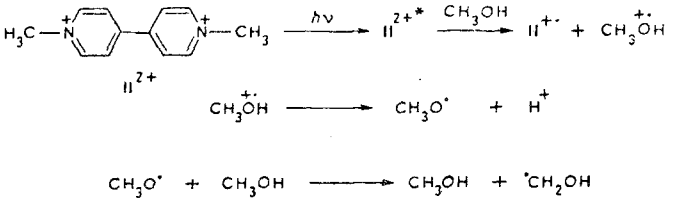
A valuable method for the generation of cation radicals and the study of their properties is the electrochemical oxidation of heterocyclic compounds [29, 30, 48-73]. The oxidation of heterocyclic substrates on a rotating disk electrode with a ring is particularly promising. The half-wave potentials and the lifetimes of cation radicals can be deter-



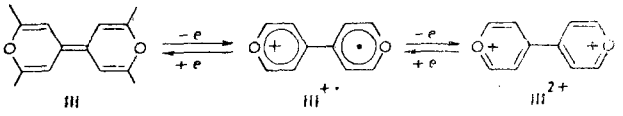
mined simultaneously by this method. In particular, data of this sort have been obtained for the cation radicals of N-methylacridan [74] and 4H-pyrans [75]. In the case of rapidly dimerized cation radicals this method makes it possible to determine the dimerization rate constants [76-78].

Chemical oxidizing agents such as I_2—$AgClO_4$ [26, 79, 80], $AlCl_3$—CH_3NO_2 [28, 81-84], $AlCl_3$—CH_2Cl_2 [85], Br_2 [24, 86-89], I_2 [55, 90-92], $HClO_4$—$(CH_3CO)_2O$ [14, 17], $FeCl_3$ [87], $NOBF_4(PF_6)$ [13, 93-95], $SbCl_5$ [18, 84, 96], H_2O_2—HBF_4 [97], H_2SO_4 [3, 6, 98-108], tris(p-bromophenyl)aminium hexachloroantimonate [109, 110], liquid sulfur dioxide [111], $Pb(CH_3COO)_4$—CF_3COOH [112], diazonium salts [113], ClO_2 [114], and potassium persulfate [115] are also used in addition to anode oxidation to convert heterocyclic compounds to cation radicals.

The one-electron reduction of heterocyclic dications, which is chronologically the first method for the preparation of heterocyclic cation radicals, is still of great value. This method has been used to reduce viologenic dications [116-123], 2,2'-dipyridyl [124], pyrazine [125], and 9,9'-diacridinyl (luzigenin) [126] bisquaternary salts, bis(pyrylium) salts [20], heterocyclic derivatives of radialene-4 [127], the 4,4'-bis(3,5-diphenyl-2-pyrazolin-1-yl)-biphenyl dication [128], bisquaternary salts of naphthyridines [129, 130], as well as diprotonated naphthyridines [130, 131], to cation radicals. The reduction is carried out with zinc, various bases, or electrochemically. The oxidative properties of the viologenic dications increase sharply on passing to the singlet excited state. In this case the viologenic dications are capable of oxidizing even aliphatic alcohols [132-135].

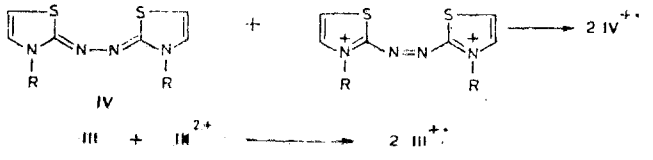


The genetic link between the two principal methods for the production of cation radicals becomes apparent when one examines a redox triad in which a cation radical is the central link [136]:



The high stability of the cation radicals from bis(pyrylium) salts is due to the high degree of delocalization of the unpaired electron, as a consequence of which the free valence and the positive charge are distributed uniformly in both symmetrical fragments of the molecule. The presence of direct conjugation between the cationic centers is necessary in dications of this type; if these centers are separated by a nonconducting grouping, the reduction of the dication takes place in one two-electron wave, i.e., it leads to uncharged diradicals [137].

The reduction of "twinned" heterocyclic compounds by conjugated dications can evidently serve as a general method for the preparation of cation radicals [128, 138]:



An extremely promising but as yet little-studied area of the chemistry of heterocyclic cation radicals entails the reactions involved in their photo- and radiochemical formation. Cation radicals are the usual intermediate particles in many photo- and radiochemical reactions. Several cases of photo- and radiochemical generation of heterocyclic cation radicals are presented in [139-149].

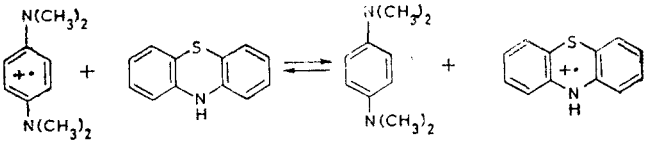
Reactivities of Heterocyclic Cation Radicals

General Characteristics. With respect to their nature, almost all heterocyclic cation radicals are oxidizing agents, i.e., they tend to accept one electron. Metals [11, 128], the iodide anion [98], and organic compounds [150, 151] can serve as the reducing agents. Under the influence of stronger oxidizing agents, heterocyclic cation radicals can act as electron donors, undergoing conversion to dications in this case [128, 138, 152]. As a rule, heterocyclic dications are stronger oxidizing agents than the corresponding cation radicals.

An important and interesting property of the $RH-RH^{+\bullet}$ and $RH-R'H^{+\bullet}$ system is the possibility of rapid electron exchange between the cation radicals and the neutral compound. However, in contrast to electron exchanges with the participation of anion radicals ($RH + R'H^{-\bullet} \rightleftarrows RH^{-\bullet} + R'H$), such processes have as yet received little study.

The rate constants of electron exchange in the phenothiazine–phenothiazine cation-radical system [$k = (6.7 \pm 0.4)\cdot10^9$ [153] and $(4.33 \pm 0.65)\cdot10^9$ liters/mole-sec [154]] show that the processes involving degenerate electron exchange in heterocyclic cation radicals evidently take place at rates that are close to the rate of diffusion and require virtually no activation.

The equilibrium constant of electron exchange in the reaction between phenothiazine and the N,N,N',N'-tetramethyl-p-phenylenediamine cation radical has been determined [151].



$K = 0{,}96 \cdot 10^{-6}$; $\Delta G^\circ = 7$, kcal/mole

A factor that determines the position of the equilibrium in the case of nondegenerate electron exchange is evidently the difference in the oxidation potentials of the neutral forms.

The degree of dissociation of heterocyclic cation radicals is evidently not very high. It has been pointed out that the constant of the equilibrium is only $(9.7 \pm 2)\cdot10^{-2}$ (at −20°C

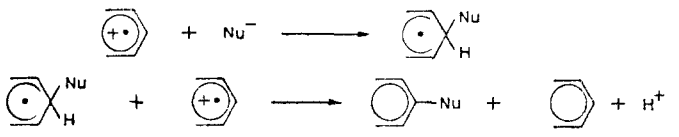
$$\text{phenothiazine}^{+\bullet}\,\|\,I_3^- \rightleftarrows \text{phenothiazine}^{+\bullet}\,I_3^-$$

in nitromethane) [155].

Reactions with nucleophiles, in the process of which the cation radicals are reduced, are characteristic for heterocyclic cation radicals. Both the nucleophile itself and the

$$HetH^{+\bullet} + Nu^- \longrightarrow HetH + Nu$$

product of its addition to the cation radical (a radical σ complex), which is aromatized due to oxidation of a second molecule of the cation radical (a "half-regeneration" mechanism) may be the one-electron reducing agent [156-159].



Transformations of the latter type are evidently very widespread in the chemistry of heterocycles; the so-called "nucleophilic" hydrogen-substitution reactions ("S_NH") [160] are closely allied to them. This stepwise mechanism of the reduction by nucleophiles (and, in

particular, anions) is general in character and is realized in those cases when direct oxidation of the anion is hindered thermodynamically. The reduction of quinones to semiquinones under the influence of the OH^- anion, e.g., proceeds in this way [161]. However, one should bear in mind that the formation of addition products in itself does not exclude possible preceding steps involving electron transfer from the nucleophile to the cation radical [162].

The available data on the relative reactivities of nucleophiles with respect to cation radicals are contradictory. According to theoretical estimates [157], the rates of reactions of the nucleophile with cation radicals are determined by the ratio of the oxidation potentials of the nucleophile and the neutral form that is associated with the cation radical. However, the data on the kinetics of such reactions indicate the absence of such a correlation: The reactivities of nucleophiles with respect to cation radicals vary in the same order as in the case of nucleophilic substitution of iodine in methyl iodide by these nucleophiles (S_N2).

A disproportionation mechanism has also been proposed for reactions between cation radicals and nucleophiles (in the case of cation radicals of thianthrene [17, 163-165] and polyphenylpyrroles [57]):

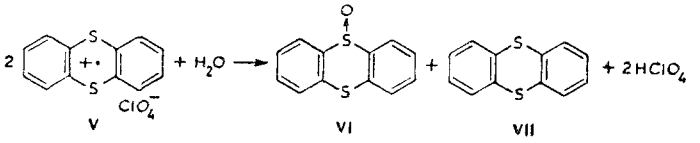
$$2\,HetH^{+\cdot} \rightleftharpoons HetH^{2+} + HetH$$
$$HetH^{2+} + Nu^- \longrightarrow HetHNu^+ \xrightarrow{-H^+} HetNu$$

Kinetic data, according to which the reactions of thianthrene cation radicals with nucleophiles are second-order in the cation radicals, have served as the chief argument in favor of this scheme [163]. However, these results were subsequently not confirmed [157, 166].

Reactions of Heterocyclic Cation Radicals. As compared with other heterocyclic cation radicals, the reactions of phenothiazine, thianthrene, phenoxathiin, and dibenzodioxin cation radicals have been studied in greatest detail.

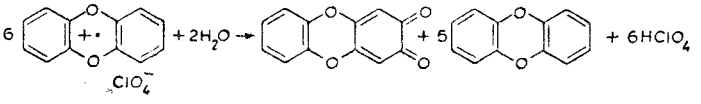
Attack at the sulfur atom and the formation of derivatives of these heterocycles with an altered sulfur function occur extremely frequently in the case of the action of nucleophiles on sulfur-containing cation radicals.

Water converts the thianthrene cation radical (V) to thianthrene 5-oxide (VI) [17]:

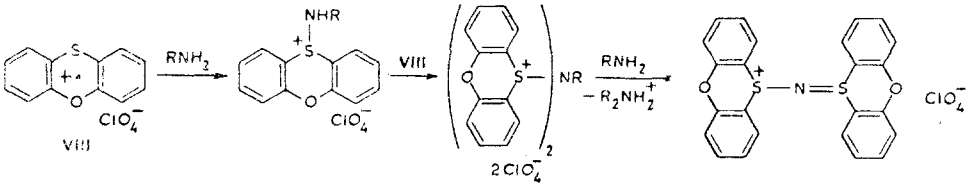


V VI VII

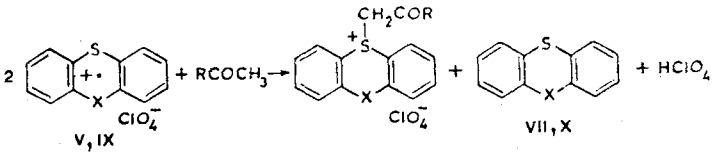
On treatment with water, the dibenzodioxin cation radical forms a mixture of dibenzodioxin and its 2,3-quinone [16, 58]. This complex reaction is evidently the result of a series of several half-regeneration steps:



Like the reaction with water, the reaction of sulfur-containing cation radicals with ammonia [164, 165], aliphatic amines [167, 168], ketones [169-172], and a number of active aromatic compounds [157, 163, 166] leads to the formation of products of addition to sulfur:

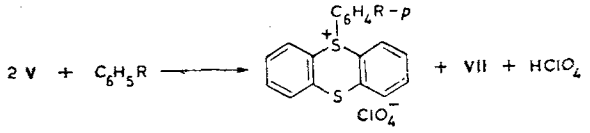


VIII

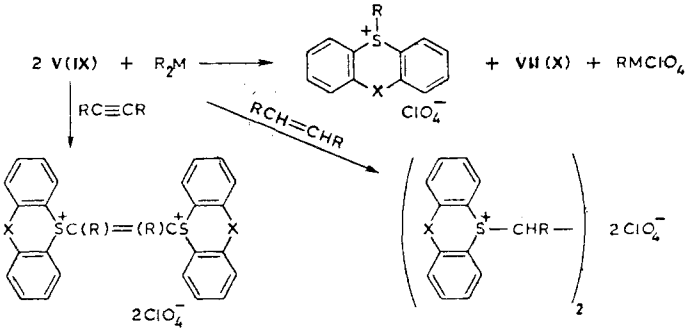


V, IX

V, VII X=S ; IX, X X=O

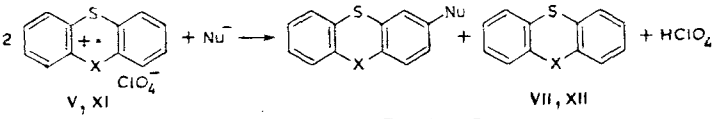


Some organometallic compounds [173], as well as olefins [174], also form sulfonium salts in reactions with thianthrene and phenoxathiin cation radicals:



M = Hg, Zn ; X = O, S

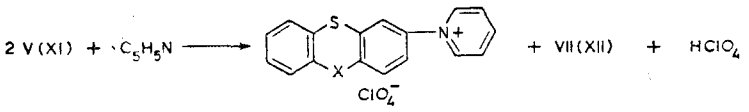
However, there are nucleophiles that form products of substitution in the benzene ring in reactions with sulfur-containing cation radicals [164]:



V, XI

V, VII X=S ; XI, XII X=NH , $Nu^- = Cl^-, Br^-, NO_2^-$

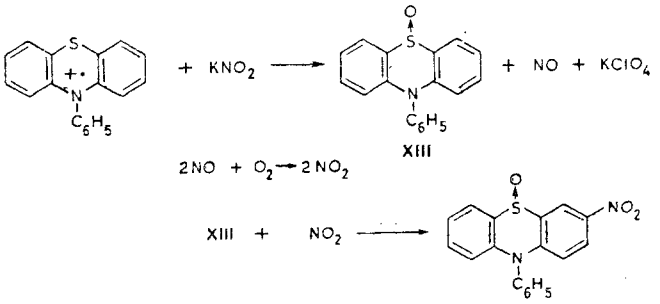
Pyridine reacts extremely vigorously with thianthrene (explosively!) and phenothiazine perchlorate cation radicals and, in contrast to ammonia and aliphatic amines, forms pyridinium salts corresponding to attack on the benzene ring [164,175]:



The reaction of 10-phenylphenothiazine perchlorate cation radicals leads mainly to 10-phenylphenothiazine 5-oxide (XIII) (40%) and 3-nitro-10-phenylphenothiazine 5-oxide (37%) [176]: (scheme, see top, following page.)

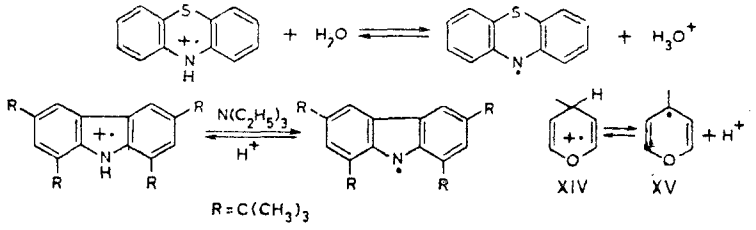
In conformity with the scheme presented [176], the reaction in an inert atmosphere leads exclusively to S-oxide XIII (82%).

Fragmentation of Heterocyclic Cation Radicals. One of the most characteristic pathways in the decomposition of cation radicals is deprotonation with the formation of neutral free radicals: $RH^{+\bullet} \rightleftarrows R^{\bullet} + H^{+}$. Many of the presently known cation radicals thus have the proper-

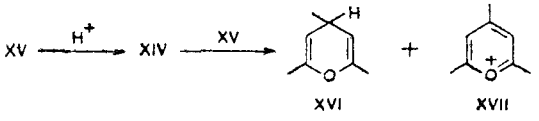


ties of true Brønsted acids, the conjugate bases of which are free radicals. Thus, the constant of the equilibrium $R^{\bullet} + BH^{+} \rightleftarrows RH^{+\bullet} + B$, where B is a reference base (water for example), can serve as a measure of the basicities of free radicals.

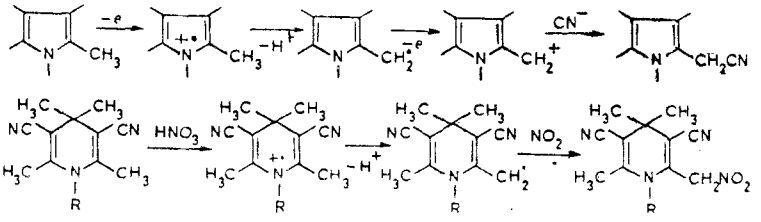
In the heterocyclic cation-radical series the cation radicals of, for example, phenothiazine [177], 1,3,6,8-tetra-tert-butylphenoxazine [178], 1,3,6,8-tetra-tert-butylcarbazole [32], and 4H-pyrans [179, 180] are deprotonated via the scheme presented above,



It should be emphasized that in the general case the deprotonation of cation radicals is reversible; the reverse reaction with time may become an important method for the preparation of cation radicals. A situation of this sort is realized particularly in the case of stable pyranyl radicals: the cation radicals that are formed when they are protonated are reduced by unprotonated radicals, and this ultimately leads to disproportionation of the free radicals:

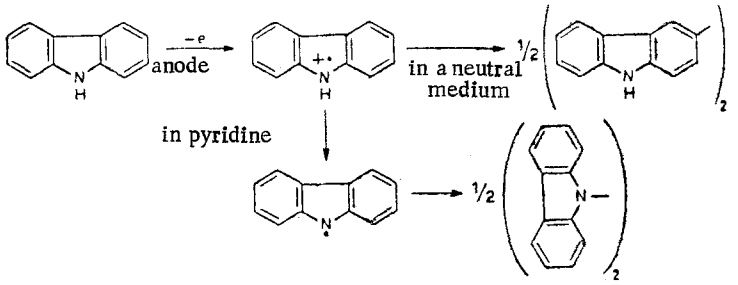


The deprotonation of the methyl groups of the cation radicals of C-methyl-substituted pyrroles, indoles, and 2,4,4,6-tetramethyl-3,5-dicyano-1,4-dihydropyridines is one of the steps in the electrochemical cyanation [181] and nitration [182] in the methyl groups described for these compounds:

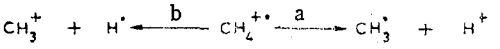


The cation radicals of carbazole and the corresponding neutral radical form dimers with various structures [22, 25, 61]. Owing to this, it becomes possible to direct the oxidative dimerization by changing the proton-acceptor properties of the medium [61]: (For scheme, see top next page.)

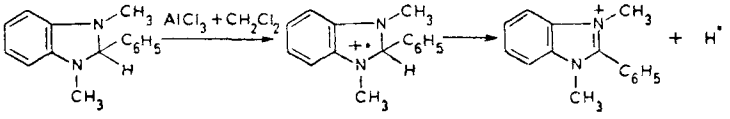
A similar effect of the proton-acceptor properties of the medium on the direction of the oxidative process has been described for the reaction of 1,3,5-triphenyl-2-pyrazoline with pyridinium hexachloroantimonate [128].



In principle, another pathway for the fragmentation of cation radicals, which leads to the formation of an organic cation and a hydrogen atom, is possible. This type of fragmentation predominates, for example, in the case of the gas-phase fragmentation of methane cation radicals [183]:



In the case of 1,3-dimethyl-2-phenylbenzimidazoline cation radicals it was demonstrated for the first time that the fragmentation of cation radicals via pathway b is also possible in solution [85]. The cation radical obtained by oxidation of a substrate with the $AlCl_3$–CH_2Cl_2 system was identified reliably by EPR spectroscopy; the ease of splitting out of atomic hydrogen in this case was associated with the unusually high spin density on the "hydride-like" hydrogen atom in the 2 position (a_H ~ 40 Oe).



It has been assumed that the aromatization of benzimidazolines proceeds as hydride-ion "transfer" [184].

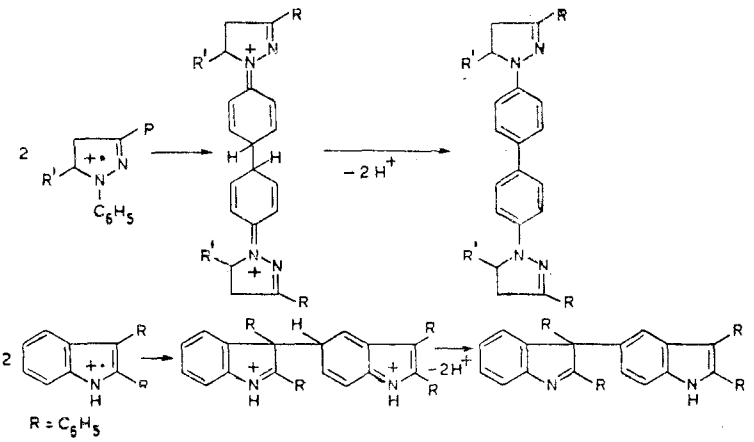
The ability of the cation radical to undergo fragmentation with the formation of hydrogen leads to a paradoxical situation in which the one-electron oxidizing agent (the cation radical) simultaneously has reductive properties, being a source of weakly bonded atomic hydrogen.

Heterocyclic Cation Radicals As Intermediates

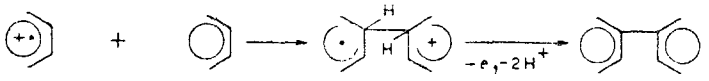
Formation of C–C Bonds. One of the extremely characteristic features of many cation radicals is their tendency to form dimeric products. This reaction is an extremely valuable preparative method for the formation of new C–C bonds.

The oxidative dimerization of carbazoles [22, 30, 61], 2-pyrazolines [128, 185, 186], 2,3-diphenylindole [187], and dibenzodihydroazepine [62] has been described in the heterocyclic series. These reactions include the oxidation of the starting compound to a cation radical and its dimerization, which leads to the development of a new carbon–carbon bond. Symmetrical dimers (dimerization of the "head-to-head" type) are usually formed; however, an example of unsymmetrical dimerization of the "head-to-tail" type also exists (2,3-diphenylindole) [187]. (See scheme, top, next page.)

The positions with the maximum density of the unpaired electron should evidently usually be the most reactive in reactions involving dimerization of cation radicals. It should also be especially emphasized that the formation of dimeric products is evidently also pos-

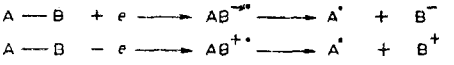


sible in the reaction of the cation radical with the neutral compound associated with it:

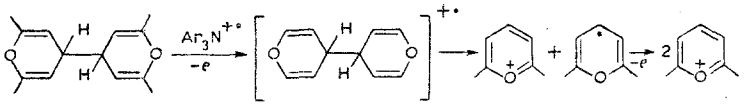


Difficulties arise during an attempt to interpret reactions of this type in classical terms: they can equally successfully be regarded as electrophilic and free-radical substitution reactions.

"One-Electron" Cleavage of the C—C Bond. In the development of concepts regarding electron transfer as the elementary act of organic reactions [188] two types of cleavage of the covalent bond, viz., reductive and oxidative cleavage, were postulated [189]:



As applied to cleavage of C—C bonds [190], this means that the fragmentation of cation radicals also leads to the synchronous formation of a carbonium ion and a radical. The oxidative dehydrogenation of dipyranyls with triethyl perchlorate leads to bis(pyrylium) cations; however, cleavage of the C—C bond occurs under the influence of the cation radicals of triarylamines, which are not capable of subsequently capturing hydrogen [136]:

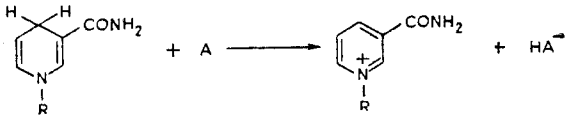


It is apparent that the known instances of cleavage of C—C bonds in the oxidation of heterocycles are associated with the intermediate formation of cation radicals and their subsequent fragmentation. This is the case, for example, in the cleavage of bis(isochromenyls) [191] and in the dealkylation during aromatization of 4H-pyrans [192] and, possibly, 1,2-dihydroperimidines [193].

It is characteristic that cleavage of C—C bonds in the case of electrocyclic reactions, which is prohibited by theorbital symmetry rule for the neutral substrate, takes place readily in cation radicals [194, 195].

Dehydroaromatization. Processes involving the dehydrogenation of hydroheteroaromatic compounds play an extremely important role in living systems in which they are responsible for numerous biochemical reactions involving electron transfer along the conjugated donor-acceptor chains and thus the functioning of the entire energy system of the living organism. However, in spite of this, the problem of the mechanism of the dehydrogenation of hydroheteroaromatic compounds and of hydroaromatic compounds in general still remains open to discussion.

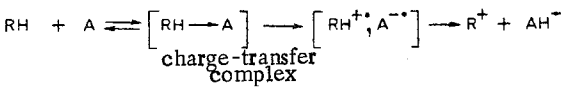
It is usually assumed that in the course of dehydrogenation a hydride ion is transferred from the hydroaromatic compound to the dehydrogenating agent, which acts as a hydride-ion acceptor:



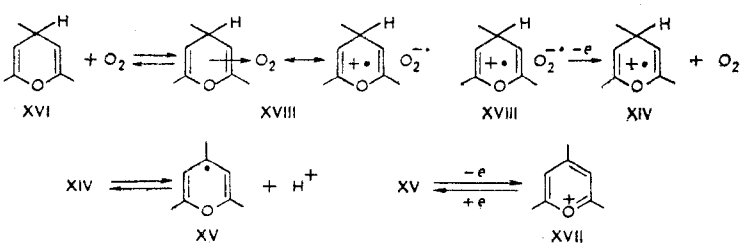
The ability to capture a hydride ion is ascribed in this case to all compounds that display dehydrogenating properties, even up to silver cations [184, 196, 197].

It should be emphasized that the possibility of the realization of a hydride mechanism for dehydrogenation is extremely unlikely. This mechanism, as well as the ability of the C–H bond to act as a hydride-ion donor, essentially has not been proved in even a single case. Hydride-ion transfer in the course of deuteration reactions has been postulated only on the basis of a purely formal approach to an examination of the experimental results of such reactions.

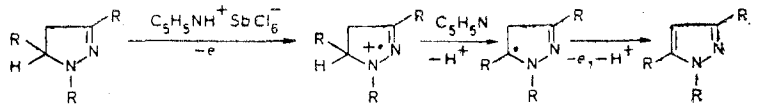
Among the opponents of this approach to dehydrogenation processes, one should single out Kosower [198], who has logically proved an overall stepwise mechanism for the aromatization of dihydropyridines and hydrogenated aromatic cations:



It is apparent that the character of the transformations that take place in an ion-radical pair should depend substantially on the nature of the solvent, i.e., on the degree of separate character of the pair. Experimental evidence in favor of the existence of one-electron steps in the course of the aromatization of dihydropyridines was recently obtained in the electrochemical research of Stradyn', Dubur, and co-workers [199]; however, as before, studies that cast doubt on the Kosower scheme have been published (e.g., see [200]). Inasmuch as we do not have space to present a list of all of the papers dealing with these two points of view, let us note only that the argumentation presented in the overwhelming majority of the studies is not exhaustive. For example, the cation radical of the substrate is recorded by EPR spectroscopy [201], but it remains unclear whether it lies on a reaction coordinate; the intermediate formation of cation radicals follows from electrochemical data [74, 202, 203], but there is no assurance that the electrode sufficiently accurately models the action of the oxidizing agent; the potential barrier to electron transfer has been estimated on the basis of kinetic data [200], but it is necessary to acknowledge here that the height of this barrier may depend decisively on the catalyst. In this sense the use of a combination of methods applied to experimental subjects of the same type seems most convincing. This was accomplished in the case of the dehydroaromatization of 4H-pyrans. The formation of cation radicals was proved by EPR spectroscopy, their conversion to stable pyranyl radicals was traced, and the ability of the latter to undergo oxidation to the final dehydro products, viz., pyrylium salts, was demonstrated [179]. The dehydrogenation of pyrans has been modeled electrochemically, the formation of cation radicals has been proved, and their conversion to stable pyranyl radicals has been traced [75]; from kinetic data on dehydrogenation by one-electron oxidizing agents it follows that the reaction is catalyzed markedly by oxygen [75]. All of this makes it possible to assert that dehydroaromatization is a stepwise process and that one-electron oxidation of the substrate occurs in the decisive steps:



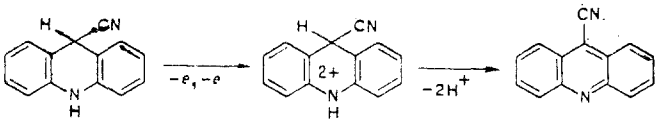
Direct oxidation of the dihydro derivative without the participation of oxygen is also possible when one uses sufficiently strong one-electron oxidizing agents. The fact that hydrogen is split out in the form of a proton becomes apparent in the case of the oxidative dehydrogenation of 1,3,5-triphenyl-2-pyrazoline in the presence of pyridine:



In the presence of bases, dimerization takes place in the cation radical step [128].

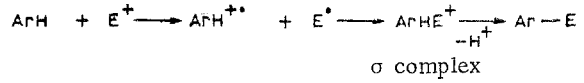
Thus, the most likely mechanism of dehydroaromatization is a $-e, -H^+, -e$, or $-e, -H\cdot$ mechanism. If the product of one-electron reduction of the dehydrogenating agent is sufficiently basic or is capable of detaching a hydrogen atom, splitting out of hydrogen from the cation radical may evidently occur immediately after electron transfer in the solvent "cage" without significant formation of a cation radical as a kinetically independent particle.

The $-e, -e, -H^+$ mechanism (see the electrochemical model in [204]) is also evidently possible in some cases.



The dehydrogenation of 4H-pyrans with carbon tetrachloride, which can be formally described as hydride-ion transfer, is, as demonstrated in [205], a free-radical chain process. The dehydrogenation of 1,2-dihydroquinolines with carbon tetrachloride also evidently proceeds similarly [206]. It is thus clear that true hydride-ion "transfer" does not occur in any of the examples mentioned above.

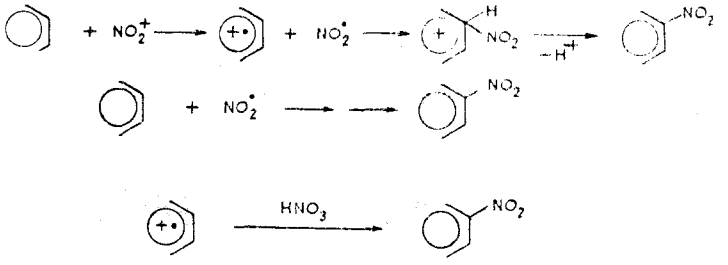
Electrophilic and Radical Substitution in the Heterocyclic Series. The assumption of the possibility of electron transfer inprocesses involving electrophilic aromatic substitution was expressed by Nagakura and Tanaka, according to whom the final product of electrophilic substitution may have a cation radical of the aromatic substrate as its precursor [207, 208]:



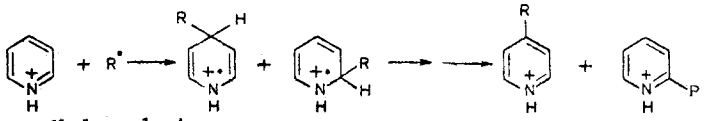
σ complex

However, because of the absence of reliable experimental evidence, these concepts have not been widely recognized.

Nevertheless, the authors of the present review have no doubt that cation radicals play an important role in nitration reactions in the case of aromatic and particularly heteroaromatic compounds [209-211]. The formation of significant amounts of cation radicals by the action of nitric acid on phenoxazine, phenothiazine, 1-phenyl-2-pyrazolines, and N-methylcarbazole has been proved by EPR and UV spectroscopy [211]. It was demonstrated in [211, 212] for the first time that a cation radical of the compound undergoing nitration in the case of nitration with nitric acid participates in the formation of a nitro derivative by reacting with nitric acid and nitrogen dioxide (in the case of the nitration of phenothiazine). With allowance for the available data, the following scheme for the nitration of aromatic and heteroaromatic compounds with nitric acid was proposed [211]:



Preparative methods for highly selective homolytic substitution (alkylation, acylation, carboxamidation, etc.) in the protonated forms of azaaromatic compounds have been developed in recent years [213-224]. Data that provide evidence for the intermediate formation of cation radicals of dihydro derivatives of azaheterocycles in such processes were recently obtained [225]:



The high selectivity of substitution in the 2 and 4 positions in protonated pyridines, quinolines, and quinoxalines is evidently due to the considerably higher rate of formation of cation radicals of dihydroazaheterocycles as compared with the protonated forms of azacyclohexadienyl radicals corresponding to attack at the unreactive positions.

Cation Radicals of Natural Heterocyclic Compounds and Their Analogs

The cation radicals of nicotine-adenine dinucleotide (NADH) and nicotine-adenine dinucleotide phosphate (NADPH) — complex natural 1,4-dihydropyridines that are evidently formed in processes involving dehydrogenation of these universal biochemical substrates — should be included among the most valuable cation radicals of this class. In fact, as we have already noted above, the oxygen analogs of 1,4-dihydropyridines, viz., 4H-pyrans, undergo dehydroaromatization to pyrylium salts through the intermediate formation of cation radicals of pyrans [179]. Nevertheless, virtually nothing is as yet known regarding the cation radicals of dihydropyridines. It has only been noted that the electrochemical oxidation of NADH is accompanied by the development of radical particles that give an unresolved EPR signal and are evidently NADH cation radicals. The low degree of reversibility of the electrochemical oxidation of 1,4-dihydropyridines [200] indicates the low stability of the cation radicals, which is evidently the chief obstacle to proof of their existence.

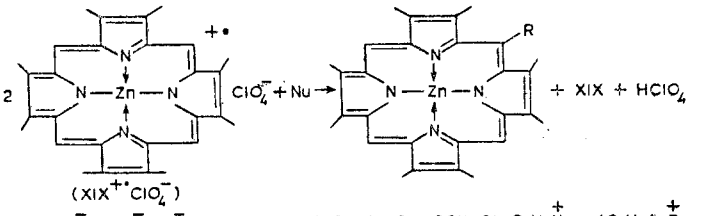
The cation radicals of metalloporphyrins and, in particular, chlorophyll are other biochemically cation radicals of heterocyclic compounds.

A noteworthy property of many metalloporphyrins is their ability to undergo facile and frequently reversible transformations of the porphyrin ligand that surrounds the metal [226-239]. It has been shown that, depending on the nature of the metal, in the case of one-electron oxidation of metalloporphyrins an electron can be removed both from the π system of the porphyrin ligand (with the formation of cation radicals of the metalloporphyrin) and from the metal atom, which undergoes conversion to a higher oxidation state. The oxidation of metalloporphyrins to cation radicals is carried out both by chemical means (by means of I_2 [91], Br_2 [26, 89], $Tl(NO_3)_3$ [91], XeF_2 [26], dichlorodicyanobenzoquinone [87], etc., as oxidizing agents) and electrochemically at a controllable potential [26, 55, 56, 89]. A number of cation-radical salts of metalloporphyrins have been isolated in the individual state [26, 27, 53]. The cation radical salt of chlorophyll is known only in solution [8, 240].

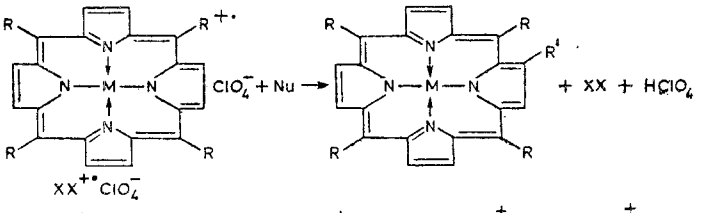
It is assumed that the cation radicals of chlorophyll are formed in the initial step of photosynthesis by photodetachment of an electron from the chlorophyll molecules (or its various associates) [8] and are the so-called primary oxidizing agent, the subsequent transformations of which lead to the liberation of oxygen from water. It is extremely important in this respect that the oxygenated forms of chlorophyll (the cation radical and the dication), according to the data in [241, 242], are actually capable of reacting with water to given oxygen. Unfortunately, there are as yet no data available regarding the mechanism of this process.

The cation radicals of metalloporphyrins evidently also play an important role in the functioning of other biochemical substrates that contain a metalloporphyrin prosthetic group. Thus, a spectroscopic study has shown that the mechanism of the of the action of catalases and peroxidases includes the intermediate formation of the cation radicals of these ferroporphyrins [243]; in this case the electron-transfer processes that take place in the course of the enzymatic action of catalases and peroxidases evidently occur through the porphyrin ring [243].

As in the case of other heterocyclic cation radicals, the study of the reactivities of cation radicals was begun with an investigation of their reactions with various nucleophiles. Products corresponding to the addition of a nucleophile to the cation radicals are usually formed in these reactions. The nucleophile may be added in both the meso positions [91, 109] and in the β positions of the pyrrole rings of the cation radicals [27].



Nu = CN^-, SCN^-, Cl^-, C_5H_5N, $(C_6H_5)_3P$; R = CN, SCN, Cl, $C_5H_5\overset{+}{N}-$, $(C_6H_5)_3\overset{+}{P}-$



Nu = SCN^-, NO_2^-, C_5H_5N, $(C_6H_5)_3P$; R' = SCN, NO_2, $C_5H_5\overset{+}{N}-$, $(C_6H_5)_3\overset{+}{P}-$;
R = C_6H_5 ; M = Zn, Mg

The reactions of cation radicals of metalloporphyrins with nucleophiles can be used for the preparative synthesis of various substituted porphyrins and, in particular, their meso derivatives. The possibility of direct cyanation and thiocyanation of porphyrin cation radicals is of particular interest in a synthetic respect.

Rather convenient methods for the generation of various ion radicals and efficient methods for the study of their electron structures (EPR and molecular spectroscopy and other methods) have been developed at the present time. Nevertheless, we still know relatively little about their strictly chemical properties and we have almost no knowledge of how to use ion radicals in preparative chemistry. However, there is no doubt that the development of this research trend is capable of revolutionizing the entire area of the chemistry of heterocyclic compounds and of opening up new prospects in the synthesis of heterocycles.

LITERATURE CITED

1. L. Michaelis and E. S. Hill, J. Gen. Physiol., 16, 859 (1933).
2. L. Michaelis and M. Granick, J. Am. Chem. Soc., 63, 351 (1941).
3. M. Hirshon, D. M. Gardner, and G. K. Fraenkel, J. Am. Chem. Soc., 75, 4115 (1953).
4. J. E. Wertz and J. L. Vivo, J. Chem. Phys., 23, 2193 (1955).
5. A. Fava, P. B. Sogo, and M. Calvin, J. Am. Chem. Soc., 79, 1678 (1957).
6. M. Kinoshita and H. Akamatu, Bull. Chem. Soc. Jpn., 35, 1040 (1962).
7. M. Kinoshita, Bull. Chem. Soc. Jpn., 35, 1137 (1962).
8. D. C. Borg, J.Fager, R. H. Felton, and D. Dolfin, Proc. Nat. Acad. Sci. USA, 67, 813 (1970).
9. D. Dolfin and R. Felton, Accounts Chem. Research, 7, 26 (1974).
10. J. P. Billon, Bull. Soc. Chim. Fr., No. 10, 1923 (1961).
11. A. S. Morkovnik, O. Yu. Okhlobystin, Z. S. Morkovnik, and E.Yu. Belinskii, Khim. Geterotsikl. Soedin., No. 12, 1696 (1979).
12. B. K. Bandlish, A. G. Padilla, and H. J. Shine, J. Org. Chem., 40, 2590 (1975).
13. B. K. Bandlish and H. J. Shine, J. Org. Chem., 42, 561 (1977).
14. S. R. Mani and H. J. Shine, J. Org. Chem., 40, 2756 (1975).
15. U. Schmidt, K. Kabitzke, and K. Markau, Chem. Ber., 97, 498 (1964).
16. H. J. Shine and L. R. Shade, J. Heterocycl. Chem., 11, 139 (1974).
17. Y. Murata and H. J. Shine, J. Org. Chem., 34, 3368 (1969).
18. E. A. C. Lucken, J. Chem. Soc., No. 12, 4963 (1962).
19. H. J. Keller, W. Moroni, D. Nothe, M. Scherz, and M.Z. Weiss, Naturwiss., 33, 838 (1978).

20. S. Hünig, B. J. Carner, G. Ruider, and W. Schenk, Ann., Nos. 5/6, 1036 (1973).
21. V. V Bessonov, O. Yu. Okhlobystin, T. P. Panova, and L. Yu. Ukhin, Teor. Eksp. Khim., 12, 829 (1976).
22. D. H. Iles and A. Ledwith, Chem. Commun., No. 9, 498 (1968).
23. B. I. Buzykin, A. Sh. Mukhtarov, A.V. Il'yasov, and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2167 (1973).
24. D. Farquhar, T. T. Gough, and D. Leaver, J. Chem. Soc., Perkin Trans. I, No. 3, 341 (1976).
25. S. F. Nelsen and C. R. Kessel, J. Am. Chem. Soc., 99, 2392 (1977).
26. J. Fajer, D. C. Borg, A. Forman, D. Dolfin, and R. H. Felton, J. Am. Chem. Soc., 92, 3451 (1970).
27. A.G. Padilla, Wu Shi Ming, and H. J. Shine, Chem. Commun., No. 4, 236 (1976).
28. C. M. Camaggi, L. Lunazzi, and G. Placucci, J. Chem. Soc., Perkin Trans. II, No. 10, 1491 (1973).
29. G. Cauquis and M. Genies, Bull. Soc. Chim. Fr., No. 9, 3220 (1967).
30. J. F. Ambrose and R. F. Nelson, J. Electrochem. Soc., 115, 1159 (1968).
31. W. Klopffer,G. Kaufmann, and G. Z. Naundorf, Naturforsch., 26A, 897 (1971).
32. F. A. Neugebauer,H. Fischer, S. Bamberger, and H. O. Smith, Chem. Ber., 105, 2694 (1972).
33. A. V. Dushkin, T. V. Leshina, O. I. Shubaeva, R. Z. Sagdeev, A. I. Rezvukhin, M. V. Kazankov, N. M. Makshanova, and S. M. Shein, Zh. Org. Khim., 13, 1231 (1977).
34. A. Ledwith and P. J. Russell, J. Chem. Soc., Perkin Trans. II, No. 6, 582 (1974).
35. C. Utsutomija, T. Kobayashi, and S. Nagakura, Bull. Chem. Soc. Jpn., 51, 3482 (1978).
36. R. A. Abramovitsh and J. G. Saha, Tetrahedron, 21, 3297 (1965).
37. M. Farcasiu and D. Farcasiu, Chem. Ber., 109, 2294 (1976).
38. B. H. Bakker and W. N. Speckamp, Tetrahedron Lett., No. 46, 4065 (1975).
39. E. M. Kosower and J. L. Cotter, J. Am. Chem. Soc., 86, 5524 (1964).
40. E. Weitz, Ber., 75, 1927 (1942).
41. M. de Sorgo, B. Wassermann, and M. Szwarc, J. Phys. Chem., 76, 3468 (1972).
42. A. G. Evans,J. C. Evans, and M. W. Bakker, J.Chem. Soc., Perkin Trans. II, No. 12, 1310 (1975).
43. A. G. Evans, J. C. Evans, and M. W. Bakker, J.Am. Chem. Soc., 99, 5882 (1977).
44. I. B. Goldberg, H. R. Crowe, G. S. Wilson, and R. S. Glass, J.Phys. Chem., 80, 988 (1976).
45. P. Hanson and R. O. C. Norman, J.Chem. Soc., Perkin Trans. II, No. 3, 264 (1973).
46. Y. Tsujino, Nippon Kagaku Zasshi, 90, 809 (1969); Chem. Abstr., 71, 101795 (1969).
47. Y. Tsujino, Tetrahedron Lett., No. 21, 2545 (1968).
48. J. P. Billon, G. Cauquis, J. Combrisson, and A. M. Li, Bull. Soc. Chim. Fr., Nos. 11-12, 2062 (1960).
49. L. H. Piette, P. Ludwig, and R. N. Adams, J. Am. Chem. Soc., 83, 3909 (1961).
50. L. H. Piette, P. Ludwig, and R. N.Adams, Anal. Chem., 34, 916 (1962).
51. C. Barry, G. Cauquis, and M. Maurey, Bull. Soc. Chim. Fr., No. 8, 2510 (1966).
52. A. Zweig, A. Maurer, and B. G.Roberts, J. Am. Chem. Soc., 89, 4091 (1967).
53. A. N. Sidorov, V. N. Kholmogorov, R. P. Evstigneeva, and G. N. Kol'tsova, 13, 143 (1968).
54. S. Hünig, H.Schlaff, G. Kieslich, and D. Dshentzow, Tetrahedron Lett., No. 27, 2271 (1969).
55. J. H. Fuhrop and D. Mauzerall, J.Am. Chem. Soc., 91, 4174 (1969).
56. D. Dolfin, R. H. Felton, D. C. Borg, and J. Fajer, J. Am. Chem. Soc., 92, 743 (1970).
57. M. Libert, C. Caullet, and M. S. Longchamp, Bull. Soc. Chim. Fr., No. 6, 2367 (1971).
58. G. Cauquis and M. M. Mey, Bull. Soc. Chim. Fr., No. 9, 3588 (1972).
59. G. M. Brown, F. R. Hopf, J. A. Ferguson, T. J. Meyer, and D. H. Whitten, J. Am. Chem. Soc., 95, 5939 (1973).
60. S. Hünig, F. Linhart, and D. Siegfrid, Ann., No. 11, 2102 (1975).
61. J. F. Ambrose, L. L. Carpenter, and R. F. Nelson, J. Electrochem. Soc., 122, 876 (1975).
62. S. Frank, J. A. Bard, and A. Ledwith, J. Electrochem.Soc., 122, 898 (1975).
63. I. N. Borukhova, V. F. Gryazev, I. Ya. Yarysheva, and Z. V. Pushkareva, Khim. Geterotsikl. Soedin., No. 4, 548 (1976).
64. M. Libert and C. Caullet, Bull. Soc. Chim. Fr., Nos. 3-4, 345 (1976).
65. R. M. Harhden, P. R. Moses, and J.Q. Chambers, Chem. Commun., No. 1, 11 (1977).
66. M. Neptune and R. L. McCreery, J. Org. Chem., 43, 5006 (1978).
67. A. Vogler, B. Rethwisch, H. Kunkelv, J. Huttermann, and O. Besenhard, Angew. Chem., 90, 1004 (1978).
68. S. Hünig, and P. Hermann, Chem. Ber., 110, 2524 (1977).

69. G. Cauquis and A. Deronzier, Chem. Commun., No. 19, 809 (1978).
70. F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, J. Am. Chem. Soc., 100, 4612 (1978).
71. E. T. Seo, J. K. Howie, and D. T. Sawjer, J. Am. Chem. Soc., 100, 207 (1978).
72. S. F. Nelsen, C. R. Kessel, and H. N. Brall, J. Am. Chem. Soc., 101, 1874 (1979).
73. L. A. Tinker and A. J. Bard, J. Am. Chem. Soc., 101, 2316 (1979).
74. I. M. Sosonkin, V. A. Subbotin, V. N. Charushin, and O. N. Chupakin, Dokl. Akad. Nauk SSSR, 229, 888 (1976).
75. N. T. Berberova, A. A. Bumber, M. V. Nekhoroshev, V. B. Panov, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 246, 108 (1979).
76. F. Pragst and W. Jugelt, J. Prakt. Chem., 316, 981 (1974).
77. R. Ziebig, F. Pragst, and W. Jugelt, Z. Phys. Chem. (Leipzig), 259, 1009 (1978).
78. B. D. Baigrie, T. A. Joslin, and D. W. Sopher, J. Chem. Soc., Perkin Trans. II, N . 1, 77 (1979).
79. M. H. Litt and J. Radovic, J. Phys. Chem., 78, 1750 (1974).
80. B. K. Bandlish and H. J. Shine, J. Heterocycl. Chem., 12, 287 (1975).
81. D. Clarce and B. C. Gilbert, J. Chem. Soc., Perkin Trans. II, NO. 10, 1078 (1975).
82. D. H. Eargle and M. de Carvalho, J. Phys. Chem., 77, 1716 (1973).
83. M. F. Chiu and B. C. Gilbert, J. Chem. Soc., Perkin Trans. II, No. 3, 258 (1973).
84. L. Lunazzi, G. Placucci, and M. Tiecco, Tetrahedron Lett., No. 36, 3847 (1972).
85. N. T. Berberova, E. P. Ivakhnenko, A. S. Morkovnik, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 12, 1696 (1979).
86. A. P. Bobrovskii and A. N. Sidorov, in: Spectroscopy of Phototransformations in Molecules [in Russian], Nauka, Leningrad (1977), p. 149.
87. J. H. Furhop and D. Mauzerall, J. Am. Chem. Soc., 90, 3875 (1968).
88. H. Sun Chou, R. C. Reeves, and E. R. Biehl, J. Heterocycl. Chem., 13, 77 (1976).
89. R. H. Felton, D. Dolfin, D. C. Borg, and J. Fajer, J. Am. Chem. Soc., 91, 196 (1969).
90. D. M. Lemal and K. I. Kawano, J. Am. Chem. Soc. 84, 1761 (1962).
91. G. H. Barnett, B. Evans, K. M. Smith, S. Besecke, and J. H. Fuhrhop, Tetrahedron Lett., No. 44, 4009 (1976).
92. D. C. Borg, A. Forman, and J. Fajer, J. Am. Chem. Soc., 98, 6889 (1976).
93. W. Musker and T. L. Wolford, J. Am. Chem. Soc., 98, 3055 (1976).
94. W. Musker and P. B. Roush, J. Am. Chem. Soc., 98, 6745 (1976).
95. W. Musker, T. L. Wolford, and P. B. Roush, J. Am. Chem. Soc., 100, 6416 (1978).
96. I. Baciu, M. Hillenbrand, and E. M. Sahini, J. Chem. Soc., Perkin Trans. II, No. 9, 986 (1974).
97. M. L. Kaplan, R. C. Haddon, and F. Wudl, Chem. Commun., No. 11, 388 (1977).
98. C. Lagercrantz, Acta Chem. Scand., 15, 1545 (1961).
99. B. Lamotte, A. Rassat, and P. S. Gavin, C. R., C, 255, 1508 (1962).
100. H. J. Shine and L. H. Piette, J. Am. Chem. Soc., 84, 4798 (1962).
101. L. D. Tuck and D. W. Schiesser, J. Phys. Chem., 66, 937 (1962).
102. M. Tomita, S. Ueda, Y. Nakai, Y. Deguchi, and H. Takaki, Tetrahedron Lett., No. 18, 1189 (1963).
103. H. J. Shine, C. F. Dais, and R. J. Small, J. Org. Chem., 29, 21 (1964).
104. F. Gerson, Helv. Chim. Acta, 47, 1484 (1964).
105. H. J. Shine and E. E. Mach, J. Org. Chem., 30, 2130 (1965).
106. H. J. Shine and R. J. Small, J. Org. Chem., 30, 2140 (1965).
107. M. Raileanu, I. Radulianu, and S. Radu, Collect. Czech. Chem. Commun., 37, 478 (1972).
108. D. Deavenport, J. T. Edwards, A. L. Ternay, E. T. Strom, and S. A. Evans, J. Org. Chem., 40, 103 (1975).
109. B. Evans and K. M. Smith, Tetrahedron Lett., No. 35, 3079 (1977).
110. O. V. Drygina, G. N. Dorofeenko, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 9, 1172 (1977).
111. M. Nojima, G. Nagano, N. Kekeya, M. Takagi, and N. Tokura, Chem. Commun., No. 9, 486 (1976).
112. S. Bamberger, D. Hellvinkel, and F. A. Neugebauer, Chem. Ber., 108, 2416 (1975).
113. J. M. Bisson, P. Hanson, and D. Slocum, J. Chem. Soc., Perkin Trans. II, No. 12, 1331 (1978).
114. E. E. Ertsbrunner, R. B. Girling, W. E. Grossmann, and R. E. Hester, J. Chem. Soc., Faraday II, 74, 501 (1978).
115. S. Ohnishi and H. M. McConnel, J. Am. Chem. Soc., 87, 2293 (1965).
116. R. M. Elofson and R. L. Edsberg, Can. J. Chem., 35, 646 (1957).

117. O. Dimroth and F. Fister, Ber., 55, 1223 (1922).
118. P. Krumholz, J. Am. Chem. Soc., 73, 4449 (1951).
119. S. Hünig and J. Grob, Tetrahedron Lett., No. 21, 2599 (1968).
120. J. Volke, Collect. Czech. Chem. Commun., 33, 3044 (1968).
121. J. A. Farrington, A. Ledwith, and M. F. Stam, Chem. Commun., No. 6, 259 (1969).
122. B. N. Shapiro, V. V. Minin, and Ya. K. Syrkin, Zh. Strukt. Khim., 14, 642 (1973).
123. I. V. Shelepin, V. N. Gavrilov, V. A. Barachevskii, and N. I. Karpova, Elektrokhimiya, 13, 404 (1977).
124. P. D. Sullivan and M. L. Williams, J. Am. chem. Soc., 98, 1711 (1976).
125. T. J. Curphey, J. Am. Chem. Soc., 87, 2063 (1965).
126. K. Maeda, T. Kashiwabura, and M. Tokuyama, Bull. Chem. Soc., Jpn., 50, 473 (1977).
127. M. Horner and S. Hünig, Angew. Chem., 89, 424 (1977).
128. A. S. Morkovnik and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 1, 128 (1979).
129. L. A. Summers and J. E. Dickeson, Chem. Commun., No. 22, 1183 (1967).
130. P. D. Sullivan and W. W. Paudler, Can. J. Chem., 51, 4095 (1973).
131. L. Roulliener and E. Laviron, Electrokhim. Acta, 23, 773 (1978).
132. C. S. Johnson and H. S. Gutowsky, J. Chem. Phys., 39, 58 (1963).
133. A. S. Hopkins, A. Ledwith, and M. F. Stam, Chem. Commun., No. 8, 494 (1970).
134. A. Ledwith, P. J. Russell, andL. H. Sutcliffe, Chem. Commun., 964 (1971).
135. P. Hyde and A. Ledwith, J. Chem. Soc., Perkin Trans. II, No. 15, 1768 (1974).
136. L. A. Polyakova, K. A. Bilevich, N. N. Bubnov, G. N. Dorofeenko, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 212, 370 (1973).
137. N. T. Berberova, G. N. Dorofeenko, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 3, 318 (1977).
138. S. Hünig and G. Sauer, Ann., 748, 173 (1971).
139. V. Zanker and G. Prell, Ber. Bunsenges. Phys. Chem., 73, 791 (1969).
140. V. V. Ryl'kov and V. E. Kholmogorov,Khim. Vys. Energ., 4, 311 (1970).
141. D. Gegiou,J. R. Huber, and K. Weiss, J. Am. Chem. Soc., 92, 5058 (1970).
142. M. Aubailly, M. Byzin, and R. Santus, Chem. Phys. Lett., 14, 442 (1972).
143. S. A. Alkaitis, G. Beck, and M. Gratzel, J. Am. Chem. Soc., 97, 5723 (1975).
144. V. A. Brovkova, Kh. S. Bagdasar'yan, V. F. Pikel'ni, V. A. Kolosov, and Yu. I. Kiryukhin, Dokl. Akad. Nauk SSSR, 224, 616 (1975).
145. V. I. Skvortsov and M. V. Alkhimov, Opt. Spektrosk., 41, 493 (1977).
146. E. M. Evleth, O. Chalvet, and P. Pamiere, J. Phys. Chem., 81, 1913 (1977).
147. T. Shida, Y. Nosaka, and T. Kato, J. Phys. Chem., 82, 695 (1978).
148. E. Amougal, A. Bernas, and D. Grand, J. Photochem., 9, 236 (1978).
149. S. Navaratnam,B. J. Parsons, G. O. Phillips, and A. K. Davies, J. Chem. Soc., Faraday Trans. I, 74, 1811 (1978).
150. K. Kim, V. J. Hull, and H. J. Shine, J. Org. Chem., 39, 2534 (1974).
151. A. Yamagishi, Bull. Chem. Soc. Jpn., 48, 3475 (1975).
152. S. Hünig, H. Balli, H. Conrad, and A. Schott, Ann., 676, 36 (1964).
153. B. A. Cowert, L. Marcoux, and A. J. Bard,J. Am. Chem. Soc., 94, 5538 (1972).
154. S. P. Sorensen and W. H. Bruning, J. Am. Chem. Soc., 95, 2445 (1973).
155. I. J. Ocasio and P. Sullivan, J. Am. Chem. Soc., 101, 295 (1979).
156. J. F. Evans and H. N. Blount, J. Am. Chem. Soc., 100, 4191 (1978).
157. U. Svanholm and V. D. Parker, J. Am. Chem. Soc., 98, 997 (1976).
158. L. Eberson and K. Nyberg, Acta Chem. Scand., B, 32, (1978).
159. L. Eberson, Chem. Commun., No. 20, 826 (1975).
160. O. N. Chipakhin and I. Ya.Postovskii, Usp. Khim., 46, 908 (1976).
161. L. A. Blyumenfel'd, L. V. Bryukhovetskaya, and S. M. Shein, Zh. Fiz. Khim., 40, 931 (1970).
162. H. J. Shine, B. K. Bandlish, and M. T. Stephenson, Tetrahedron Lett. No. 8, 733 (1978).
163. H. J. Shine, J. J. Silber, R. J. Bussey, and T. Okuyama, J. Org. Chem., 37, 2691 (1972).
164. J. J. Silver and H. J. Shine, J. Org. Chem., 36, 2923 (1971).
165. H. J. Shine and J. J. Silber, J. Am. Chem. Soc., 94, 1026 (1972).
166. U. Svanholm, O. Hammerich, and V. D. Parker, J. Am. Chem. Soc., 97, 101 (1975).
167. H. J. Shine and K. Klein, Tetrahedron Lett., No. 1, 99 (1974).
168. B. K. Bandlish, S. R. Mani,and H. J. Shine, J. Org. Chem., 42, 1538 (1977).
169. K. Kim and H. J. Shine, J. Org. Chem., 39, 2537 (1974).
170. K. Kim and H. J. Shine, Tetrahedron Lett., Nos. 49-50, 4413 (1974).
171. K. Kim, S. R. Mani,and H. J. Shine, J. Org. Chem., 40, 3875 (1975).
172. A. G. Padilla, B. K. Bandlish, and H. J. Shine, J. Org. Chem., 42, 1833 (1977).

173. B. K. Bandlish, W. R. Porter, and H. J. Shine, J. Phys. Chem., 82, 168 (1978).
174. H. J. Shine, B. K. Bandlish, S. R. Mani, and A. G. Padilla, J. Org. Chem., 44, 915 (1979).
175. J. F. Evans, J. R. Lenhard, and H. N. Blount, J. Org. Chem., 42, 983 (1977).
176. B. K. Bandlish, K. Kim, and H. J. Shine, Heterocycl. Chem., 14, 209 (1977).
177. B. C. Gilbert, P. Hanson, R. O. C. Norman, and B. T. Sutcliffe, Chem. Commun., No. 6, 161 (1966).
178. H. B. Stegmann and K. Scheffer, Chem. Ber., 101, 262 (1968).
179. O. Yu. Okhlobystin, V. A. Samarskii, M. V. Nekhoroshev, and V. D. Pokhodenko, Zh. Org. Khim., 15, 1110 (1979).
180. O. Yu. Okhlobystin, V. A. Samarskii, M. V. Nekhoroshev, and V. D. Pokhodenko, Summaries of Papers Presented at the All-Union Conference on the Chemistry of Carbonium Ions [in Russian], Novosibirsk (1979), p. 103.
181. K. Yoshida, J. Am. Chem. Soc., 99, 6111 (1977).
182. J. Kuthan and A. Kurfurst, Tetrahedron Lett., No. 24, 2071 (1976).
183. M. Dewar and R. Dougherty, The PMO Theory of Organic Chemistry, Plenum (1975).
184. A. V. El'tsov and Kh. L. Muravich-Aleksandr, Zh. Org. Khim., 1, 1673 (1965).
185. F. Pragst, J. Prakt. Chem., 315, 549 (1973).
186. F. Pragst and I. Schwertfeger, J. Prakt. Chem., 316, 795 (1974).
187. G. T. Check and R. F. Nelson, J. Org. Chem., 43, 1230 (1978).
188. K. A. Bilevich and O. Yu. Okhlobystin, Usp. Khim., 37, 2162 (1968).
189. V. Ts. Kampel', K. A. Bilevich, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 197, 95 (1971).
190. O. Yu. Okhlobystin, in: Mechanisms of Heterolytic Reactions [in Russian], Nauka, Moscow (1976), p. 21.
191. G. N. Dorofeenko, G. P. Safaryan, V. F. Voloshinova, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 7, 999 (1976).
192. M. V. Nekhoroshev and O. Yu. Okhlobystin, Zh. Org. Khim., 13, 1294 (1977).
193. A. F. Pozharskii, N. M. Starshikov, F. T. Pozharskii, and Yu. I. Mandrykin, Khim. Geterotsikl. Soedin., No. 7, 980 (1977).
194. E. Haselbach, T. Bally, and Z. Lanyiova, Helv. Chim. Acta, 62, 577 (1979).
195. M. L. Gross and D. H. Russell, J. Am. Chem. Soc., 101, 2082 (1979).
196. Z. N. Parnes and D. N. Kursanov, Hydride-Transfer Reactions in Organic Chemistry [in Russian], Nauka, Moscow (1969).
197. Z. N. Parnes, Summaries of Papers Presented at the All-Union Conference on the Chemistry of Carbonium Ions [in Russian], Novosibirsk (1979), p. 12.
198. E. Kosower, Introduction to Physical Organic Chemistry, Wiley (1968).
199. G.Ya. Dubur, Yu. I. Beilis, E. M. Belash, and A. E. Fasin', Summaries of Papers Presented at the Seventh All-Union Conference on Polarography [in Russian], Tbilisi (1978), p. 53.
200. F. M. Martens, I. W. Verhoven, R. A. Gase, U. K. Pandit, and T. I. de Boer, Tetrahedron, 34, 443 (1978).
201. Y. Ohnishi and A. Ohno, Chem. Lett., No. 7, 697 (1976).
202. F. Pragst, Z. Chem., 14, 236 (1974).
203. V. Skala, J. Volke, V. Ohanka, and J. Kuthan, Collect. Czech. Chem. Commun., 42, 292 (1977).
204. I. M. Sosonkin, O. N. Chupakhin, and A. I. Matern, Zh. Org. Khim., 15, 1976 (1979).
205. M. V. Nekhoroshev, V. B. Panov, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 249, 622 (1979).
206. Y. Sato, H. Kojima, and H. Shirai, Tetrahedron, 30, 2695 (1974).
207. S. Nagakura and J. Tanaka, J. Chem. Phys., 22, 563 (1954).
208. S. Nagakura, Tetrahedron, 19, Suppl. 2, 361 (1963).
209. V. D. Pokhodenko, V. A. Khizhnyi, V. G. Koshechko, and O. I. Shkrebtii, Zh. Org. Khim., 11, 1873 (1975).
210. C. L. Perrin, J. Am. Chem. Soc., 99, 5516 (1977).
211. A. S. Morkovnik, N. M. Dobaeva, V. B. Panov, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 251, 125 (1980).
212. A. S. Morkovnik, O. Yu. Okhlobystin, and E. Yu. Belinskii, Zh. Org. Khim., 15, 1565 (1979).
213. T. Caronna, G. P. Gardini, and F. Minisci, Chem. Commun., No. 5, 201 (1969).
214. F. Minisci, R. Galli, V. Malatesta, and T. Caronna, Tetrahedron, 26, 4083 (1970).
215. F. Minisci, T. Caronna, R. Galli, and V. Malatesta, J. Chem. Soc., C, No. 10, 1747 (1971).

216. F. Minisci, R. Mondelli, G. P. Gardini, and O. Porta, Tetrahedron, 28, 2403 (1972).
217. F. Minisci and A. Selva, Tetrahedron, 28, 2415 (1972).
218. T. Caronna, A. Citterio, and M. Bellatti, Chem. Commun., No. 20, 987 (1976).
219. T. Caronna, A. Citterio, T. Crolla, and M. Ghirardini, J. Heterocycl. Chem., 13, 955 (1976).
220. A. Citterio, M. Girardini, and F. Minisci, Tetrahedron Lett., No. 3, 203 (1976).
221. M. M. Fiorentino, L. Testaferri, M. Tiecco, and L. Troisi, Chem. Commun., No. 9, 317 (1977).
222. M. Braun, G. Hanel, and G. Heinisch, Monatsh., 109, 63 (1978).
223. G.Heinisch, A. Jetzsch, and I. Kirchner, Tetrahedron Lett., No. 7, 619 (1978).
224. I. A. Borisova, V. V. Zorin, S. S. Zlot-skii, and D. L. Rakhmankulov, Khim. Geterotsikl. Soedin., No. 7, 990 (1979).
225. A. Porta and G. Sesana, Tetrahedron Lett., No. 38, 3571 (1978).
226. E.I. Rabinovith and J. Weiss, Proc. R. Soc., 162A, 251 (1937).
227. H. Linschitz and J. Rennert, Nature, 169, 193 (1952).
228. G.L. Closs and L. E. Closs, J. Am. Chem. Soc., 85, 818 (1963) .
229. R. H. Felton, G. W. Sherman, and H. Linschitz, Nature, 203, 637 (1964).
230. A. Stanienda, Z. Phys. Chem. (Leipzig), 229, 257 (1965).
231. A.K. Chibosov and A. V. Karyakin, Biofizika, 11, 991 (1966).
232. A.K. Chibisov, A. V. Karyakin, and V. B. Evstigneev, Biofizika, 11, 983 (1966).
233. B. Diehn and G. R. Seely, Biochem. Biophys. Acta, 153, 862 (1968).
234. A. N. Sidorov and V. G. Maslov, Usp. Khim., 44, 577 (1975).
235. A. P. Kostikov, N. A. Sadovnikova, and V. B. Evstigneev, Biofizika, 21, 803 (1976).
236. Y. Nakato, K. Abe, and H. Tsubomura, Chem. Phys. Lett., 39, 358 (1976).
237. S. V. Vul'fson, O. L. Kaliya, O. L. Lebedev, and E. A. Luk'yanets, Zh. Obshch. Khim., 46, 179 (1976).
238. M. Tezuka, Y. Ohkatsu, and T. Osa, Bull. Chem. Soc., Jpn., 49, 1435 (1976).
239. R. C. Brown, A. Harriman, and L. Harris, J. Chem. Soc., Faraday Trans. II, 74, 1193 (1978).
240. J. C. Waterton and J. K. M. Sanders, J. Am. Chem. Soc., 100, 4044 (1978).
241. V. M. Kutyurin, I. Yu. Artamkina, N. P. Mel'nikov, and I. A. Anisimova, Teor. Eksp. Khim., 11, 831 (1975).
242. M. Aizawa, M. Hirano, and S. Suzuki, Electrochim. Acta, 23, 1185 (1978).
243. D. Dolphin, A. Forman, D. C. Borg, J. Fajer, and R. H. Felton, Proc. Nat. Acad. Sci. USA, 68, 614 (1971).